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METALLOGRAPHIC PREPARATION OF PLUTONIUM

A. L. RAFALSKI

ABSTRACT

Procedures are given for electropolishing and electroetching pure plutonium and delta phase stabilized plutonium alloys. The electrolytes used in this investigation are based on orthophosphoric acid. Photomicrographs are included which are representative of results obtainable using the techniques described.

INTRODUCTION

Until recently at Rocky Flats the procedure for preparing plutonium specimens for metallographic examination had been to use the electrolytic swab techniques described by Greeson, et. al.¹ The swab method, unfortunately, was found to be unsatisfactory because of the difficulty in consistently producing acceptable results. The purpose of this study, therefore, was to develop a more reliable method for revealing plutonium microstructures. This report describes an electrolytic apparatus and polish-etch conditions which were used to routinely produce metallographic results of the highest quality. The materials studied were alpha phase plutonium and delta-stabilized Pu-1 w/o Ga alloys.

EQUIPMENT

The experimental apparatus used for this work consisted of two commercial units, 1) the electrolytic cell of the Struers* Disa-pol

*Struers Scientific Instruments, Copenhagen, Denmark

electropolisher and 2) a Buehler** direct current power supply. The most important component of the apparatus is the polishing cell, the pertinent features of which are shown in the schematic drawing in Figure 1. The sample to be polished (a in Figure 1) which is the anode is clamped to the top of a mask (b) over an orifice which has a specific area. A stainless steel cathode (c) located beneath the specimen is fixed, therefore, a constant anode-cathode distance is always maintained. The electrolyte (d) which is contained in a glass bowl is projected upward onto the surface of the sample by the action of the pump (e). Hence, during polishing, the electrolyte is constantly being recirculated. The recirculation system is one of the most desirable features of the Disa-pol because not only is the sample always exposed to fresh electrolyte but also reaction products are flushed away and the sample surface cooled somewhat by the flow of the electrolyte.

EXPERIMENTAL PROCEDURE

Prior to electrolytic preparation, specimens were mounted in a cold-setting resin known as Koldmount.*** Since this material is a non-electrical conductor, a copper clip was attached to the sample to provide electrical continuity. The mounted samples were mechanically polished by 1) sanding on 180, 320, 400 and 600 grit SiC papers, 2) rough lapping with 6 μ m diamond paste on metcloth and 3) final polishing with 1 μ m diamond abrasive on nylon cloth. Carbon tetrachloride was the lubricant used in all the mechanical preparation steps.

**Buehler Ltd., 2120 Greenwood St., Evanston, Illinois

***Vernon-Benshoff Co., 413 N. Pearl St., Albany, New York

Before electropolishing the desired voltage was selected on the power supply and the proper electrolyte placed in the polishing unit. The electrolyte used for alpha plutonium contained 8 parts phosphoric acid, 5 parts glycerol and 5 parts alcohol. For the delta phase alloys a solution made up of 2 parts phosphoric acid, 1 part glycerol and 1 part 2-ethoxyethanol was used. These are essentially the same mixtures described by Greeson, et. al.¹

Electropolishing commenced when the pump was activated. After a predetermined time interval polishing was completed and the specimens were etched by simply decreasing the voltage to the proper setting. No handling of the specimens was required at any time during electropolishing or electroetching. Etched samples were rinsed with alcohol and dried by an air blast.

RESULTS AND DISCUSSION

The parameters for polishing and etching the materials studied are given in Table I. All procedures were carried out at room temperature.

Polishing voltages were determined from curves relating cell resistance to cell voltage. According to Tegar² the voltage which corresponds to the maximum cell resistance is the optimum polishing voltage. The time periods listed in Table I correspond to the amount of polishing necessary to completely dissolve the worked surface layer produced during mechanical polishing.

Voltages used for etching were determined by trial and error. Since etching characteristics vary slightly from sample to sample, the times listed are average values.

Figures 2 through 5 are examples of microstructures commonly encountered at Rocky Flats. Figure 2 is a micrograph showing the grain structure of alpha plutonium. Grain structures of homogenized high purity and recrystallized nominal purity Pu-1 w/o Ga alloys are exhibited in Figures 3 and 4, respectively. Figure 5 illustrates a Pu-1 w/o Ga alloy in the cored condition. Although inclusions are not retained in etched specimens, the artifacts usually seen in micrographs of plutonium are notably absent.

CONCLUSIONS

It has been shown that by using the techniques described high quality results can be obtained on both alpha and delta plutonium. Due to the automatic nature of the equipment and efficiency of the metallographic operations has been greatly increased.

ACKNOWLEDGMENT

The author would like to thank D. V. Ferrera for his aid in preparing the specimens used for this research. The work reported here was performed under AEC contract AT(29-1)-1106.

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Figure I- Schematic drawing of the Electrolytic Cell.

TABLE I

CONDITIONS FOR POLISHING AND ETCHING
ALPHA AND DELTA PLUTONIUM

Pu Phase	Electrolyte	Micro- Structure	<u>Polish</u>		<u>Etch</u>		Illumination
			Volts	Time min.	Volts	Time min.	
Alpha	8-5-5*	grain structure	9	4	2	4	Polarized
	8-5-5	inclusions	9	2			Bright field
Delta	2-1-1**	inclusions	9	2			Bright field
Delta	2-1-1	worked structure	9	4	4	4	Bright field
Delta	2-1-1	cored structure	9	4	4	4	Bright field
Delta	2-1-1	recrystal- lized grain structure	9	4	2	4	Bright field
Delta	2-1-1	homogenized grain structure	20	2	9	4	Polarized
					2	4	

*8 parts phosphoric acid, 4 parts glycerol, 4 parts alcohol

**2 parts phosphoric, 1 part glycerol, 1 part 2-ethoxyethanol

Figure 2. Grain Structure of Alpha Plutonium
Polarized Illumination X250

Figure 3. Grain Structure of Homogenized High
Purity Delta-Stabilized Pu-1 w/o Ga Alloy.
Polarized Illumination X250

Figure 4. Grain Structure of Normal Purity
Delta-Stabilized Pu-1 w/o Ga Alloy in the
Recrystallized Condition.
Bright Field X250

Figure 5. As Cast Delta-Stabilized
Pu-1 w/o Ga Alloy Showing Coring.
Bright Field X500

ELECTROLYTIC POLISHING AND ETCHING OF ALPHA PLUTONIUM

D. G. Rencken

ABSTRACT

Alpha plutonium microstructures that reveal sharply delineated grain boundaries have been produced with an electrolytic polisher-etcher. A microscope was used for observing the surface during polishing and etching. Specimens could be satisfactorily electrolytically polished at 3.0 A/cm^2 for 10 to 30 sec in a solution of 10% nitric acid, 20% ethylene glycol, and 70% methanol, and electrolytically etched at 30 mA/cm^2 for 1.5 to 3 min. This technique also provides a very rapid means for polishing and etching alpha plutonium directly from the as-machined condition. The microstructures reveal more detail than is generally shown by either grain-relief etches or etches for polarized light illumination. The microstructures are comparable to those that can be obtained by ion bombardment, but electrolytic polishing and electrolytic etching provide more consistent results and are much simpler.

INTRODUCTION

An electrolytic polishing and etching procedure has been developed for delineating alpha plutonium grain boundaries and for polishing plutonium specimens rapidly. Generally, alpha plutonium is mechanically polished and electrolytically etched to reveal the grain structure by polarized light illumination of an adherent surface oxide layer produced during etching.^(1,2) However, a perennial question is whether or not polarized light illumination reveals the actual grain structure of alpha plutonium. Examination of etched specimens for bright field illumination has been limited, since bright-field etching produces only a grain relief.⁽³⁾ Ion bombardment has been used somewhat successfully to delineate grain boundaries,⁽⁴⁾ but it has received limited use because the specimens transform to beta at about 120°C unless they are externally cooled. Consequently, ion bombardment is a slow process. The need for good electrolytic polishing and etching techniques for bright field examination is clearly necessary since the delineation of the grain boundaries in alpha plutonium is quite difficult.

SPECIMEN PREPARATION

Specimens were prepared three different ways. The first method, which is the normal procedure for polishing alpha plutonium (α -Pu), was to mount the specimen in cold-setting resin, machine the specimen surface flat with a lathe, grind through 600 grit silicon carbide, rough polish on a vibratory polisher using silk with 0.3 μ alumina, and final polish on a vibratory polisher using microcloth with 0.3 μ alumina as the abrasive. By the second method, the specimen surface was machined as smoothly as possible with a lathe and then electrolytically

polished to remove all effects of machining. Third, instead of electrolytically polishing the machined surface, the specimen was rough ground through 600 grit silicon carbide and then electrolytically polished to remove all effects of machining and grinding.

The electrolytes and procedures were developed using a glovebox-enclosed Zeiss Optical Electro-polisher-etcher (Figure 1), which microscopically reveals the changes in the specimen surface during polishing and etching. Magnifications ranged from 200X to 500X. The best operating voltage using a direct current power supply could be selected very quickly by observing the specimen surface microscopically during polishing and etching. Another advantage of being able to microscopically observe the process is that electrolytes could be evaluated in a very short time and either discarded or further developed.

RESULTS AND DISCUSSION

A process was developed for electrolytically polishing and etching α -Pu, and different electrolytes were evaluated for delineating grain boundaries without surface relief. The resulting microstructures of α -Pu were compared to the microstructures obtained from other polishing and etching processes.

An electrolyte of nitric acid, methanol, and ethylene glycol was determined to be satisfactory for both electropolishing and electrolytic etching to delineate the grain boundaries. Different percentages were used to accomplish different purposes. For example, the grain boundaries could be delineated more easily by increasing the acid and ethylene glycol contents, but better polishing could be obtained by decreasing the acid and ethylene glycol contents. The best electrolyte for both etching and polishing was a solution containing 10% nitric acid, 20% ethylene glycol, and 70% methanol. Although this concentration is a compromise between polishing and etching, satisfactory surfaces were prepared using the same electrolyte for both polishing and etching.

FIGURE 1
Zeiss Electropolisher-Etcher Enclosed in a Glovebox for
Electrolytic Polishing and Electrolytic Etching of Alpha
Plutonium

FIGURE 2
Current Density-Voltage Curve for a 6 mm Diameter α -Pu
Specimen Using an Electrolyte of 70% Methanol, 20% Ethylene
Glycol and 10% Nitric Acid

by heating a polished specimen to 115°C (Figure 3c).⁽⁵⁾ Good microstructures can be obtained by ion bombardment but this technique is very slow, particularly since alpha transforms to beta about 120°C. Bright field etching shows more detail in the microstructure than can be seen with polarized light illumination (Figure 3c) and the conventional electrolyte of 17% water, 23% tetraphosphoric acid, and 60% 2-ethoxy ethanol. Notice that the microstructures, particularly the grain size, obtained by the different etching techniques are quite similar. However, the procedure using the Zeiss-Optical Electro-polisher-etcher provides the most sharply defined grain boundaries.

A very significant advantage of using the Zeiss-Optical Electro-polisher-etcher is the short time required to prepare the metal for examination. An alpha plutonium specimen can be prepared for examination within 15 min. For example, the microstructure shown in Figure 4 was electrolytically polished and etched rapidly. The electropolishing time of either machined or rough-ground surfaces is 45 sec to 2 min compared to 10 to 30 sec for a specimen polished on the vibratory polisher. The quality of the microstructures is somewhat lowered, however, as can be seen by comparing Figure 3a with Figure 4b and Figure 3b with Figure 4c. When the rapid technique is used, the grain boundaries are not as clearly defined, the specimens show more surface relief, and the areas surrounding the inclusions and microcracks were etched away considerably leaving large pits. Even so, the quality is satisfactory for many visual examinations, and one can have a grain boundary etch revealing the metal's thermal and mechanical history, such as either as-cast, recrystallized, textured, or deformed microstructures.

Other electrolytes that were investigated were citric acid, ethanol, water, and potassium nitrate, which is used to etch delta stabilized plutonium; hydrochloric acid, methanol, and ethylene glycol; nitric acid, ethanol, and ethylene glycol; and sulfuric acid, methanol, and ethylene glycol. These electrolytes were found to be unsatisfactory. Of these, the solution of nitric acid, ethanol, and ethylene glycol was the best, but it caused excessive pitting.

Specimens that had been mechanically polished on the vibratory polishers could be further polished and etched electrolytically according to the current density-voltage curve (Figure 2), which was experimentally determined for α -Pu. As the voltage and current were increased from zero, a reaction layer (or anodic film) formed on the surface. Below 3 A/cm^2 the polishing action was too slow to flush away this reaction layer. Current densities between 3.0 and 7.0 A/cm^2 removed the reaction layer, but caused excessive surface relief. Voltages beyond the plateau, which is between 60 and 75 volts at 7 A/cm^2 , caused very extensive pitting. Thus the best condition for electrolytic polishing was 3 A/cm^2 for 10 to 30 sec. The precise current density was quite critical and could be determined only by observing the surface microscopically. The microstructure, however, shows some surface relief (Figure 3a). The round black areas reveal locations of inclusions, which were removed during polishing and the irregular black areas near the top of the photomicrograph are small microcracks.

The specimen was then etched by reducing the current density to about 30 mA/cm^2 . The etching time varied from 1.5 to 3 min depending on the grain size and heat treatment. This combination of electrolytic polishing and electrolytic etching produced a microstructure having sharply defined grain boundaries (Figure 3b). These microstructures show grain boundaries that are more sharply defined than previously published microstructures of bright field electrolytically etched specimens.⁽³⁾ They are comparable to microstructures obtained

a) Electrolytically Polished 10 Sec. at 3 A/cm² Using Technique Described in Text b) Electrolytically Etched 3 Min. at 30 ma/cm² Using Technique Described in Text

c) Electrolytically Etched 30 Sec. at 50 Volts in 23% Tetraphosphoric Acid, 17% Water and 60% 2-Ethoxy Ethanol

d) Etched by Ion Bombardment e) Polished Surface Heated to 115°C

FIGURE 3
Microstructure of α -Pu Prepared by Different Techniques (250X)

a) Machined Surface

b) Electropolished 3 min.
at 3 A/cm^2

c) Electroetched 3 min. at 30 mA/cm^2 After Electropolishing

FIGURE 4

Microstructures Showing Electropolishing and Electroetching
of a Machined Surface for Rapid Metallographic Preparation

CONCLUSION

Microstructures revealing sharply delineated grain boundaries of alpha plutonium have been produced, and a technique was developed for rapidly electrolytically polishing and electrolytically etching either machined or rough-ground surfaces of alpha plutonium.

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The author thanks Dr. R. D. Nelson and D. D. Hays for their advice and consultations and his colleagues, G. H. Giddings, H. E. Kjarmo and H. W. Arrowsmith for their assistance.

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QUALITATIVE METALLOGRAPHY OF URANIUM-
PLUTONIUM MIXED CARBIDE FUELS*

By

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ABSTRACT

A metallographic technique that distinguishes between the metallic, dicarbide, and sesquicarbide phases and precipitates of plutonium silicide in sintered uranium-plutonium carbide fuels is described. This includes general sample preparation, the multiple techniques required, and the interpretation of results.

INTRODUCTION

Sintered ceramic fuels of the composition $(U_{0.8}Pu_{0.2})C_{1.0}$ are among those proposed for use as fuel in the LMFBR (Liquid Metal Fast Breeder Reactor) program. The program includes compatibility studies in the sodium bonding of the fuel to container materials.

Metallographic examination is one of the primary methods for evaluating the compatibility of fuels with cladding when the phases and precipitates present in $(U,Pu)C$ can be absolutely identified. A step procedure of stain-etching, microhardness testing, and preferential etching has been developed that identifies the metallic, dicarbide, and sesquicarbide phases of $(U,Pu)C$ and precipitates of $PuSi$.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

EXPERIMENTAL PROCEDURE

Specimen Preparation

The (U,Pu)C fuel pellets (0.265-in. o.d. by 0.25-in. long) were sectioned longitudinally and vacuum-impregnation mounted in epoxy resin.* The mounted sections were wet-ground on SiC papers through 600 grit with lapping oil* as the lubricant. Polishing was performed by hand and with automatic equipment on synthetic napless lap coverings using 15 μ , 6 μ , and 1 μ diamond paste with silicone oil** as the lubricant. The sample mounts were ultrasonically cleaned with methyl chloroform between each preparative step.

Because of hydrolysis problems¹ with (U,Pu)C specimens, the grinding, polishing, and cleaning liquids were analyzed for their water content, and molecular sieves were placed in the lubricant containers to absorb the small percentage (< 0.04 wt %) of water present.

The prepared samples were then electrolytically etched[†] with 1:1:1 lactic, nitric, and acetic acids (2.5 V dc, 9 sec, touch probe) to distinguish grain boundaries and precipitates.

RESULTS

Known samples of hypo- and hyperstoichiometric composition (by electron microprobe analysis) were visually examined following the stain-etch.

The differentiation of metallic, dicarbide, and sesquicarbide phases, by optical means utilizing distinctive grain and precipitate shapes, proved effective only with the dicarbide phase, which appears as needle-shaped precipitates within the grains as shown in Fig. 1.

*Product of Buehler, Ltd.

**Product of Dow-Corning Corp. (Dow #200)

†Disa Electropol, Struers Scientific Instruments.

Preferential etches to remove metallic precipitates² proved effective on 65% of the samples tested. The unreliability of this technique is attributed to the metallic particles occasionally retaining an oxide film that prevents dissolution by the etchant.

Diamond point microhardness testing of precipitates and the surrounding matrix proved valid in detecting the metallic phase; i.e., the metallic phase had lower hardness numbers than the matrix. However, the crystal faces of matrix grains in polished and normal stain-etched specimens vary in hardness as color tone varies; i.e., the faces that etch darker are an average of 150 numbers lower in hardness than the crystal faces that etch light in color. Therefore, matrix grains of both shades adjacent to precipitates were DPH tested (25 g, 50 g loads) to determine accurately the presence of the metallic phase.

Precipitates with higher hardness numbers than the matrix have been determined by analysis to be sesquicarbides, plutonium silicides, or agglomerates of the metallic phase and plutonium silicide. The plutonium silicides range from 100 to 300 numbers higher in hardness than the matrix and are comparable in hardness to sesquicarbides.

A preferential etch for PuSi (1:1:3 hydrofluoric acid, nitric acid, and methanol)³, swab-applied after the usual electro-etch, colors the PuSi precipitates green, red, or orange, removes all coloration of the matrix grains, and leaves the metallic or sesquicarbide phase precipitates white.

The qualitative metallographic procedure that delineates the phases and precipitates in sintered (U,Pu)C specimens thus consists of the following three steps:

1. Sample is etched with the usual electrolyte to distinguish grain boundaries, porosity, and precipitates. A typical hypostoichiometric

(U,Pu)C sample is shown in Fig. 2, and a hyperstoichiometric sample is shown in Fig. 3.

2. The microhardnesses of precipitates and matrix grains are measured to distinguish between the metallic phase and harder phases or precipitates.

3. Samples are re-etched with the PuSi preferential etch. If a precipitate or a segment of it develops a color, PuSi is present; no color indicates that the precipitates are sesquicarbide. Figure 4 is typical of an agglomerate containing the metallic phase and PuSi in a hypostoichiometric sample. Figure 5 exhibits precipitates of the sesquicarbide phase in a hyperstoichiometric sample. Typical results obtained from this three-step technique are listed in Table I.

Table I
Microhardness and Etch
(25 g load)

<u>Matrix Grains</u>	<u>Precipitates</u>	<u>PuSi Color</u>	<u>Analysis</u>
860	580	No	M
698	450	No	M
960	464	No	M+
814	1081	Yes	PuSi
958	1189	Yes	PuSi
1090	1238	Yes	PuSi
960	1288	No	M_2C_3
1080	1246	No	M_2C_3

SUMMARY

A three-step technique; electro-etch, microhardness testing and preferential etching has proved effective in metallographically determining the metallic, dicarbide and sesquicarbide phases of (U,Pu)C and PuSi precipitates in sintered (U,Pu)C fuels.

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Fig. 1. Hyperstoichiometric (U,Pu)C.
Matrix = MC. Needle phase = MC_2
Electro-etched, 300X.

Fig. 2. Hypostoichiometric (U,Pu)C.
Electro-etched, 300X.

Fig. 3. Hyperstoichiometric (U,Pu)C.
Electro-etched, 300X.

Fig. 4. Hypostoichiometric (U,Pu)C.
 Precipitate shaded areas = PuSi
 Precipitate colorless areas = M.
 PuSi etch, 400X.

Fig. 5. Hyperstoichiometric (U,Pu)C.
 Colorless precipitates = M_2C_3 .
 PuSi etch, 400X.

CERAMOGRAPHIC FACILITY AND SPECIAL TECHNIQUES
FOR EXAMINATION OF
UNIRRADIATED PLUTONIUM-URANIUM CERAMIC FUEL MATERIALS^(a)

F. M. Smith and R. V. Olson^(b)

Battelle Memorial Institute
Pacific Northwest Laboratory
Richland, Washington

- (a) This paper is based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830.
- (b) Research Scientist and Senior Technician, respectively, Materials Department.

Ceramography is used in the Materials Department of the Pacific Northwest Laboratory in several areas:

- Quality control of fuel pellets used in production or developmental fuel elements
- Microstructural studies of experimental materials such as advanced fuels or certain isotopic heat sources
- Support of applied research projects such as compatibility studies of fuel/cladding couples, phase studies, etc.

To conduct the ceramography required, a gloved facility was constructed and has been in use for about four years. It is 22 feet long and about 4 feet wide with an inside height of 30 inches. Top and side views showing the general equipment layout of the box are shown in Figure 1. All samples are transferred into the sample receiving end of the box by either bag-in or sphincter pass-through methods.

As in any ceramographic procedure, the transport of grit from one stage of grinding or polishing to the next must be strictly minimized. To this end, the box is compartmented so that after mounting, the different stages of grinding and polishing are physically separated from one another. This, of course, minimizes the transfer of grit contaminants and also serves to clean the specimen of loose radioactive material as it proceeds through the facility.

One compartment, separated from the others by nitrogen locks, is devoted to chemical and electrolytic etching. The last compartment, next to the metallograph, is essentially free of loose contaminants and attests to the cleanliness observed during the preceding stages of sample preparation. In this area, surface replication, microscopic examination, and some

FIGURE 1. General layout of ceramographic facility showing equipment positions.

FIGURE 2. Open hood over metallograph stage. Note airlock into box.

photomacrography are done. In addition, the last compartment is connected by means of an airlock to an open faced hood situated over and around the metallograph stage as shown in Figure 2. This rather unique arrangement and the careful technique used in the box allow specimens to be brought through the airlock into the open hood and placed on the metallograph stage without any containment other than the mount itself. Occasionally contamination has been transferred to the metallograph stage but this is easily cleaned up, and the advantages gained through such a procedure far outweigh the disadvantages. In the time required for viewing and photomicrography, no evidence has been found to show that the hypostoichiometric mixed oxides, nitrides or carbides undergo any chemical or structural change because of air oxidation.

A convenient method for photomacrography has been devised by attaching a small plastic blister, equipped with lights, a sample stage, and an optical flat glass viewing plate to the side of the hood. A B&L Model L camera is mounted above so photographs can be made through the optical flat on top of the blister. Figure 3 shows this equipment. Figure 4 shows a view of the whole box. The overall plan of the facility has proven to be very flexible, and has met the laboratory needs with the possible exception of ceramography involving some of the high specific activity isotopes considered for use as heat sources. Each one of these materials presents its own special problems as to shielding and control.

A continuous flow of dry nitrogen is maintained throughout the box with the exception of the etch chamber. The nitrogen enters near the metallograph end in the clean compartment and is exhausted from the sample receiving end. This flow path also serves to concentrate dust and grit toward one end of the box. A certain amount of moisture is picked up by the nitrogen on its flow through the box even though nonaqueous lubricants for polishing and grinding are used.

During recent months, several new ceramographic techniques have been developed to meet new ceramics research problems. These are described below.

FIGURE 3. Macro camera and sample blister.

FIGURE 4. Ceramographic facility.

Out-of-Reactor Compatibility Studies

Out-of-reactor tests are being conducted at the Pacific Northwest Laboratory to determine the compatibility of mixed uranium-plutonium oxide and nitride fuel candidates sodium bonded to 304 stainless steel. Test capsules are assembled and heated at 650°C and 1000°C for time periods up to 5000 hours. After testing, ceramography is done to determine if any evidence of a reaction has occurred at or near the fuel-cladding interface or if any change has occurred in the fuel material itself. Much of this work has been reported in recent progress reports. (1,2,3,4)

The procedure used is to first determine the location of the pellet-sodium interface in the capsule by radiography. Using a tube cutter, the capsule wall is scored just above the interface to a depth so that only about one mil of solid metal remains uncut. While holding the capsule in a vertical position with a fixed clamp, it is arranged so that the end containing the pellet is submerged in epoxy mounting resin just to the score line. Once the resin has hardened completely, the capsule portion above the resin is "snapped off" showing the transverse face of the pellet. At this point, the specimen mount is placed in a vibratory polishing holder which makes the sample easier to manipulate with rubber gloves.

The hand polishing is done on kerosene-lubricated 2/0 and 3/0 emery paper. Use of the coarser papers, 280-400-600 grit, must be avoided because the coarse debris created during polishing lodges in the soft sodium. Even so, the sodium layer still entraps a certain amount of pellet, stainless steel, and plastic particles, but some of these can be removed by ultrasonically cleaning the specimen in kerosene for 15 minutes. From here, the specimen goes directly to the final polish on a vibratory polisher for 16-18 hours using kerosene lubricant and 0.3 micron alumina (Linde A) on a nylon cloth. After polishing, the sample is again cleaned ultrasonically and rinsed with clean kerosene. A cover glass is immediately placed over the polished surface while insuring that air bubbles are excluded from between the sample surface and cover glass. There is enough adhesion between the sample mount, kerosene, and cover glass so that the assembly can be inverted for metallographic examination without danger of the cover glass

falling off. This procedure serves to protect the sodium from corrosion due to atmospheric attack and from the accelerated attack due to the heat of the metallograph. A maximum magnification of about 250X can be attained through the cover glass. Polarized light has proven to be better than bright field; all filters are removed for maximum light. Sodium will polish away faster than the surrounding fuel and cladding so its polished surface will be lower than the other two surfaces; thus two pictures may be required of an area, one focussed on the sodium, the other on the stainless steel and pellet.

Because of the reaction between sodium and etchant solution, the sodium must be removed if pictures of the etched structure of the stainless steel or the pellet are required. Sodium can eventually be removed by controlled reaction with butyl alcohol, and the pellet can be lifted from the mount. This method will not completely remove all the sodium from the interior of the pellet; however, enough is removed near the surface so that any reaction between the sodium and fresh mounting resin is minimized. The pellet can then be remounted in resin by normal mounting procedures. After filling the void left by the pellet removal with resin, the separated components are polished and etched by their normal procedures since no sodium problems now exist. Figure 5 shows a flow diagram of the overall procedure. Figures 6, 7, and 8 show photomicrographs of specimens taken at various stages of the procedure using polarized light.

Transmission Electron Microscopy of Oxide Fuel Materials

Daniel and co-workers^(2,3,4,5) of the Pacific Northwest Laboratory have developed methods for uniform thinning of polycrystalline oxide fuel materials for examination by transmission electron microscopy. By combining careful ceramographic polishing with a light chemical etch, sintered UO_2 specimens have been prepared containing clean, transparent areas of up to a millimeter in diameter. The best method to date is a modification of the technique of Doherty and Leombruno,⁽⁶⁾ and currently includes the following steps:

1. Pre-cut the specimens to about 1 mm thickness, with parallel faces;

FIGURE 5. Ceramographic procedures for examination of sodium bonded compatibility capsule with sodium in place.

749E

250X

FIGURE 6. Interfaces between stainless steel cladding, sodium, and $\text{UO}_2 - 25 \text{ wt\% PuO}_2$ fuel after being polished on 3/0 paper. Stainless steel at top, fuel at bottom. Note debris trapped in sodium layer. Polarized light. Taken through cover glass.

764A

250X

FIGURE 7. Interfaces between stainless steel cladding, sodium, and $\text{UO}_2 - 25 \text{ wt\% PuO}_2$ fuel after being ground with 280-400-600 grit papers then polished with 3/0 paper. Note extra large grit particles trapped in sodium layer. Polarized light. Taken through cover glass.

7122B

100X

7122C

100X

FIGURE 8. Photomicrographs after polishing on Syntron. Sodium in focus on top and stainless steel cladding and UN - 20 wt% PuN fuel in focus on bottom. Polarized light. Taken through cover glass.

2. Carefully thin with diamond wheels, fine emery cloth, and vibratory polishers (with the specimen cemented to the surface of a Lucite or other suitable mount for polishing the second side, instead of being cast in a resin);
3. Treat each face briefly with a chemical polishing agent or etchant such as H_2O_2 - H_2SO_4 after final vibratory polishing to remove remaining scratches and surface artifacts; and
4. Clean carefully in a solvent refluxing unit before in-microscope examination.

Extreme care in handling the relatively large thinned sections is necessary to prevent breakage during the final polishing and recovery stages, especially for pneumatically impacted UO_2 . Total elapsed preparation time required is 5 to 10 days, though generally several specimens are thinned simultaneously. Success rate, as determined in the electron microscope, is about 75% for dense sintered UO_2 .

Mechanical thinning without any chemical treatment enroute leaves an appreciable residue of shallow dislocations, polishing marks, and surface artifacts, but produces a large area suitable for study of grain boundaries, inclusions or pull-out holes, and grain identification. The addition of brief periods of chemical polishing significantly reduces the apparent polishing damage, but may produce a slightly etched surface.

Extension of the thin section work to mixed oxides (UO_2 - 20 wt% PuO_2) has been only partially successful to date. Mechanical thinning of low-density (85% T.D.) specimens proceeded in a manner similar to that of pure UO_2 but the final thin sections showed more tendency to spall. Most of the sufficiently thinned edges were lost or destroyed during final recovery from the mounting cement, with a few narrow edges remaining for cursory microscopy. The limited observations suggest somewhat less internal defect structure than for the sintered UO_2 . Successful thinning of UO_2 - 25 wt% PuO_2 specimens of high density ($\sim 95\%$ T.D.) has been done recently. Figures 9 and 10 are photomicrographs of the results on one sample. These were taken by reflected light and show interference fringes in the portions photographed.

4884L

250X

FIGURE 9. UO_2 - 25 wt% PuO_2 mechanically mixed and sintered to 95% T.D. Thinned by mechanical and etch methods. Photographed by reflected light. Note interference fringes.

4884E

1000X

FIGURE 10. A portion of the same area shown in Figure 9 but at higher magnification. Photographed by reflected light.

Etching of PuO_2 , $\text{UO}_2\text{-PuO}_2$, and UN-PuN

In applying standard ceramographic procedures to plutonium ceramics, the etching step is most troublesome. Cathodic etching is frequently used, but is relatively inconvenient to apply. A brief search has been conducted for suitable chemical etchants. Generally, the stoichiometric mixed uranium-plutonium oxides are most difficult to etch, hypostoichiometric oxides are faster, and the mixed uranium-plutonium nitrides rapid. Daniel and others^(1,2,5) have demonstrated that the following etchants appear to be applicable at least under the conditions shown. Extensive tests have not been attempted, but evaluations are being made during applications to semi-routine ceramography.

PuO_2

40 ml HF (conc.)
10 ml HNO_3 (conc.)

Immerse for 60 to 90 minutes (shorter time for hypostoichiometric oxide). Rinse, neutralize thoroughly with dilute NaOH solution and rinse well.

UN-PuN, $\text{UO}_2\text{-PuO}_2$, and Irradiated $\text{UO}_2\text{-PuO}_2$

80 ml H_2O
20 ml HNO_3
3 drops HF
0.1 gm cerium nitrate

For UN-PuN swab etch for 60 to 90 seconds. Rinse well. Photomicrographs should be taken within one hour after etching. The unirradiated mixed $\text{UO}_2\text{-PuO}_2$ is etched by immersion for 60 to 90 minutes only. Rinse well. The irradiated mixed oxide fuel specimens require sequential etching for periods of approximately 4, 8, and 12 minutes to reveal microstructural details in each major area successively.

As a point of interest, the following two etchants were in use for mixed oxides before the etch listed above.

$(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{2.00}$

5 ml H_2O
15 ml HNO_3 (conc.)
3 drops HF (conc.)

Etch by immersion for three to five minutes.

9 ml H_2O_2 (30%)
1 ml H_2SO_4 (conc.)

Etch by immersion for three to five minutes.

These last two etches were difficult to control and sometimes resulted in over-etching.

Replication of Unirradiated Ceramic Fuel Materials for Electron Microscopy

All the replication done in the gloved facility for electron microscopy is carried out in the "clean" or the last compartment. Polyvinyl chloride solution (4% PVC in tetrahydrofuran and methylisobutylketone) is placed drop-wise on the surface of the specimen and mount to be replicated, and allowed to set until the solvent has evaporated. The PVC film remaining is stripped off and decontaminated by ultrasonic cleaning. If the contamination is stubborn, strong acid may be used since it does not attack the PVC. After decontamination, the PVC replica is removed from the glove box and shadowed in a contamination-free evaporator. The PVC is removed from the shadow material by extraction with tetrahydrofuran in a refluxing apparatus. One must make sure the PVC solution is compatible with the specimen mount material so that no reaction occurs between the two to cause adherence of the replica to the mount.

In the near future, a new high vacuum evaporator will be installed in the ceramography facility for the coating of replicas for electron microscopy, thin-film studies, and to make conductive coatings for specimens for examination with the electron microprobe and the scanning electron microscope.

Radioactive Materials of High Specific Activity

Since it is necessary to remove specimens and replicas from the ceramographic facility from time to time, strict control of contamination must be observed at all times. For this reason, the use of the facility has been mostly limited to those isotopes with specific activities in the same order of magnitude as the plutonium-239 normally examined. An exception has been

allowed in the case of the examination of promethium oxide microspheres. By careful cleaning after each step in the procedure and using a lubricant of low volatility such as kerosene to entrap all grinding debris generated during the grinding and polishing operations, examination of these microspheres was accomplished without wide spread of beta contamination. Of course, gross quantities of promethium are avoided at all times.

Although plutonium-containing specimens are viewed on the metallograph without any protection on the specimen itself, viewing of high specific activity materials is always done through a cover glass to minimize spread of contamination. Polonium-210 presents special problems for viewing because of its extremely high specific activity; it has a half life of 0.38 years compared with 2.6 years for promethium-147 and 24,000 years for plutonium-239. Specimens are prepared in a special gloved facility and the mount decontaminated. A cover glass is applied and the mount and cover glass are wrapped with enough plastic tape until one obtains, virtually, a plastic tape cocoon with a window for viewing the specimen.

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Current Metallographic Practices on Plutonium-rich
Plutonium-Hafnium Alloys*

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ABSTRACT

The plutonium-hafnium phase diagram is under current investigation at LASL. The metallography of the plutonium-rich alloys of this system is challenging because of the existence at room temperature of two intermetallic compounds and two metastably retained allotropes of plutonium (β and δ -Pu). The procedures used in preparing the specimens for optical metallography, diffractometry and hardness testing are described.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

INTRODUCTION

Binary plutonium alloys ranging in composition between 0 and 10 a/o hafnium have been examined metallographically in support of a study of the plutonium-hafnium phase diagram. The metallography of this portion of the system was especially challenging because of the occurrence, within a composition range of 6 a/o, of five phases: α -Pu, metastably retained β and δ -Pu, and the intermediate phases ζ and θ . Metallographic examination included optical metallography, X-ray diffractometry and microhardness testing of both arc-cast and heat-treated buttons, thermal analysis specimens and dilatometric specimens.

ALLOY PREPARATION

The plutonium stock used in making the alloys contained the following impurities (in ppm by weight): 5 Al, 10 Ni, 1 Sn, 7 Am, 12 H and 20 O₂. The hafnium stock contained 3 B, 20 Mg, 30 Al, 20 Si, 300 Fe, 10 O₂ and ~ 2% Zr.

The metallographic specimens consisted mainly of ~ 4-g buttons prepared either by simply arc melting the alloy components together in a helium atmosphere or by first arc melting the alloy components together and then inductively remelting the resulting arc-cast button in vacuum. Each ingot was cut in half, one of the halves being prepared for immediate optical examination, the other for X-ray powder studies and later optical examination after heat treatment.

The X-ray specimens were sealed within evacuated SiO₂ capsules for heat treatment in resistance furnaces.

All thermal analysis and dilatometric specimens were examined metallographically after completion of the thermal measurements.

METALLOGRAPHIC MOUNTING AND POLISHING

The metallographic specimens were wire brushed in a glove box before being transferred to an open-front hood for mounting. Each specimen was placed on a Teflon disk within a 1-in. ID Teflon mounting ring. Geomount,^{*} a cold setting resin that sets up in 30-45 minutes, was used as the mounting resin. This resin has a hardness of 23 DPH and is resistant to alcohols, carbon tetrachloride and numerous acids.

The mounted specimen was pushed out of the Teflon ring and transferred into the glove-box train where it was marked for identification. The sharp edges of the mount were then rounded to prevent cutting the drybox gloves and polishing cloths, and a hole was drilled through the back of the mount to allow electrical contact to be made between the specimen and a stainless steel probe used in electropolishing and etching.

The specimens were rough ground manually on 180, 240 and 320 SiC papers and then fine ground on 400 and 600 SiC paper and on 4/0 emery paper.

The specimens were rough polished on Metcloth[†] with Geoscience 6 μ and Buehler 3 μ diamond, while the fine polishing was done with 1/4 μ Geoscience diamond on Astromet[‡] cloth. A Buehler 2-speed polishing wheel was used for both the rough and fine polishing. The specimens were cleaned ultrasonically between each grinding and polishing stage.

Carbon tetrachloride was used as the lubricant in all grinding and polishing operations, and was also used in the ultrasonic cleaners.

^{*} Geo-Science, 435 East 3rd Street, Mount Vernon, New York.

[†] Buehler Ltd., 2120 Greenwood Street, Evanston, Illinois.

[‡] Precision Scientific Co., 3737 West Cortland Street, Chicago, Illinois.

ELECTROPOLISHING AND ETCHING

All electropolishing and etching was performed in an open-front hood. The electropolishing and etching apparatus consists essentially of two power supplies (a DC power supply, having a maximum output of 30A at 120V and an AC power supply having a maximum output of 10A at 110V), a small crystallizing dish to hold the electrolyte, a stainless steel screen for the cathode and a stainless steel probe for making electrical contact with the specimen.

Most of the alloys were etched in a 10 v/o Nital solution (10 ml HNO_3 and 90 ml methanol) with alternating current. Initially, a small amount of the Nital was "doped" by passing a 50V current through the solution, between the stainless steel probe and the fine stainless steel screen, for 20 sec, after which the etchant was brought to the proper level by the addition of fresh Nital. Voltages used ranged between 6 and 30 and the etching times varied between $1/2$ and 10 sec. Surface areas of the specimens ranged between 30 and 330 mm^2 . Etching was quickly followed by a water and then a methanol rinse to prevent the formation of a tightly adherent oxide layer on the etched surface. It was found during the latter part of this work that both β and δ -Pu that had been ground through 4/0 paper could be electropolished satisfactorily by use of the Nital solution at 20V AC for 10 sec.

Other etchants used in this work included two swab etchants (by volume: 2 Hf - 1 HNO_3 - 2 H_2O and 10 H_3PO_4 - 10 $\text{C}_3\text{H}_6\text{O}_3$ - 5 HNO_3 - 20 HAc) which were used to etch the hafnium stocks and to reveal primary hafnium and a hafnium oxide; and the following electrolytic etchants: DC 10 v/o Nital, DC 7 $\text{H}_6\text{P}_4\text{O}_3$ - 36 H_2O - 57 2-ethoxyethanol, and AC 50 $\text{C}_3\text{H}_6\text{O}_3$ - 15 H_2O - 6 H_2SO_4 .

OPTICAL EXAMINATION AND PHOTOMICROGRAPHY

The specimens were examined on a Zeiss metallographic microscope in the open laboratory. Particular care was taken to ensure that the mounted specimens were free of all loose contamination. Specimens that were to be photographed were transferred within closed containers to an American Optical Co. metallograph, also in the open laboratory. Inverted stages were used on both the microscope and the metallograph.

X-RAY DIFFRACTOMETRY

All metallographic specimens were examined by X-ray diffractometry to identify the phases present in the bulk samples. Most of the specimens were AC etched with Nital to remove the cold worked surface and any oxide layers. After being etched, the specimens were wrapped in Cut-Rite^{*} to prevent escape of contamination and were mounted on a Philips diffractometer in the open laboratory.

This technique provided excellent patterns for α , β and δ -Pu as well as for the ζ and θ phases. Some difficulties encountered in identifying the different phases in the multiphase alloys, because of the coincidence of strong lines in the diffractometer traces, were overcome through the use of X-ray powder data.

MICROHARDNESS MEASUREMENTS

Microhardnesses of the phases in the alloys were determined with a Leitz microhardness tester. The alloys were etched to remove the work hardened surface and to delineate the phases present, since most of the

* A plastic film produced by Scott Paper Company, Chester, Pennsylvania.

alloys were multiphase. However, hardness was not necessarily a differentiating factor, as can be seen by the hardness ranges obtained for the different phases listed below.

DPHN (25-g load)

Phase	Hardness Range	Average
α	258 - 311	290
β	83 - 168	115
δ	40 - 73	55
ζ	109 - 166	131
θ	159 - 268	190

RESULTS

The results of the optical metallography are best shown in the following series of photomicrographs (Figs. 1-20). Correlations of the results shown in these photomicrographs with the partial phase diagram (Fig. 1) may not be entirely straightforward because of the metastable retention of the β and δ -Pu allotropes.

SUMMARY

The metallographic preparation of plutonium-hafnium alloys containing up to about 10 at/o hafnium, and the interpretation of their structures, is difficult because of the room temperature existence of two intermediate compounds, ζ and θ , and the metastable retention of β and δ -plutonium. Of several etchants that were used with some success, 10 vol/o Nital and an AC electroetching technique gave the best results. This technique was also used successfully to electropolish and etch β and δ -plutonium that had been ground through 4/0 paper.

Figure 1. Plutonium-hafnium partial phase diagram.

Figure 2. Plutonium stock metal, etched AC - N,
6V - 10 sec. 50X.

Figure 3. Hafnium stock metal, swab etched
2 HF - 1 HNO₃ - 2 H₂O ~ 20 sec. 50X.

Figure 4. Pu - 2 a/o Hf alloy, arc melt, heat treated 275°C for 1440 h, air cooled, etched AC - N, 20V ~ 2 sec, showing θ in a α -plutonium matrix. 1000X.

Figure 5. Pu - 2 a/o Hf alloy, induction melt, heat treated 250°C for 200 h, air cooled, etched AC - N, 30V - 5 sec, showing mostly δ plus a small amount of α . 200X.

Figure 6. Pu - 2 a/o Hf alloy, arc melt, heat treated 266°C for 720 h, air cooled, etched AC - N, 15V - 3 sec, showing α in δ matrix. 1000X.

Figure 7. Pu - 2 a/o Hf, dilatometric specimen, slow cooled, etched AC - N, 10V - 10 sec, 3 phases, α needles in δ matrix plus θ . 200X.

Figure 8. Pu - 2.5 a/o Hf alloy, arc melt, heat treated 250°C for 1366 h, air cooled, etched AC - N, 6V - 10 sec, showing $\alpha + \gamma$ duplex structure in γ matrix. 500X.

Figure 9A. Pu - 3 a/o Hf, induction melt, heat treated 475°C for 120 h, air cooled, etched AC - N, 30V - 1/2 sec, essentially single phase β . 500X.

Figure 9B. Pu - 3 a/o Hf, induction melt, heat treated 475°C for 120 h, air cooled, etched AC - N, 30V - 1/2 sec, plus overnight oxidation, single phase β . 500X.

Figure 10. Pu - 3 a/o Hf, arc melt, heat treated 300°C for 838 h, air cooled, etched DC - N, 10V - 5 sec, showing θ in β matrix. 500X.

Figure 11. Pu - 3 a/o Hf, arc melt, heat treated 250°C for 2880 h, air cooled, etched DC, 7 $\text{H}_6\text{P}_4\text{O}_3$ - 36 H_2O - 57 parts 2-ethoxyethanol, 10V ~ 3 sec, θ in ζ matrix. 500X.

Figure 12. Pu - 3 a/o Hf, arc melt, heat treated 250°C for 1322 h, air cooled, etched AC, 50 lactic - 15 H_2O - 6 H_2SO_4 , 40V - 5 sec, α Pu (bright) plus δ Pu (dark) in ζ matrix. 1000X.

Figure 13. Pu - 3.5 a/o Hf, dilatometric specimen, slow cooled from ϵ , etched AC - N, 30V - 2 sec, shows δ (dark), ϵ (bright, smooth) plus θ (feathery). 500X.

Figure 14. Pu - 4 a/o Hf, induction melt, heat treated 250°C for 200 h, air cooled, etched AC - N, 30V - 5 sec, δ (dark) plus $\epsilon + \theta$ (feathery). 500X.

Figure 15. Pu - 5 a/o Hf, dilatometric specimen, slow cooled from δ , etched AC - 20 v/ Nital, 10V ~ 5 sec, showing δ (dark) plus ζ (light grey) in θ matrix (light). 1000X.

Figure 16. Pu - 5 a/o Hf, thermal analysis, slow cooled from 1000°C, etched DC - N, 10V - 5 sec, 3 phases, δ (dark) plus θ (light) plus ζ (light grey). 500X.

Figure 17. Pu - 6 a/o Hf alloy, induction melt, heat treated 250°C for 200 h, air cooled, etched AC - N, 30V - 5 sec, δ (dark) plus θ (bright). 1000X.

Figure 18. Pu - 8 a/o Hf, arc melt, heat treated 300°C for 838 h, air cooled, etched DC - N, 10V - 15 sec, δ grain plus intergranular θ. 500X.

Figure 19. Pu - 10 a/o Hf, arc melt, heat treated 200°C for 3600 h, air cooled, etched AC - N, 20V - 1 sec, Hf in θ matrix. 500X.

Figure 20. Pu - 15 a/o Hf, arc melt, heat treated 325°C for 1531 h, air cooled, etched AC - N, 20V - 1 sec, showing δ Pu (dark) plus Hf (bright) in θ matrix. 1000X.

Figure 21. Pu - 2 a/o Hf, arc melt, heat treated 450°C for 102 h, air cooled, etched AC - N, 20V - 10 sec, off 4/0 emery, β Pu. 500X.

Figure 22. Pu - 5 a/o Hf, arc melt, heat treated 450°C for 102 h, air cooled, etched AC - N, 20V - 10 sec, off 4/0 emery, δ Pu. 500X.

ELECTRON MICROPROBE EXAMINATION OF

Pu-Al ALLOYS

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INTRODUCTION

Accurate quantitative analyses with the electron microanalyzer depend on valid expressions for converting observed relative intensities into concentrations. These expressions contain corrections for absorption, fluorescence, and atomic number differences which in turn rely on experimental values. Generally the expressions are most accurate with systems in which the elements do not differ a great deal in atomic number. Problems arise however, in both the correction expressions and the numbers to be used in systems containing light elements and where a substantial difference in atomic number exists. In the first case the mass absorption data are usually very poor or nonexistent. In the second case the correction terms for fluorescence cannot be applied and the poorly understood atomic number correction is usually large. Analysis for aluminum in plutonium-aluminum alloys is a good example where the previously mentioned problems are evident. The mass absorption coefficient of aluminum in plutonium is reported to be zero¹ which is almost certainly incorrect. In addition, no fluorescence correction can be applied to intensity data because of the large number of plutonium X-ray lines with energies greater than aluminum $K\alpha$.

A solution to the problem is to make homogeneous standards close to the composition of the unknown specimen. This may be difficult however, so a variation of the standards technique is to utilize the empirical Ziebold-Ogilvie² equation for a binary system

$$\frac{C_A}{K_A} = a_{AB} + (1 - a_{AB}) C_A \quad (1)$$

where C_A is the concentration (weight fraction) of element A, K_A is the observed intensity of A relative to pure A, and a_{AB} is the conversion parameter (assumed constant) for element A in the alloy. One procedure is to determine K_A from a single standard and evaluate a_{AB} . A better method is to determine the extrapolated value of C_A/K_A as $C_A \rightarrow 0$ from the curve determined from several compositions in the system being studied. This also has the advantage of verifying the Ziebold-Ogilvie equation for the system.

The objective of this study was to determine if alloys and intermetallic compounds in the Pu-Al system could be correlated with equation (1) and to determine the conversion parameters of aluminum and plutonium for our instrument. (The parameter will vary with different instruments, but this will not affect the correlation.)

EXPERIMENTAL PROCEDURE

The Pu-Al system³ is characterized by five intermetallic compounds and a limited solubility of aluminum in the delta (FCC) phase of plutonium. Four intermetallic compounds (Pu_3Al , $PuAl_2$, $PuAl_3$, and $PuAl_4$) and one Pu-1.1 w/o Al solid solution alloy were made by arc melting and annealing at the appropriate temperatures. With

the exception of PuAl_2 all intermetallics were multiphase after annealing. However, there was no problem with identification in the probe because the specimen currents were monitored and matched with the linear relationship between specimen current and composition. The samples were metallographically polished, cleaned, and examined in a Materials Analysis Company Model #400 microanalyzer. Plutonium-M α and Aluminum-K α radiation lines were monitored.

RESULTS AND DISCUSSION

Figure 1 shows that the data can be correlated with equation (1). The reason for the increased scatter in the aluminum-K α plot is not known, however, it was noted that the X-ray intensity appeared to be extremely sensitive to the optical focus.

The conversion parameters calculated on an individual basis are shown in Table I. These numbers and those obtained from the extrapolation demonstrate several things to note when determining a_{AB} . The first is that equation (1) is very sensitive to small errors in concentration for low values of C_A (<10 w/o). The second is that a small error in concentration at high concentrations (>90 w/o) leads to large errors when calculating a_{AB} from each standard.

The value of the aluminum conversion parameter $a_{\text{Al,Pu}} = 2.30$ is noteworthy because of its extremely high magnitude. Values of

the conversion parameter greater than one are usually attributed to an overriding absorption effect. In this case the absorption must be very high.

SUMMARY

1. Aluminum $K\alpha$ and plutonium- $M\alpha$ radiation can be correlated with the empirical Ziebold-Ogilvie equation.
2. The data indicate a very strong absorption effect which is not predicted by mass absorption data. Therefore the Ziebold-Ogilvie technique must be used to obtain accurate analyses of aluminum in plutonium-aluminum alloys.

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TABLE I CALCULATED CONVERSION PARAMETERS OF Pu-Al

Sample	Concentration	Relative Intensity	Conversion Parameter
	<u>wt % Al</u>		<u>$a_{Al,Pu}$</u>
Pu-1.1 w/o Al	1.1	0.0048	2.31
Pu ₃ Al	3.6	0.0153	2.40
PuAl ₂	18.4	0.0887	2.32
PuAl ₃	25.3	0.129	2.29
PuAl ₄	31.1	0.161	2.35
	<u>wt % Pu</u>		<u>$a_{Pu,Al}$</u>
Pu-1.1 w/o Al	98.9	0.980	1.83
Pu ₃ Al	96.4	0.962	1.06
PuAl ₂	81.6	0.754	1.45
PuAl ₃	74.7	0.671	1.45
PuAl ₄	68.9	0.599	1.48

FIGURE 1.
Ziebold-Ogilvie Plot of Al-K α
and Pu-M α Radiation Obtained
from Pu-Al Standards

TECHNIQUES FOR IDENTIFICATION OF MICROQUANTITIES OF
CORROSION PRODUCTS ON MINIATURIZED ELECTRONIC COMPONENTS

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ABSTRACT

A technique is discussed for removing and identifying microquantities of corrosion products on miniaturized assemblies. This technique involves extraction replication and use of electron microscopy, electron diffraction and microprobe analyses. In the case studied in this investigation, the corrosion product was found to consist of both Pb_2O_3 and Cu_2S . The presence of the Cu_2S led to a detailed study of the entire production process and the eventual solution of a serious production corrosion problem.

*Mound Laboratory is operated by Monsanto Research Corp. for the Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

● Miniature electronic components which consist of pure copper and soft solders were observed to exhibit corrosion of an undetermined origin. This corrosion was in sufficient quantity to cause rejection of the completed part although the quantity of corrosion product was extremely small. Since the corrosion appeared to occur randomly and at different steps in the production process, identification of the components of the corrosion product was essential to solution of the problem.

The components studied in this investigation consisted specifically of high purity copper electrodes molded in asbestos-filled diallyl phthalate between which a precious metal bridge-wire was soldered with a soft solder of composition (wt %) 37.5 Pb - 37.5 Sn - 25 In.

Two forms of corrosion product were most prevalent on these assemblies. The solder mound was partially covered by a brown adherent film with a black crystalline appearing material around the base. Figure 1 (80X) shows a typical corroded sample, although the amount of material present on this sample is sufficient to cause rejection, it is still a very small quantity where the usual identification or analytical techniques must be applied.

A number of different analytical techniques were used in the study of this corrosion problem, but the small quantity of material present limited the type of analyses which could be performed. Emission spectroscopy on the product was attempted but the results were inconclusive and no regular chemical analyses could be obtained on these samples. Ordinarily x-ray powder diffraction techniques will furnish identification of small quantities of crystalline materials but the x-ray results on samples removed from these assemblies were generally inconclusive and good patterns were not obtained because of the microquantity of sample.

In light of these limitations on sample quantities, electron microscopy techniques were then investigated as a method of studying the product. Extraction replicas were made of the corroded assemblies using standard cellulose acetate tape and acetone solvent. Figure 2 (80X) shows a typical solder mound extraction replica with the location of the corrosion product clearly defined. Carbon was then vapor deposited on the replica surface at an angle of approximately 75° . The replica was rotated 180° and a second carbon deposition made to a total thickness of approximately $400 \text{ \AA}$. Rotation of the replica was necessary because the sides of the solder mound would be

parallel to a 90° deposition angle, and at any angle less than 90° there will be a shadowing effect which would prevent complete coverage of the replica.

After the carbon deposition step was completed the cellulose acetate replicas were dissolved away from the carbon substrates using successive acetone rinses. The corrosion product was retained in the carbon film and studied directly in the electron microscope.

Using these techniques to study a number of the corroded assemblies the primary components of the corrosion products were identified as Pb_2O_3 and Cu_2S . Figure 3 (5600X) is an electron micrograph showing both types of the corrosion product. Diffraction patterns associated with Pb_2O_3 were obtained from areas showing predominantly the acicular phase and patterns associated with Cu_2S were obtained from the globular masses. Figure 4 is a portion of a microprobe trace which was made of the globular particles with the electron microprobe attachment of the electron microscope at ORNL. The characteristic reflections are those of copper and sulfur; no other elements were detected.

The process of extraction replication also removes some of the components of the inert plastic. For example a segment of the asbestos fiber filler material outside of the corrosion area was identified as serpentine. This points out the importance

of locating the corrosion product on the replica at moderate magnifications on the light microscope so that only the materials of importance to the corrosion problem are studied in the electron microscope.

In the corrosion problem studied here replication and electron microscopy techniques furnished a convenient and successful method of identification of microquantities of corrosion products.

I would like to express my thanks to Ralph Gehlbach, Oak Ridge National Laboratory, Oak Ridge, for obtaining the microprobe analyses of the corrosion product.

Figure 1 Typical corroded sample (80X).

Figure 2 Plastic replica showing corrosion product removed from the part (80X).

Figure 3 Electron micrograph showing both types of corrosion product (5600X).

Figure 4 Microprobe trace showing characteristic reflections obtained on typical globular corrosion particle.

Metallography of Helium-Embrittled Incoloy 800

by

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Abstract

Helium was injected into small tensile samples of Incoloy 800 by α bombardment to the level of 4×10^{-5} atom fraction. Subsequent tensile testing between 500°C and 800°C revealed a loss in ductility, as measured by elongation at failure, with increasing temperature.

Reduced ductility was always accompanied by partial or total intergranular failure, as determined by light and electron metallography techniques. Intergranular cracks originated as small voids adjacent to grain-boundary carbide particles, presumably through grain-boundary sliding. The presence of helium bubbles at grain-boundary carbide particles reduces the time required to nucleate a void through grain-boundary sliding, thus causing premature failure.

This embrittlement mechanism is the same as that described for types 304 and 316 stainless steel.

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Introduction

The loss of high temperature ductility in stainless steel, when used as a cladding material in nuclear reactors, has been the subject of several investigations.^(1, 2, 3, 4, 5) The problem of helium embrittlement is of major importance with regard to fast breeder reactors where all the major alloy constituents of a fuel cladding will transmute to other isotopes yielding helium and hydrogen⁽⁶⁾ as by-products. Embrittlement is manifested as a loss in ductility at elevated temperatures ($> 500^{\circ}\text{C}$) and can be brought about with as little as 10^{-6} atom fraction helium.

Experimental

In order to study helium embrittlement without resorting to lengthy reactor irradiations, small tensile samples (.009" x .040" x 1.0") were injected with helium by cyclotron irradiation to a concentration of 4×10^{-5} atom fraction. The composition of Incoloy 800 and the heat treatment given to the samples prior to injection are shown in Table I.

Table I

Composition (wt %)

<u>Ni</u>	<u>Cr</u>	<u>C</u>	<u>Cu</u>	<u>Al</u>	<u>Ti</u>	<u>Si</u>	<u>Mn</u>	<u>Fe</u>
32.4	19.3	0.03	0.16	0.10	0.20	0.26	1.05	Bal.

Heat Treatment

1 hr 1010°C then 100 hr 760°C

The combined techniques of light and electron metallography were used to examine samples tested at 500°C to 800°C . Light photographs were

taken and used to determine the overall density and distribution of the larger voids. They also give some measure of gross intergranular cracking. Fractographic impressions were taken (using a two-stage replica technique) and examined to determine the mode of failure.

The sites where the macro-voids (as seen in light microscopy) originated were determined by making a replica of a plane parallel to the tensile axis. Great care was taken to achieve a surface free of artifacts. These replicas revealed incipient voids not resolvable using light microscopy techniques. They are usually adjacent to grain-boundary carbide particles and can be as small as $2000\text{\AA}$.

The foils were first chemically thinned to 50-75 microns and then brought to electron transparency electrolytically using 10 parts acetic acid to one part perchloric acid. The cell voltage applied varied from 10 to 15 volts.

Results and Discussion

The total elongation during tensile testing is plotted as a function of test temperature in Figure 1. At 500°C , both the control and helium containing samples failed transgranularly by the shear-rupture mechanism (microvoid coalescence).

Fractographs of the control and helium-containing samples tested at 700°C are seen in Figures 2 and 3. The control sample (Fig. 2) failed transgranularly as evidenced by the shear-rupture dimples (though not well developed). The helium-containing sample (Fig. 3) failed intergranularly.

This is clearly indicated by the grain-boundary triple point at point A. Lines drawn to points, B, C, and D delineate the actual boundaries. The control sample tested at 800°C, as seen in Figure 4, failed in a mixed mode (intergranular and intragranular) and the helium-containing sample failed in an intergranular manner (Figure 5). Again a grain-boundary triple point is clearly discernible.

Replicas taken on a plane parallel to the tensile axis reveal incipient voids not resolvable using light microscopy. Figure 6 shows a void adjacent to a grain-boundary carbide particle in the helium-containing sample tested at 700°C. Samples tested at 800°C with and without helium have voids at grain-boundary carbides, as seen in Figure 7. The number of voids present in the helium-containing sample is far greater than in the control sample.

The thin foil (Figure 8) shows helium bubbles ranging from 40Å to 300Å in size. The smaller bubbles were primarily in the matrix with the larger ones either isolated in a grain-boundary or attached to a grain-boundary carbide particle.

Conclusions

- 1) The loss of ductility is associated with premature intergranular cracking which originates at grain-boundary carbide particles, presumably through grain-boundary sliding.
- 2) The presence of helium bubbles at grain-boundary carbide particles is responsible for this premature failure by reducing the time required to nucleate a void.

- 3) This embrittlement mechanism is the same as that described for types 304 and 316 stainless steel.

Acknowledgment

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Figure 1. Total elongation as a function of test temperature for Incoloy 800.

Figure 2. Fractograph of Incoloy 800 without helium tested at 700°C, showing shear-rupture dimples.

Figure 3. Fractograph of Incoloy 800 containing 4×10^{-5} atom fraction helium showing intergranular failure. Tested at 700°C.

Figure 4. Fractograph of Incoloy 800 tested at 800°C showing mixed (intergranular and intragranular) failure.

Figure 5. Fractograph of Incoloy 800 containing 4×10^{-5} atom fraction helium showing intergranular failure. Tested at 800°C.

Figure 6. Replica electron micrograph of Incoloy 800 containing 4×10^{-5} atom fraction helium showing a void adjacent to a grain-boundary carbide particle. Tested at 700°C.

Figure 7a. Replica electron micrograph of Incoloy 800 tested at 800°C and containing no helium showing voids adjacent to grain-boundary carbide particles.

Figure 7b. Replica electron micrograph of Incoloy 800 containing 4×10^{-5} atom fraction helium showing voids adjacent to grain-boundary carbide particles. Tested at 800°C.

Figure 8. Transmission electron micrograph of Incoloy 800 containing 4×10^{-5} atom fraction helium showing helium bubbles. Tested at 800°C.

THE METALLOGRAPHY OF A VARIETY
OF UC AND (U,Pu)C MATERIALS

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ABSTRACT

The metallography facility and procedures used for the metallographic preparation of a variety of UC and (U,Pu)C samples are described. UC and (U,Pu)C samples having a wide range of carbon and oxygen contents and also the same materials stabilized either with Fe or Cr_{23}C_6 are examined. Compatibility couples, comprising the above carbide materials against a variety of stainless steels and vanadium alloys are also evaluated.

The preparation procedures described include mounting, grinding and polishing as well as chemical, electrolytic and vacuum cathodic etching of samples for optical microscopy.

Note: Work performed under AEC Contract AT(30-1)-3791.

1. INTRODUCTION

Metallographic facilities for handling plutonium-containing materials at various laboratories have been described by several authors. (1-6) This paper describes such a facility operated by the Ceramic Development Group of Westinghouse Advanced Reactors Division. The principal function of this group is to manufacture and characterize various potential fast reactor ceramic fuels of interest to the Division. These include oxides, nitrides, but currently all work is being undertaken on uranium and mixed uranium-plutonium carbides, having compositions ranging from stabilized hypostoichiometric to hyperstoichiometric. The stabilizers used to date have been Cr_{23}C_6 and Fe, although programs including the latter have recently been de-emphasized. The metallography facility has been developed not only to examine such ceramic materials, but also compatibility couples comprising these and potential cladding materials. The philosophy of design was such that all necessary metallographic procedures could be accomplished within the confines of gloveboxes, and at no time would specimens be brought out into the open laboratory as is the practice in certain facilities. (2)

2. LABORATORY DESCRIPTION

The plutonium facility contains a total of 11 double-faced gloveboxes which are constructed of stainless steel and arranged in two parallel lines. The facility is considered "permanent" and consequently easy access for maintenance and replacement of equipment has been allowed for. In the first line of interconnected gloveboxes, all fabrication of carbide materials is undertaken. Work in the second line, consisting of five boxes, each 8 ft. long by 4 ft. wide by 3 ft. high, is concerned with the characterization of these materials. Characterization facilities include analytical chemistry, metallography,

immersion density, and particle characteristics; differential thermal analysis, thermogravimetric analysis, and thermal dilatometer equipment are currently being installed.

Four of the five boxes in the characterization line are interconnected and employ continuously-flowing, recirculated dry argon to provide an inert atmosphere. The metallography facilities are contained in this section of the line. The dry, purified argon is passed through these boxes at a maximum rate of 50 cu. ft./min., producing a total atmosphere change of approximately 18 times/hour. Argon purity is usually maintained at <1 ppm water and 100 ppm oxygen and the pressure held in the boxes at about 1/2-inch water negative with respect to room pressure. It has been observed with carbide samples of all compositions, that relatively large increases in oxygen content, e.g., 300-400 ppm, do not adversely affect them. However, a relatively small increase in water content, e.g., 10-20 ppm, causes rapid oxidation of sample surfaces. Unfortunately for metallographic operations, the design of the overall facility did not permit the use of a once-through type of inert atmosphere when first commissioned, i.e., the one which is generally employed at other laboratories. Although the technique of using recirculated argon causes some restrictions in practice, e.g., all solvents and lubricants have to be dried before entry into the line and aqueous acid etching must be kept to a minimum, these are not too great when considered in the light of the overall glovebox operation. Furthermore, a small single box located away from the line and employing a once-through type inert atmosphere, is currently being considered for all electrolytic and swab etching operations. However, for someone embarking only on the design of a metallography facility, the use of a recirculated atmosphere is questionable.

Because of criticality hazards and for accounting purposes, all samples are weighed prior to their entry into the facility. Pellet dimensions and metallographic mount thickness before and after examination are recorded so that at any time the total amount of plutonium in the boxes is known. Estimates of plutonium content of etchants and polishing slurries can also be made.

The present layout of the laboratory is shown in Figure 1, and it can be seen that the metallography facility occupies one whole box and approximately half of two others in the characterization line. The "dirty" section of the metallography facility, i.e., a cut-off wheel, etching facilities, and a sludge filter is located in one box; mounting, grinding, polishing equipment in the middle box; and the vacuum cathodic etcher and microscope in the third box. A large plexiglass screen, with closable transfer doors is placed across the middle box, so that the fine polishing is separated from the mounting and grinding operations. The flow of argon is in the direction from the polishing to the grinding areas to minimize possible contamination of the polishing wheels with mounting and grinding debris. Figure 2 is a general view of the suite of boxes in the characterization line and a section of those in the fabrication line. The Zeiss-Polaroid camera seen in the foreground fits into the eyepiece tube of the Unitron microscope and is currently the only technique available for obtaining photomicrographs.

Standard commercial metallographic equipment has been used in the facility in every instance and no major problems have been encountered in running such equipment in a dry argon atmosphere. It was thought that the motors used in the polishers would burn out readily, as they were the brush type. However, after nine months of almost continuous use, no such failure has occurred. Tools

and electric leads are suspended from hooks in the ceiling of the boxes to keep as many items off the floor as possible. This greatly assists in keeping the box tidy and enables equipment to be moved relatively easily.

As with all facilities of this type, a rigorous discipline is necessarily maintained in the areas of cleanliness and metallographic procedures. This is essential not only for handling plutonium-bearing materials, but also to obtain the best metallographic results.

3. SPECIMEN MOUNTING

Three types of specimen mounting have been successfully used:

a. Conventional Hot Mounting with Bakelite

This technique was employed before the installation of the vacuum cathodic etcher. A standard Buehler hot mounting press is used, producing 1-1/4-inch diameter mounts. The press is firmly attached to the box floor by studs which run through the press base, so that it is rigidly held when a sample is being mounted.

Various bakelite powders were investigated and it was found that the "black" type marketed by Buehler gave the best results with carbide materials. This was anticipated to some extent as it is the hardest of the species when fully cured.

Numerous UC and (U,Pu)C samples have been mounted using this technique, and in no instance has damage to the sample been observed. The nature of the samples ranged from portions of arc melted buttons to longitudinal and transverse sections of sintered pellets. Indeed, the very limited amount of cracking that has been observed in pellets could in all instances be attributed to pressing or sintering defects.

b. Hot Mounting with Pre-Molds for Use in Conjunction with the Vacuum Cathodic Etcher

This is the conventional technique used when samples are to be vacuum cathodically etched. Samples are hot mounted as in (a) above, but instead of using bakelite powder, pre-molded bakelite sections of the mount are employed with a plug of copper impregnated bakelite to provide back-electrical contact. A variation of this technique, which has been successfully employed in producing samples for vacuum cathodic etching, and circumvents the use of expensive pre-molds, has been to lay down a layer approximately half the sample thickness of conventional bakelite powder and fill the rest of the die with copper impregnated bakelite, the latter being electrical conducting. This method has also been very successful in providing back contact to samples for electrolytic etching.

It has been found that a serious drawback to the use of pre-molds in a glovebox environment is that after 24-36 hours in a dry argon atmosphere, the molds begin to crumble and eventually collapse. This is presumably caused by the removal of water, which has acted as a binder. Consequently, only the number of pre-molds that are required immediately are posted into the box.

c. Cold Mounting

A variety of cold setting resins has been investigated and the most successful for our applications was found to be AB plastic epoxide. Following the manufacturer's instructions, it cures completely in 3-4 hours with little or no shrinkage away from the sample, thus minimizing the chances of staining during later operations. This type of resin has also been used to vacuum impregnate low density samples that required strengthening for metallographic preparation. A mount arrangement similar to the one described

by Hodkin and Haines⁽¹⁾ in providing back electrical contact for electrolytic etching has been successfully tried, and once again AB epoxide was used as the filler material.

Having investigated the various mounting techniques available, it has been found that method (b) outlined above provides the best and most versatile mount for our requirements, i. e., one in which the sample can be vacuum cathodically, electrolytically, or swab etched without problems.

4. MECHANICAL GRINDING AND POLISHING

Standard Buehler equipment is employed for this work, all completely enclosed in the glovebox. Figure 3 is a view of the low speed grinder with the mounting press in the foreground. Additional corner feet have been fitted to the grinder to lift it some 3 inches further from the floor. This was found necessary to provide sufficient ventilation to the gearbox and motor and prevent their breakdown by overheating. Coupled to the grinder is the Automet attachment, which takes five samples at one time, the head fitting conveniently into the cylindrical stainless steel tank of the ultrasonic cleaner. Dried kerosene, which is applied at a drip feed, has been found to be satisfactory as a lubricant in this operation with dried Xylene in the ultrasonic cleaner. After cleaning, specimens are washed in "200"-proof absolute alcohol and dried by a pressure pad of tissue or cotton.

Conventional adhesive-backed silicon carbide grinding papers (120-600 mesh) are used. Diamond impregnated grinding discs have been investigated, but the only one found to be satisfactory was the 120 mesh. The latter is used when the longitudinal section of a pellet has to be examined and excessive grinding is consequently required.

Some difficulty has been experience in the operation of the ultrasonic beaker because of the easier electrical discharge possible in an argon environment-- in particular, breakdown of insulation in the amphenol plug fitting mounted on the side of the beaker. This has been overcome by removing the amphenol fitting, running a continuous lead from the connectors in the roof of the box directly into the beaker, and then packing the whole of the vibrator unit, located in the base of the beaker, with epoxy resin. Power is transmitted through the box shell by means of insulated 3/8" diameter copper rods. Figure 4 shows the installed polishing equipment, i.e., both mechanical and vibratory polishing. The high speed mechanical polisher is raised approximately 3 inches, as per the grinder, and the Automet attachment is also used. The polishing media are diamond pastes in grades ranging from 6 micron down to $\frac{1}{4}$ micron. Metadi fluid was originally used as the lubricant, but was observed to cause rapid oxidation of both UC and (U,Pu)C samples. Subsequent analysis of the fluid revealed it contained large quantities of water, despite assurances to the contrary by the vendors. Since that time, the technique has been to saturate the cloths with high quality silicone oil, add and smear the diamond paste, and during polishing, lubricate with a drip feed of dried kerosene. AB metcloth is used with the 6 micron wheel to give better cutting, and microcloth used on the 1 and $\frac{1}{4}$ micron wheels to give a good, scratch-free polish. Approximately 20 minutes on each wheel is required to give the best results on five samples at one time. This technique gives excellent results and consequently little vibratory polishing work has been undertaken. In fact, the vibratory polisher was bought in anticipation of compatibility samples going through the line,

where both hard and relatively soft materials have to be polished concurrently in one mount, and this type of polishing is probably preferable to mechanical. Slurries of γ -alumina in dried Xylene have given excellent results with the vibratory polisher--also a very thin slurry of a $\frac{1}{4}$ micron diamond paste in silicone oil with a microcloth as the base.

One point of interest worth mentioning at this time, in connection with mechanical polishing, is the following: several samples of UC and (U,Pu)C of different compositions have exhibited an "orange-peel" effect, similar to the one observed when polishing soft metals. This invariable occurred on the 1 micron wheel, and since this stage was eliminated, the effect has not been observed.

Spillage from the grinding and polishing operations is collected directly in polyethylene bottles and then filtered through vacuum funnels. The residue is heated at 1,000°C in air to insure complete oxidation of carbide debris and reduce the overall volume. A sample is taken for plutonium and/or uranium²³⁵ content, and the remainder sent for recovery. The filtrate is then absorbed on "kitty-litter" and buried with the remainder of active trash.

5. ETCHING TECHNIQUES

Currently, three types of etching are utilized: namely (1) swab etching, (2) electrolytic etching, and (3) vacuum cathodic etching.

It had originally been hoped that all etching would be undertaken in the vacuum cathodic etcher. Not only would this eliminate the problems associated with the corrosive properties of acid solutions in the line, but also those from the standpoint of nuclear safety, i.e., introduction of liquids into plutonium-handling gloveboxes should be kept to a minimum.

Furthermore, if acid etching is undertaken in a separate box, extra capital

investment is necessarily required, and there are also the associated problems of transferring samples from one box to a separated one.

Three compositions of carbides are currently being investigated by WARD, namely, hypostoichiometric, Cr_{23}C_6 stabilized hypostoichiometric, and Fe-stabilized hypostoichiometric. Fuel samples of these compositions have recently been inserted in GETR and were characterized metallographically before insertion in pile. Swab etching with 65% orthophosphoric acid has given excellent results with the three compositions, particularly the Fe-modified and (U,Pu)C arc melted buttons. It was necessary, however, to "age" the new orthophosphoric acid before use to obtain a desired control and subsequent results.

A limited amount of swab etching has had to be undertaken in an attempt to differentiate between traces of metal and sesquicarbide phases in carbide samples. The technique proposed by Chamberlain and Paige⁽⁷⁾ has been utilized. This consists of electroetching the specimen to produce a clean, film-free surface and show delineation of phase boundaries. The surface is then etched for periods up to two minutes in a solution of 10 v/o bromine in methyl alcohol. This latter solution, which was discovered by Mahla and Nielsen⁽⁸⁾ working on carbide inclusions in steels, attacks any metallic phases, but does not attack carbides or other non-metallic constituents. Specimens have had to be prepared carefully if reproducible results are to be obtained.

For electrolytic etching, a Buehler Micromet is employed, the control unit being located outside the box line. Although it does not perhaps give the maximum desirable voltage, electropolishing and etching results to date have been more than satisfactory. Stainless steel electrodes are employed and the

etchants are contained in a polyethylene cup.

With this type of etching, the original technique consisted of totally immersing the mount in the solution and touching the probe electrode onto the center of the carbide sample. This yielded a very uneven etch. An excellent, definitive etch combined with a superior control has resulted from the use of copper impregnated mounts in conjunction with back application of the electrode, particularly with the Cr_{23}C_6 -stabilized material. Two etches have been used to date, namely equal parts of sulphuric, acetic, and lactic acids, and equal parts of nitric, acetic, and lactic acids. The latter, however, deteriorates rapidly and almost all electrolytic etching is now done with sulphuric-acetic-lactic. Typical etch conditions are 5 volts (open circuit) for 30 seconds. As with swab etching, this solution had to be "aged" prior to use to yield the best results. After wet etching, samples are washed with absolute alcohol and dried by a pressure pad as previously described. There are several potential hazards associated with this section of the work; acids, electrolytes, and solvents all attack neoprene gloves rendering them tacky and reducing their mechanical strength. Consequently, a very close watch is kept on the gloves used in these operations. To avoid pollution of the glovebox atmosphere, the various liquids are left out of their stoppered containers for as short a time as possible, and the maximum flow of argon maintained to sweep the various vapors out of the boxes and into the argon purifier. With solvent vapors, there is always the risk of fire, and solid fire extinguishants are kept at convenient places in the boxes.

A NUMEC Model 4 CVG vacuum cathodic etcher has been installed in the line, and excellent results have been obtained to date, not only with carbide materials, but also stainless steels, Inconel 600, and vanadium alloys.

Nevertheless, limitations to its use were discovered in the course of operation, which periodically caused recourse to alternative techniques. In particular, a sample having a porosity exceeding 14%, or one containing cracks became badly stained during the etching discharge. This was thought to be the result of breakdown of foreign matter which had become entrapped within the pellet during the grinding and polishing operations. Efforts to overcome this effect included prolonged ultrasonic cleaning, vacuum outgassing at 50°C, and impregnation of the polished face with an epoxy resin. This last technique excluded the presence of dirt particles, but entertained possible epoxy breakdown during vacuum cathodic etching. Mixed success with this technique points to other factors as yet not fully evaluated. For instance, it is known that a prolonged discharge causes breakdown of unprotected bakelite mount material; consequently, a teflon sheilding disc is often placed over the mount which exposes only the pellet area. Nevertheless, the use of low potentials for short durations, with lengthy cooling intervals, has resulted in good etches even when no shielding was used. Another disadvantage of the vacuum cathodic etching technique lies in the variation in the degree of etching which occurs across the face of some samples, the central area being etched more deeply. Teflon shielding discs with slit aperatures have been used in an attempt to overcome this etching gradient, but the effect has not been completely eliminated with certain samples, particularly the Fe-stabilized.

Some further development is obviously going to have to be undertaken to eliminate these problems, but we are reasonably pleased with the performance of the etcher to date.

The power supply controller(A) and vacuum equipment (B) of the cathodic

etcher are located outside the glovebox, as shown in Figure 5. Figure 6 shows the belljar, which is the etching chamber, and is the only portion of the unit located inside the glovebox. Bottle argon, having a total impurity content of 300 ppm, is fed to the etcher at a pressure of approximately 2 psi. For carbide samples, a typical etching time is 4 minutes (in cycles of 30 seconds with power on and 30 off to prevent overheating) at 1.5 kv and 150 microns indicated argon pressure.

6. MICROSCOPY

Photomacrographs, up to a magnification of approximately X20, have been taken by a Burke-James Press camera, located outside the glovebox. The sample to be photographed is held in contact with a cleaned section of the glovebox window, by means of adhesive tape and the position of the camera adjusted to obtain the best view. No spot lights are used, but some care is obviously required to prevent reflection and glare from the windows, affecting the quality of the shot. Figure 7 is a typical example of the quality obtainable. This is a photomacrograph of a sintered UC pellet (X10.5) showing the classical pressing defects of capping and pressure lining. Fortunately, this is not typical of the products from our fabrication line! A typical photomacrograph of a sound UC pellet (10.5) is shown in Figure 8, which also demonstrates the phenomenon of the orange-peel effect referred to earlier. For routine microscopical examination and photomicrography, a Unitron MeC monocular microscope has been installed in the line (see Figure 9). Because of its low cost, it is considered an expendable item. This has four magnifications, namely X50, 100, 200, and 400. In conjunction with the Zeiss camera, which fits into the eyepiece tube, photomicrographs having magnifications ranging from X75 to X600 can be produced.

The α -sealing arrangement on the microscope is similar to that described by Hodkin and Haines.⁽¹⁾ The standard eyepiece tube is brought out of a

regular gloveport in the box through a P.V.C. sleeve, this sleeve being sealed by two "O" rings into a nylon flange (see Figure 2). This flange is attached to the tube in a leak-tight manner by means of epoxy resin, the outer seal being made in the normal manner onto the gloveport. Although no leak has developed, it would be a relatively simple matter to cure one, by applying additional coatings of epoxy resin. This resin has also been applied to the lens-eyepiece tube interface such that eyepiece lenses also act as a physical barrier to prevent release of activity through the inside of the microscope, and maintain atmosphere integrity.

Routine metallographic examinations are made of carbide pellets to determine pore size and nature of distribution in the as-polished condition, e.g., Figure 10, which is a micrograph of a Cr_{23}C_6 -stabilized (U,Pu)C sample, (mag.X75). Typical etched structures are shown in the next sequence of figures. Figure 11 (mag. X300) shows the typical structure of the same sample shown in Figure 10, which was one of the first such pellets produced in the Ward Plutonium Laboratory. This pellet has been etched for six seconds in 85% orthophosphoric acid and it will be seen that gross segregation of the $\text{Cr}_{23}\text{C}_6 + \text{Cr}$ phase (white areas) has occurred in the (U,Pu)C produced by the stabilizing additions of Cr_{23}C_6 . Further from these islands are light grey areas, which comprise the original (U,Pu)C matrix. In recently produced Cr_{23}C_6 -stabilized pellets, a more uniform distribution of the $\text{Cr}_{23}\text{C}_6 + \text{Cr}$ phase has been achieved in the grain boundary regions.

Figure 12 (mag. X300) shows a typical view of an Fe-stabilized (U, Pu)C pellet. The grain boundary phase is $(\text{U, Pu})\text{Fe}_2 + \text{Fe}$. This sample has been swab etched in 85% orthophosphoric acid.

In Figures 13-15, which are the micros of the same sample, different aspects of the three etching techniques are quite apparent. The sample is a Cr_{23}C_6 -stabilized (U, Pu)C pellet and the magnification is X600 in every case. Figure 13 is the cathodically etched structure. Figure 14 is the electrolytically etched structure (1:1:1 sulphuric, acetic, lactic) and Figure 15 the swab etched.

7. FUTURE DEVELOPMENTS

The following items are considered essential to improve the metallographic facility.

- a. A Leitz MM5 metallograph is being purchased, specially modified by Leitz for glovebox operation. This is necessary for taking high quality photomicrographs.
- b. There is a necessity for an "in-line" microhardness tester, particularly as Ward is proposing to increase the number of carbide compositions. Various types are currently being examined.
- c. We propose installing an optical particle size analyzer in conjunction with the metallograph. Currently a small amount of work is being undertaken mounting powder samples in "permount" on glass slides, and examining these under the microscope.
- d. As stated previously, an out-of-line box is required for acid etching operations.

8. CONCLUSIONS

Within the time and space available, a satisfactory plutonium metallography facility has been assembled. This is currently being extended to improve the overall capability. Only a minimum number of modifications have had to be made to standard commercial equipment for use in the facility, and

during almost 12 months, no major accident has occurred justifying the procedures adopted. If the current rate of samples is maintained, the metallography facility will handle approximately 500 specimens per annum.

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Figure 1 Schematic Layout of the Laboratory

Figure 2 General View of the Characterization Suite of Boxes

Figure 3 Mechanical Grinding Machine

Figure 4 Mechanical Polishing Equipment

Figure 5 Characterization Suite Showing Power Supply Controller and Vacuum Equipment of Cathodic Vacuum Etcher

Figure 6 Belljar Etching Chamber of Cathodic Vacuum Etcher

Figure 7

Photomacrograph of a Sintered UC Pellet
Showing Pressing Defects

Figure 8

Photomacrograph of a Sintered UC Pellet
Showing an "Orange-Peel" Effect (X10.5)

Figure 9 Unitron Monocular Microscope in Box Section

Figure 10

Photomicrograph (X75) of the Pore Distribution in a Cr_{23}C_6 -Stabilized (U,Pu)C Pellet

Figure 11

Photomicrograph (X300) of a Cr_{23}C_6 -Stabilized (U,Pu)C Pellet Etched in 85% Orthophosphoric Acid

(4.34% C, 1179 ppm O_2 , 140 ppm N_2 , 17.86% Pu, 4.2% Cr)

Figure 12

An Fe-Stabilized (U, Pu)C Sample Swab
Etched in 85% Orthophosphoric Acid(300X)
(4.44% C, 3,080 ppm O₂, 1,477 ppm N₂,
21.1% Pu, 2.1% Fe)

Figure 13

A Cr₂₃C₆-Stabilized (U,Pu)C Pellet
Vacuum Cathodically Etched (600X)
(4.71% C, 2919 ppm O₂, 27 ppm N₂,
18.8% Pu, 1.9% Cr)

Figure 14

A Cr₂₃C₆-Stabilized (U,Pu)C Pellet
Electrolytically Etched in 1:1:1
Sulphuric-Acetic-Lactic Acids

(4.71% C, 2,919 ppm O₂, 27 ppm N₂, 18.8% Pu, 1.9% Cr)

Figure 15

As Figure 14, Swab Etched in 85%
Orthophosphoric Acid

ELECTRO-MECHANICAL POLISHING OF
SOME REFRACTORY CARBIDES
CONTAINING GRAPHITE

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ABSTRACT

The refractory carbides with associated graphite phases have been polished using the electro-mechanical polishing technique. This method yields a surface with less flowed material than does standard mechanical polishing methods. The procedure has been adapted for polishing graphite and predominately graphitic matrices for optical microscopic examination.

INTRODUCTION

The physical limitations of many materials at very high temperatures have led to the development of a class of materials which possess some useful characteristics under these extreme conditions. The materials developed were composites of graphite and refractory metal carbides and methods for joining graphitic materials. The high temperature materials examined were NbC + C, TaC, NbC + TaC + C and refractory metal brazed graphite.

CARBIDE COMPOSITES

In any alloy or process development, metallography has a key role in evaluating the product. In this program, the materials proved difficult to polish to a flat surface because of their great differential hardness and because of the large areas involved - up to one-third of a square inch. Published hardness values in kg/mm² are: NbC, 2000 to 2400; TaC, 1400 to 1800; Graphite, 10 to 20. Previously, the very hard pure carbides and the softer but large area specimens were polished using the Automet apparatus using Metcloth and one micron diamond abrasive. When this method was used for the composite specimens the results were unacceptable. Figure 1 shows a flake of graphite flour in a NbC matrix. The surface of the graphite was pitted, not well polished and in some instances the graphite-carbide interface was poorly defined. Figure 2 shows a specimen of NbC + C in which the carbon was varcum flour. This specimen polished quite satisfactorily with the Automet apparatus because the varcum flour was reported to have an amorphous structure and certainly appeared to be very finely divided. The Whirllymet polishing apparatus was found to give an over-all flatter surface, but still

the graphite was not well polished. Figure 3 shows a lower magnification view of the structure of the NbC + C specimen. Figure 4 shows the rough graphite surface. Figure 5 shows a not uncommon effect in which a graphite flake had been eroded or "dished out" in the polishing process.

For the past three years, these hard to polish composites have been prepared by adding an extra step to the Whirlmet polished specimens. This final polishing method has been one using the Relapol electro-mechanical apparatus made by Struers Scientific Instrument Company. With this apparatus, the specimen which is commonly the anode is polished mechanically using one micron diamond abrasive on a polishing cloth and is simultaneously attacked by the application of direct current through a suitable electrolyte. The apparatus uses a flat stainless steel disc as the cathode on which the polishing cloth is attached by means of a draw string. Of the three cloths available for this disc only the lowest nap cloth, designated RC-1, has proven satisfactory. This cloth is remotely similar to Metcloth but has a much more open weave. The three cloths are chemically resistant to many electrolytes.

One micron diamond abrasive was charged to the cloth and for these composite specimens an electrolyte consisting of 10% HF (49%) in water was used. The NbC + C composites have been successfully electro-mechanically polished using a current density of 0.1 amperes per square inch. Currents from 0.2 milliamperes to 2 amperes are readily obtained with the Relapol equipment. Figure 6 shows the general structure of a polished NbC + C composite. Figure 7 shows the as-polished microstructure at higher magnification. The graphite flakes and carbide matrix were in the same plane and the graphite particles were not eroded. The structure of the graphite flakes was revealed by what was thought to be a film deposited by the electro-mechanical polishing method. This film was resistant to nearly all solvents, acid or base, but could be removed by rubbing the specimen surface with a dry cloth or tissue. It is an obvious advantage to have the structure of the graphite revealed for optical microscopy without the actual removal of material which would tend to introduce a relief condition at the carbide-graphite interface. Polishing of graphite will be discussed later in this paper. The grain structure of the NbC may be revealed by electro-etching without appreciable damage to the film on the graphite. Figure 8 shows the grain structure of the NbC after etching in 10% HF at a current density of 0.2 amperes per square inch. In general, carbides tend to show scratch-free surfaces when polished mechanically but the scratches are revealed by etching the surface. After etching the composite specimens which had been polished electro-mechanically, no scratched carbide grains were revealed indicating the excellence of the polishing method. Figure 9 shows the eutectic-type structure of arc cast NbC + C. The long, narrow graphite phase was thought to have been precipitated from solid solution and showed no internal structure. The roundish graphite phase was thought

to be part of the original graphite charge and showed a grain structure. Figure 10 shows the arc cast NbC + C after etching. The graphite was more prominent after etching.

Tantalum carbide was prepared by an identical technique. Figure 11 shows the electro-mechanically polished and etched TaC. No graphite was associated with this pure TaC and quite a bit of porosity was evident in the grain boundaries. The remarkable tendency for TaC to form etch pits yielded this cluttered structure. Combinations of NbC + TaC + C gave excellent polished specimens with the etched specimens showing the tendency to etch pit in some proportion to the TaC content.

Other carbide materials have been prepared by this technique. Figure 12 shows the structure of a specimen containing UC, ZrC and graphite. The reactivity of this specimen was greater than NbC but polished well using 0.05 amperes per square inch in 10% HF. The graphite structure was also revealed under these conditions.

BRAZING GRAPHITIC MATERIALS

The problem of polishing the bond interface between brazed graphitic materials was also one of maintaining a flat surface between the soft graphite and the hard, refractory carbide formed during brazing. The graphite used for the brazing program was high density graphite made at the Los Alamos Scientific Laboratory. This graphite was chosen because the material preparation and analysis were better characterized than most commercial graphites. Figure 13 shows the structure of the electro-mechanically polished joint in which 0.0005 inch thick Mo sheet was used to join the LASL graphite. The same 10% HF electrolyte was used but the current density was much lower. The ratio of electrical resistivities of NbC and graphite is approximately 1 to 10. Since these specimens were predominately graphite a current density of 0.01 amperes per square inch was used and found to be satisfactory; that is, the graphite-carbide interface was flat and the graphite structure was revealed by the deposited film. Figure 14 shows the etched MoC bond. The etchant used was Murakami's etchant diluted 1 to 40 in water. Figure 15 shows the fine plate-like structure of the MoC at 2000 magnification. It can be observed that the carbide-graphite interface was remarkably flat for this magnification which had little depth-of-field accommodation. Figure 16 shows the same field at 3000 magnification with only slight loss of resolution. These photomicrographs were taken using the B & L Research II metallograph which justifiably lists magnifications to 3000. Figure 17 shows an electron micrograph of the MoC-graphite interface. This graphite had been polished electro-mechanically but not cathodically etched for electron microscopic replication. The flatness of the interface is apparent.

Figure 18 shows the etched, granular structure of WC joining the graphite. Figure 19 shows an electron micrograph of this WC bond. This electro-mechanical polishing technique has been used for graphite samples joined with Ti, Zr, V, Nb, Ta, and Cr as well as the Mo and W all of which formed carbides at the brazing conditions.

Figure 20 shows that the polishing method worked well for a pyrolytic carbon coated uranium carbide bead in a graphite matrix. All components were in the same plane of view.

CONCLUSION

The electro-mechanical method used as the final preparation step for metallographic specimens containing refractory carbides and graphite has been shown to be an excellent method for keeping all components in a flat plane simplifying the subsequent etching and examination steps. For optical microscopy the anodic-type film deposited during polishing which reveals the grain structure of graphite gives an added bonus to the process.

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Figure 1 500X

Figure 2 500X

Figure 3 100X

Figure 4 500X

Figure 5

500X

Figure 6

100X

Figure 7

500X

Figure 8

500X

Figure 9 500X

Figure 10 500X

Figure 11 500X

Figure 12 500X

Figure 13

500X

Figure 14

500X

Figure 15

2000X

Figure 16

3000X

Figure 17

6000X

Figure 18

500X

Fig 20

500X

Figure 19

6000X

A METALLOGRAPHIC PROCEDURE FOR AN EXPLOSIVE MATERIAL -
RDX DISPERSED IN TNT

by

F. E. McGrath*

ABSTRACT

A procedure for the metallographic preparation of an explosive material, RDX dispersed in TNT is described. The procedure involves conventional polishing techniques using diamond abrasive as a polishing medium. Etching to reveal the microstructure of the material is described and photomicrographs and photomicrographs are presented to illustrate the results of the metallographic procedure. Precautionary measures for the safe handling of the explosive material are enumerated and discussed.

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INTRODUCTION

The development of metallographic techniques for the examination of TNT castings containing a dispersion of RDX particles was part of a feasibility study for the analytical modeling of high-explosive castings. Analytical modeling involves developing a computer program to describe the heat transfer in a casting during solidification. By calculating the heat transfer out of a casting, the time required for the casting to solidify can be calculated. The complexity of the solidification process of slurries of liquid TNT (trinitrotoluene) carrying solid particles of constituents as RDX (cyclotrimethylene trinitramine) or aluminum had previously discouraged theoretical modeling. However, successful modeling of castings was expected to result in the establishment of casting procedures for the material and advance the understanding of TNT slurry behavior during the actual solidification process. From this information, accurate control of the casting process should be possible. It was further hoped that the studies would permit making castings which were free from pipe, blow holes and other defects, which, in the end, would lead to the production of more uniform and dependable explosives.

TNT is comparatively insensitive and one of the most stable high explosives. Various materials often are added to TNT to form what are known as permissible explosives. One common additive is RDX. This material

was first prepared in 1899 by Henning⁽¹⁾ but its value as an explosive was not discovered until 1920 by Von Herz⁽¹⁾. During World War II, RDX was used on a large scale and it is one of the most powerful high explosives in use today. RDX mixed with TNT is presently used as a bursting charge for aerial bombs, mines, torpedoes, etc.

This paper describes metallographic techniques and safe handling which were developed for the RDX-TNT material.

Handling Hazard and Procedures

RDX and TNT are comparatively insensitive explosives and normally can be handled safely with little special precautions. However, grinding, polishing, and etching procedures employed in metallographic preparation can create potentially hazardous conditions which require special procedures. In small quantities, TNT will burn quietly if not confined. If large quantities burn, the accumulation of heat can cause it to detonate. Also, sudden heating of any quantity can cause it to detonate. For example, sparks, a blow from a hard object, or contact with certain chemicals could cause detonation. It has been calculated that the impact of a 2 kg weight from a fall of 14 inches is required to detonate TNT; the impact of a 2 kg weight from a fall of 8 inches is required to detonate RDX.

Due to the possible danger to the metallographer during preparation of the material, certain safety precautions were adopted and followed during handling. These precautions were as follows:

- a. Specimens were limited in size to a range of 5 to 10 grams (a size that could still cause a serious injury to anyone handling the specimens improperly).

(1) Encyclopedia of Chemical Technology, V 6, 1951, p 39.

- b. Specimens were furnished already cut to size. If sectioning had been necessary, it would have been done remotely.
- c. Specimens were not mounted, primarily to prevent them from contacting alkalies or epoxy resins which could cause reactions with the TNT which produce toxic vapors.
- d. Power-driven equipment was not used in grinding. All grinding was done by hand with the sample submerged in water.
- e. Vibratory polishing was not done since the combination of abrasives, continual vibration, contact with the edges of the polishing containment or with other specimens, and perhaps other unknowns was thought to be potentially hazardous.
- f. All handling of the specimens was done with rubber gloves since TNT can be absorbed through the skin, presenting an internal health hazard. Careful handling while wearing rubber gloves was required to avoid dropping the specimens. Rubber gloves with rough fingers were used.
- g. All etching was done under a hood.
- h. Specimens were never permitted to be struck by hard objects.
- i. Specimens were kept away from heat, fire, and sparks. Smoking was not permitted in the storage or preparation area.
- j. All particles produced during grinding and polishing, all polishing cloths, and all liquids used in preparing the specimens were collected and safely disposed. Good house-keeping was considered a very important requirement for handling RDX-TNT explosives.
- k. Samples were never unattended while being prepared metallographically. At all other times they were locked in a safe.

Metallographic Procedure

During the first attempts to prepare metallographic specimens of the RDX-TNT material, two major problems were encountered. First, due to the soft plastic nature of TNT, the elimination of grinding and polishing

scratches was very difficult. Second, the relative hardness of the RDX particles caused them to polish in considerable relief. Many different methods of grinding and polishing were tried. The most satisfactory procedure which evolved from the experimentation was as follows:

Step 1. Specimens were hand-ground on 600-grit silicon carbide paper submerged in water in a polyethylene container. The fast removal of material on 600-grit paper did not necessitate the use of coarser papers.

Step 2. Grinding scratches were removed using 1/2-micron diamond paste on a lintless-cloth covered wheel rotating at about 60 rpm.

Step 3. Final polishing was accomplished using 1/2-micron diamond abrasive on a Gamal-cloth covered wheel rotating at about 60 rpm. During polishing a light flow of water was maintained on the wheel and frequent additions of diamond abrasive to the Gamal cloth were required.

Heavy hand pressure was used during the initial polishing. A very light pressure was used during the final polishing. Polishing cloths had to be replaced frequently due to an accumulation of small contaminant particles which produced scratches. The total time required for polishing was from 5 to 15 minutes per specimen. The bulk of the time was spent removing grinding scratches during the first polishing step. If the RDX particles polished in relief during the final polishing step, the relief effect was minimized by repeating Step 2. The polishing procedure required a heavy charge of diamond abrasive on the polishing cloths and a very light stream of water flowing on the polishing wheel. As the diamond was washed out of the cloth by the flow of water, more relief and directional polishing scratches resulted. Thus, it was necessary to add diamond abrasive to the polishing cloths frequently.

Acetone, benzene and ethyl alcohol were found to be the most satisfactory etching reagents for RDX-TNT. Some results obtained from various combinations of these reagents were as follows:

- a. Acetone full strength - overetched the specimen rapidly.
- b. 10 percent acetone in water - produced the most effective etch.
- c. Benzene full strength - etched the specimen slower than acetone but roughened the etched surface.
- d. Alcohol full strength - did not produce a selective etching attack.
- e. Etch-polish with a slurry of Linde B and 10 percent acetone in water - caused the RDX particles to appear in extreme relief.

Water used on the wheel with diamond paste produced a chemical polish and to some degree an etch-polish. The etch-polishing action proved to be more satisfactory as an etchant than any of the etching reagents that were tried. Also, the structure in the TNT became more pronounced after air etching.

Results

Figure 1 contains photomacrographs which illustrate the structure in the bottom, middle and top sections of an RDX-TNT casting made in a horizontal mold. Most of the information about the solidification process was obtained from the arrangement of the RDX particles within the TNT matrix. Pronounced orientation of the more elongated RDX particles was observed in the center of the casting, indicating that cellular convection occurred. Considerable differences in porosity can be seen in relation to the freezing front. Sections from the top of the casting, the last part of the mold to freeze, have a large amount of coarse porosity. This is best

illustrated by comparing Figures 1a and 1b. Figure 1 shows that the density of RDX particles increases from the top to the bottom of the casting, indicating that, to some extent, the solid RDX particles settled to the bottom of the mold.

Figure 2 contains photomacrographs of typical structures of various RDX-TNT castings. The etched structure, Figure 2d, shows a grain structure within the TNT matrix. The grains appeared to have nucleated at the RDX particles and grown radially from them. Some small metallic particles were observed in the microstructures of some of the castings. One of these particles is shown in Figure 3. It is not known whether these particles are contaminants that were present in the mold prior to pouring or if they were in the RDX-TNT mixture prior to melting.

Summary

Metallographic examination is a practical and safe method for examining RDX particle dispersions within a TNT matrix. However, due to the nature of the material, precautions for safe handling must be observed. Conventional polishing techniques are used which simplify metallographic preparation. With more experimentation, and the use of finer grades of diamond, it is hoped that scratch-free surfaces can be obtained. It is hoped, too, that better etching techniques can be developed.

(a) Top

(b) Middle

(c) Bottom

FIGURE 1. TYPICAL MACROSTRUCTURE OF RDX-TNT CASTINGS 20X

(a)

(b)

(c)

(d)

FIGURE 2. TYPICAL MICROSTRUCTURES OF RDX-TNT CASTINGS
Magnification 100X

500X

6B104

FIGURE 3. METALLIC CONTAMINANT PARTICLE IN THE TNT
MATRIX OF AN RDX-TNT CASTING

THE METALLOGRAPHIC PREPARATION
AND MICROSCOPIC EXAMINATION OF A MOLYBDENUM
URANIUM-DIOXIDE CERMET FUEL*

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ABSTRACT

A procedure for the metallographic preparation of tungsten-coated Mo-UO₂ cermet fuels was developed specifically for their subsequent examination by replica electron microscopy. Both polishing and etching procedures were evaluated as well as replication techniques for electron microscopy. The best polishing techniques involved the use of an alumina-chromic acid slurry on rotating cloth laps. Etching of the UO₂, as well as other portions of the material, could be accomplished with a variety of etchants which would affect only specific structures. Examination of the prepared surface by replica electron microscopy could reveal fission product voids down to 100 Å in diameter.

*Work done under the auspices of the Atomic Energy Commission

INTRODUCTION

Some nuclear fuels must operate at temperatures of 2000°K with a high degree of dimensional stability. The dimensional stability is partially dependent upon the formation of fission products and their subsequent agglomeration and movement. Other factors affecting the performance of the fuel assembly involve interactions and changes of the components due to temperature and irradiation. The Mo-UO₂ cermet fuel pin in this investigation undergoes a number of microstructural changes during high-temperature irradiation; therefore, there is a need for suitable metallographic, optic, and electron microscopic techniques.

The metallographic preparation of the cermet should allow observation of the following structural details^{(1,2)*}:

1. The UO₂ fuel, with emphasis on fission gas voids, grain growth, and migration into the Mo or the W coating.
2. The Mo matrix, with emphasis on radiation damage effects and migration into the W and interaction with the UO₂.
3. The UO₂ and Mo interface where fission gas voids may agglomerate.
4. The cermet and W interface for Mo depletion and its replacement by UO₂.
5. The loss of UO₂ from the cermet.
6. The W cladding for changes in grain structure, Mo migration into grain boundaries and small voids.

*Numbers in parentheses indicate references listed at the end of the report.

The observation of fission gas voids may be the most difficult, since they are expected to develop in the 100 to 500 Å range⁽¹⁾. A microscopic resolution must then be near 50 Å to detect them as well as follow their interactions.

The purpose of the study was to develop etching techniques (for the hot cell facilities of LASL Group CMB-14) suitable for optical and electron microscopy. As the etching study was undertaken, it became apparent that the preliminary polishing was important for the evaluation of complete microstructures as well as for preparing the surface for etching. Subsequent operations showed that replication of the surface for electron microscopy was difficult; therefore, the development of suitable polishing and replication techniques was also undertaken.

EXPERIMENTAL MATERIALS AND PROCEDURES

The polishing and etching of the cermet was designed to provide as complete an examination of the microstructure and fission gas voids as possible. The examination of the microstructure by electron microscopy was hampered by pullout of the UO_2 during polishing, and replica techniques to minimize this difficulty were also evaluated.

A. Specimen Materials

The fuel pin used in this study was number 5117-R1-5 and was in the unirradiated condition. It was approximately 1/4 in. in diameter and 1-in. long with an axial hole along two-thirds its length to vent the fission gases as they formed during irradiation. The longitudinal cross section of about one-third of the fuel pin is shown in Fig. 1. The fuel was a Mo-40 UO_2 (by volume, 9.7% enriched) cermet which was vapor coated with a 0.005-in. layer of tungsten.

The cermet fuel pin was fabricated by the following technique:

1. The starting cermet materials were 4.8- μ molybdenum powder and 4.5- μ UO_2 powder.
2. The powders were hot pressed at 2070°K and 44,000 psi.
3. The pressing was then fired at 2270°K for 4 hours in argon.
4. The resulting block, 1.5 in. in diameter, was Elox-machined to fuel pin size.
5. The tungsten coating was then vapor-deposited from a $10\text{H}_2 + \text{WF}_6$ atmosphere at 550°C.

B. Metallography

The major problem encountered in the metallographic preparation of the Mo- UO_2 cermet was the cracking and pullout of UO_2 particles from the matrix during polishing. Minor difficulties were also encountered due to the hardness difference between the UO_2 and Mo, the tendency of both materials to develop disturbed layers during polishing, and the difference in chemical activity of the materials.

1. Polishing

In the rough grind stage, extreme cracking of the UO_2 resulted from all grit sizes of SiC paper disks. Most successful were the 600 grit SiC (soft*) and 3/0 and 4/0 emery papers (16-18 micron particle size ⁽³⁾). Both emery paper abrasives, when used with no lubrication, provided the least pullout of the UO_2 .

The rough polishing stage provided the toughest situation with essentially no cure for the UO_2 pullout problem. Many combinations of abrasives, cloths,

* Buehler Ltd., Evanston, Illinois

lubricants, and polishing machines were tried with no success. Abrasives used consisted of 1- through 20- μ diamonds, 1- through 6- μ aluminas, and 1- and 5- μ chrome oxides. Cloths tried were nylon, silk, Texmet*, Metcloth*, Microcloth*, and Politex-Pre**. Lubricants involved were water, alcohol, water-soap solution, Metadi fluid*, and kerosene. Polishing was accomplished on Syntron*** and Vibromet* vibratory polishers, Whirlimet* attachments, and by hand-holding the specimens on rotating laps. Of all the tests, only the smaller size abrasives (1- and 3- μ diamond and 1- μ alumina) on a silk cloth gave acceptable results. The pullout was not eliminated but was reduced to its lowest occurrence. Epoxy resin impregnation of rough polished surfaces did not decrease the pullout.

The final polishing stage was the most successful but it, too, would not eliminate the UO_2 pullout. Many techniques were also tried, with the main additions to the rough polishing stage being the finer abrasive sizes (0.3- and 0.05- μ aluminas and 0.5- μ chromic oxide) and the use of acidic, basic or peroxide slurries of the above abrasives (Table 1).

2. Etching

The etching study was initiated to develop the microstructure of the UO_2 without affecting the other portions of the fuel pin. Several chemical etchants were tried, as well as vacuum cathodic ion bombardment techniques, but the main effort was on variations of water, hydrofluoric, and nitric acids. Several chemical combinations were also found that would

* Buehler Ltd., Evanston, Illinois

**Geoscience Instruments, New York, N. Y.

***Syntron Company, Homer City, Pennsylvania

discretely with other select portions of the W-coated Mo-UO₂ structure (Table 2).

C. Electron Microscopy

Two-stage, carbon-platinum shadowed, negative replica techniques were employed with satisfactory results. Primary replicas of the sample surfaces were cast, using either parlodion in pentyl acetate or acetyl cellulose softened with methyl acetate. This was done to determine whether one primary would offer any advantage, in speed or yield, over the other on this type of sample. The final negative replicas were formed by vacuum evaporation of platinum and carbon. Both replica techniques display a surface topography that is negative with respect to the original sample surface. A depression or pit in the sample surface would appear as a projection or raised area in the electron micrograph.

RESULTS

The inability to prepare the Mo-UO₂ cermet without the presence of voids from UO₂ pullout was found only to be a handicap for microscopic examination. With extended polishing times on a rotating lap in the range of 1 hour and on a vibratory polisher in the range of 70-100 hours, the pullout was reduced only to a low level. As experimentation with various polishing techniques proved fruitless, the literature provided a different approach to mechanical polishing. Several authors (4-9) described the use of alumina and chromic acid slurries, and others (5,10,11) suggested the use of alumina abrasives and other reagents. Modifications of these chemical-mechanical polishing techniques were found to work better than mechanical methods, but did not eliminate the pullout problem. Impregnation of the sample with epoxy resins did not help because the starting density of the material was very high.

The previous procedure used by the hot cell facilities of Group CMB-14 at Los Alamos ⁽¹²⁾ is listed in Table 1, procedure P-1. This procedure was not adequate for electron microscopic examination and, therefore, others were developed (Table 1, procedures P-2, P-3 and P-4). The optical appearance of the cermet microstructure as prepared by these procedures is illustrated in Figs. 2-4. One undesirable feature of procedures P-2, P-3 and P-4 is the development of Mo grain boundaries by relief polishing. This can be minimized during the acid slurry step by using heavier loads on the specimen or by decreasing the flow of the acid slurry during the polishing.

Preparation of samples by the last three procedures provides equivalent results for optical microscopy. If polishing is terminated prior to the vibratory step, the Mo and the UO_2 structures are marred by scratches and disturbed material. If the UO_2 is etched, it is found to have many more and sharper scratches than the Mo and can therefore be identified in the electron microscope (Fig. 5).

If the sample is carried through the vibratory polishing step, relieving of the Mo from the UO_2 is observed, as well as removal of the scratches (Fig. 6). It is obvious that, at this point, the Mo and UO_2 are not easily distinguished but that the ability to see microvoids is favorable. The appearance of the cermet surface in the as-polished condition is pitted when viewed at high magnifications (Fig. 7); this pitting is believed to result from the polishing procedure. Fission gas voids in the UO_2 or in the Mo- UO_2 interface area may then be observed down to a size of 100 Å when viewed in the as-polished state.

If the vibratory polished sample (procedure P-4) is then etched for the UO_2 (etchant E-1), well defined grain boundaries in the UO_2 may be observed which allows them to be distinguished from the Mo (Fig. 8).

The W and W-cermet interface would also be best viewed in the as-polished state when voids are to be observed. Examination of the W and the W-cermet interface, however, is best in the etched state as shown in Fig. 9 when other features are desired.

DISCUSSION

Due to the setup of the Group CMB-14 hot cell facilities at Los Alamos, polishing procedure P-2 could not be used. It was found necessary to eliminate the use of the chromic acid in the polishing and procedure P-3 was developed for an alternate method. This procedure used the finer alumina abrasive and a silk cloth to obtain better cutting action than could be gained from the use of the 0.3- μ alumina with Texmet. The silk, when used with the 0.05- μ alumina, lasted only about 20 minutes. If longer polishing times than this were required, Texmet was found to be a better substitute for the silk than nylon.

Polishing procedure P-4 was found to give a much better surface for electron microscopy than any of the others. Procedure P-2 was shorter than P-4 and was quite useful for optical examination on a quick routine basis. The use of chemicals other than chromic acid in the abrasive slurries was briefly explored with apparently equivalent success.

Only moderate success was realized in the development of polishing procedures in that surface pitting and pullout of the UO_2 were not eliminated. It became obvious, however, that chemical-mechanical polishing techniques were suited to the rapid preparation of this material for both optical and electron microscopy. The etching of the tungsten-coated cermet was found to be extremely versatile and effective because discrete portions of the microstructure could be independently revealed. The observation of fission gas voids down to 100 Å was found to be feasible, but was complicated by polishing and etching artifacts 50-100 Å in diameter.

For electron microscopy, the parlodion primary replicas consistently provided a much higher yield (less breakup during dissolution of the primary) of usable replica than did the acetyl cellulose primaries. The cellulose replicas were easier to strip, however, and provided about as much detail as the parlodion primary replicas.

ACKNOWLEDGMENTS

The discussions with D. S. Shaffer concerning the metallographic preparation of these materials and with A. J. Patrick in relation to the fabrication and examination of the cermet are gratefully acknowledged. The extensive photographic assistance rendered by C. A. Baum is also appreciated.

TABLE 1 - POLISHING PROCEDURES

Abrasive	Lubricant	Cloth	Machine	Time
<u>Procedure P-1</u>				
240 SiC	Kerosene		Automatic*	
400 SiC	Kerosene		Automatic	
600 SiC	Kerosene		Automatic	
6 μ Diamond	Kerosene	Metcloth	Automatic	1 hr
1 μ Diamond	Kerosene	Selvyt	Automatic	1 hr
<u>Procedure P-2</u>				
240 SiC	Metadi**		Whirlimet	5 min
400 SiC	Metadi		Whirlimet	5 min
600 SiC(S)**	Metadi		Whirlimet	5 min
4/0 Emery	Dry		Hand-Held	
0.3 μ Al ₂ O ₃	20% CrO ₃ ***	Texmet	Whirlimet	2-5 min
0.05 μ Al ₂ O ₃	Water	Microcloth	Syntron	2-6 hrs
<u>Procedure P-3</u>				
240 SiC	Metadi		Whirlimet	5 min
400 SiC	Metadi		Whirlimet	5 min
600 SiC	Metadi		Whirlimet	5 min
0.05 μ Al ₂ O ₃	Water	Silk	Whirlimet	10-20 min
0.05 μ Al ₂ O ₃	Water	Microcloth	Syntron	2-6 hrs
<u>Procedure P-4</u>				
240 SiC	Metadi		Whirlimet	5 min
400 SiC	Metadi		Whirlimet	5 min
600 SiC	Metadi		Whirlimet	5 min
0.3 μ Al ₂ O ₃	20% CrO ₃		Whirlimet	5 min
0.05 μ Al ₂ O ₃	5% CrO ₃ ****	Silk	Whirlimet	5 min
0.05 μ Al ₂ O ₃	Water	Microcloth	Syntron	4-6 hrs

*Los Alamos Scientific Laboratory Design

**Metadi Fluid, Buehler Ltd., 600 SiC, Soft Grade, Buehler Ltd.

***Slurries made up of lubricant and abrasive indicated in the proportion 1:1

****Either 1% NaOH or 2% H₂O₂ may be substituted for the chromic acid for equivalent results

TABLE 2 - ETCHING PROCEDURES

Etchant Code	Etch Conditions
E-1	Etches UO_2 : Composed of 3:1:1/ H_2O : HF : HNO_3 ; Immersion agitate for 30-60 seconds; handle in plastic labware.
E-2	Etches UO_2 : Vacuum Cathodic Ion Bombardment; Krypton gas at 20 microns pressure and 2.3 kv and 0.15 ma for 30 minutes.
E-3	Etches Mo: Composed of 1:1/ H_2O : HNO_3 ; Immersion agitate for 5-10 seconds.
E-4	Etches Mo, Mo-W and Mo- UO_2 boundaries: Composed of 2:1:1/ H_2O : HF : HNO_3 ; Immersion agitate for 2-5 seconds.
E-5	Etches Mo-W boundaries: Composed of 1:1:1/ H_2O : HF : HNO_3 ; Swab for 10-20 seconds.
E-6	Etches Mo-W and Mo- UO_2 boundaries: Composed of 3:2:2/ H_2O : HF : HNO_3 ; Immersion agitate for 5-10 seconds.
E-7	Etches Mo and W grain boundaries: Composed of 10 grams KOH, 10 grams $\text{K}_3\text{Fe}(\text{CN})_6$ and 300 mls. H_2O (modified Murakami's etch); Immersion etch for 5-10 seconds at room temperature.
E-8	Etches W: Composed of 1 gram CuSO_4 , 60 mls. NH_4OH and 20 mls. H_2O ; Immersion etch for 30-60 seconds.

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Fig. 1 - Longitudinal Cross Section of the Tungsten Coated Cermet Fuel Pin. Note the Tungsten Coating at (A) Cermet Fuel at (B) and the Vent Hole at (C). Procedure P-4. 15X

Fig. 2 - Cermet Fuel, Illustrating the Typical Appearance of the Tungsten Coating at (A) the Cermet at (B) and a Molybdenum-Rich Area at (C). Procedures P-2 and E-1. 100X

Fig. 3 - Cermet Fuel, Illustrating the Typical Appearance of the Microstructure at the Outside Edge. Note the Pullout Voids (Arrows). Procedures P-2 and E-1. 500X

Fig. 4 - Cermet Fuel, Illustrating the Typical Appearance of the Microstructure at the Center. Procedures P-4, E-1, E-7 and E-8. 1000X

Fig. 5 - Cermet Fuel, Electron Micrograph Illustrating the Effect of Etching the Cermet Subsequent to the Acid-Slurry Step of Procedure P-4. Note the Appearance of the Scratches on the Uranium-Dioxide (A) as Opposed to the Molybdenum (B). Etchant E-1. 10,000X

Fig. 6 - Cermet Fuel, Electron Micrograph Illustrating the Microstructure after Vibratory Polishing Step of Procedure P-4. Note Pullout Voids (A) and Grain Boundaries. The Uranium-Dioxide is not Distinguishable from the Molybdenum at this Stage. Procedure P-4. 10,000X

Fig. 7 - Cermet Fuel, Electron Micrograph of the Cermet Structure of Fig. 6 at a Higher Magnification. Note Surface Pitting and the Inability to Distinguish the Uranium-Dioxide and the Molybdenum. Procedure P-4. 50,000X

Fig. 8 - Cermet Fuel, Electron Micrograph of the Etched Structure After Procedure P-4. Note Some Uranium-Dioxide Grains Well Outlined by Etching. Procedures P-4, E-1 and E-8. 10,000X

Fig. 9 - Tungsten Coating and Cermet Interface, Electron Micrograph of the Etched Structures After Procedure P-4. The Tungsten is the Columnar Grain Structure on the Right. Procedures P-4, E-1 and E-8. 10,000X

Metallographic Techniques for Vacuum-Cast Rolled Ingot Beryllium Sheet

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Abstract. Two techniques developed for the metallographic preparation of vacuum-cast ingot beryllium sheet are described. Both methods yield metallographically prepared surfaces considered to be of the highest quality. The first method retains inclusions and requires polarized illumination for structural delineation. The second method is an electrolytic swab-etch technique which yields bright-field delineation of the microstructure; however, inclusions are not retained. Emphasis in the report is mainly on illustrating the effects that improper preparation can have on the resulting microstructure.

INTRODUCTION

Commercial grade, scrap S-200 beryllium, made by powder metallurgy techniques, has been converted to vacuum-cast ingots and to rolled sheets. The Rocky Flats Metallography Laboratory group is responsible for providing representative metallography of such beryllium through the various stages of the process. A comparison of the chemistry of the powder-pressed scrap beryllium feed to that of the vacuum-cast ingot beryllium is shown in Table I.

A search of the literature revealed a number of beryllium metallographic techniques for the preparation of the powder-pressed material.^{1,2,3} Such work efforts were relied upon in developing the procedures given. Only one report is available on a technique developed for vacuum-cast ingot beryllium sheet.⁴

The science of metallography, in part, is the study of microstructural characteristics of metals by the aid of a reflecting microscope. Little can be learned relative

to the structure, unless the surface of the specimen is first prepared according to an explicit procedure.

In the preparation of vacuum-cast ingot beryllium rolled sheet specimens, the Metallography Laboratory experience has shown that specific methods are necessary. Beryllium specimen preparation is also a technical art and to carry out the specific procedures properly requires skill and dexterity on the part of a technician.

DISCUSSION AND RESULTS

Two methods are described to resolve the grain structure of the vacuum-cast ingot beryllium rolled sheet.

Method A: To be used where inclusions must be retained and for polarized light examination and photography of the microstructure.

Method B: An electrolytic swab-etch technique which will resolve the grain structure, such that bright-field illumination can be used for examination and photography. Inclusions are not retained.

There are certain operations that are common to both Methods A and B. The operations of sectioning, mounting, and grinding are first discussed. Later, the specific Methods A and B are examined.

The essential factor leading to a metallographically prepared beryllium sample of high quality relates to the care exercised while preparing a surface for final polishing and etching. Much of the emphasis of the report is on illustrating the effects which improper preparation can have on the resulting microstructure.

PROCEDURES

Specimen Sectioning and Mounting: The sectioning of a representative area from the parent beryllium sheet will induce mechanical deformation. A carefully machined surface will have a deformation from 100 to 200 microns deep (Figure 1). A more severe cutting action, such as a band saw, will effect deformation to a considerable depth (Figure 2). It is therefore suggested that the technician remove approximately $\frac{1}{16}$ of an inch of metal during the rough grinding operation.

¹ G. E. Darwin and J. H. Buddery. *Beryllium*. Butterworths Scientific Publication, London, England. 1960.

² D. W. White, Jr. and J. E. Burke. *The Metal Beryllium*. The American Society for Metals, Metals Park, Ohio. 1955.

³ G. A. Wheeler and C. W. Price. "Metallographic Technique for Polishing and Etching Beryllium." Battelle Memorial Institute, Columbus, Ohio. 1967. (To be published in the proceedings of the Twenty-First Metallography Group Meeting of the U.S. Atomic Energy Commission held at Brookhaven National Laboratory, Upton, Island, New York. May 1967.)

⁴ R. J. Jackson, W. L. Johns, and A. E. Calabra. *Simplified Metallographic Techniques for Uranium Alloys and Other Metals*. RFP-862. Rocky Flats Division, The Dow Chemical Company, Golden, Colorado. January 20, 1967.

For ease of handling and for edge retention⁵ the sample should be mounted in a suitable potting material prior to grinding.

Grinding Procedure: The grinding procedure is tabulated in Table II. Precautions which must be taken during the grinding of the specimen are:

1. The grinding matrix under excessive pressure will form deep-seated scratches. These are difficult and sometimes impossible to remove in subsequent grinding and polishing steps. Excessive pressure will also promote the formation of a considerable amount of

disturbed metal and the embedding of particles of the grinding media. It is difficult to give a numerical value to excessive pressure. An experienced technician can, however, give the contact pressure a "feel-value." Such a nebulous value comes only with experience.

2. The grinding media must be changed several times at each grit size used. A worn-grinding paper tends to smear the metal forming somewhat of a polished surface (Figures 3 and 4). The surface deformation causes the furrow edges to fold over resulting in hidden furrows. Remnants of a scratch following improper grinding appears after polishing as a series of small cross-hatched acicular twins across several grains (Figure 5).

⁵ A. E. Calabra, *Maraset Epoxy Resin and Coors Pelletized Alumina as a Metallographic Specimen Potting Mixture*, RFP-545. Rocky Flats Division, The Dow Chemical Company, Golden, Colorado. 1965.

TABLE I. Comparison of the Chemistry of the Scrap Feed to the Chemistry of the Ingot Sheet. Values are in Percent by Weight.

	Feed Scrap	Vacuum Cast		Feed Scrap	Vacuum Cast
Beryllium (Be) ^a	98.6	99.29	Copper (Cu)	0.010	0.010
Beryllium Oxide (BeO) ^{a,b}	1.65	0.260	Nickel (Ni)	0.020	0.025
Aluminum (Al)	0.090	0.075	Titanium (Ti)	0.040	0.013
Iron (Fe) ^a	0.150	0.170	Calcium (Ca)	0.010	<0.004
Magnesium (Mg)	0.040	<0.002	Cadmium (Cd)	<0.003	<0.003
Silicon (Si)	0.050	0.050	Cobalt (Co)	<0.003	<0.003
Carbon (C) ^a	0.080	0.070	Molybdenum (Mo)	<0.003	<0.003
Nitrogen (N) ^a	0.037	0.015	Lead (Pb)	<0.003	0.004
Manganese (Mn)	0.010	0.010	Tungsten (W)	<0.006	<0.008
Chromium (Cr)	0.010	0.010	Zinc (Zn)	0.010	0.006

^a Wet chemical analyses. All other impurities are determined by spectrographic techniques.

^b The analyses are made by the bromine-methanol method. There is doubt in the levels reported. Neutron-activation analysis indicates that substantially less than 1000 parts per million of total oxygen is present in the wrought material, 1.5 to 2.0 percent BeO in the feed scrap.

TABLE II. Mechanical Grinding.

Grinding Steps	Grit Size (silicon carbide paper)	Lubricant
Coarse ^{a,b,c,d}	60	Water
Intermediate	180, 240, 320, 400, 600	Water
Final	600 Soft ^e	Water

^a Remove approximately $\frac{1}{16}$ of an inch of metal.

^b Grinding papers must be fresh; change several times at each grit size.

^c After each grit size, etch for 10 seconds in a 10-percent sulfuric acid (H₂SO₄) aqueous solution.

^d Clean the specimen thoroughly between each step.

^e Buehler (Microcut) paper; Adolph I. Buehler, Inc., Evanston, Illinois.

FIGURE 1. Mechanical Deformation as Affected by Machining Out a Beryllium-Metallography Specimen. Polarized Illumination. Magnification 80X.

FIGURE 2. Mechanical Deformation as Affected by Band-Saw Sectioning of a Beryllium Specimen. Note the Microcracks, Which Often Occur, in the Upper Portion of the Photomicrograph. Polarized Illumination. Magnification 80X.

FIGURE 3. Normal Appearance of the Beryllium Surface from a Fresh 240-Grit Silicon, Carbide-Grinding Paper. Note the Well-Defined Furrows Made by the 240-Grit Particles. Magnification 80X.

FIGURE 4. Prolonged Grinding on a Worn 240-Grit Silicon, Carbide-Grinding Paper. The Surface Appears "Polished" Due to a Fold-Over of Furrows. Magnification 80X.

FIGURE 5. Series of Small Cross-Hatched Acicular Twins across Several Grains Affected by Improper Grinding. Sample Polished thru the Vibratory Polish. Polarized Illumination. Magnification 200X.

METHOD A — The particulars for Method A are outlined in Table III. Such a procedure will preserve inclusions for examination by bright-field illumination and will delineate the microstructure under polarized light.

For hand-polishing, the technician must use a firm pressure during the first third of each polish cycle. The pressure is thereafter decreased and only a light pressure used during the last third of the cycle. Figure 6 is an example of smeared metal caused by excessive polishing pressure. The polishing cloths, media, lubricant, time, and revolutions per minute

(rpm), shown in Table III, are applicable for hand-polishing.

After the polishing steps listed in the table are completed the vacuum-cast ingot beryllium sheet specimen is now ready for examination. Figures 7, 8, 9, and 10 are typical of beryllium samples prepared by Method A. Figure 7 is a photomicrograph illustrating the excellent retention of small inclusions. Figure 8 shows how the procedure has resolved a relatively large agglomeration of different types of inclusions. Delineation of the grain structure by polarized illumination is shown in Figures 9 and 10. There is no evidence of induced flowed metal or remnants of grinding scratches, and results are of the highest quality.

TABLE III. Polish Procedure, Method A (for automatic polishing units).

Polishing Steps	Cloth (1)	Media (2)	Lubricant (3)	Time	Load (grams)	Revolutions per Minute (rpm)
* Rough Mechanical	nylon	6-micron diamond	water-soluble oil	15 minutes	500	250
* Fine Mechanical	low nap	3-micron diamond	water-soluble oil	15 minutes	300	150
* Fine Mechanical	low nap	1-micron diamond	water-soluble oil	5 minutes	300	150
* Fine Mechanical	low nap	1/4-micron diamond	water-soluble oil	3 minutes	300	150
Vibratory Polish	low nap	200-cubic centimeter, 0.05-micron gamma alumina	600 milliliters of distilled water (H ₂ O) plus 20 milliliters of 10-percent chromic acid	24 hours (Additional time may be desired; and will not be injurious to the sample.)	350 mount holder	3 to 5
Final Polish (chemical)				5 second (Swab with 2-percent hydrofluoric acid and 48-percent ethol-alcohol solution.)		

* Swab with two-percent hydrofluoric — ethol-alcohol solution for five seconds between each mechanical polish step; clean thoroughly before proceeding.

FIGURE 6. A Fully Annealed Beryllium Specimen Showing Surface-Smeared Metal Intentionally Formed by Heavy Pressure on the Polish Cycle. The Variation in Shading across many Single Grains is Indicative of Surface Smear. It Takes on an Appearance of Subgrains Which They Probably are. It is Noted That the Acicular Twins are at 45° and 90° to the "Subgrains." Twins Too were Induced by the Heavy Mechanical Polishing Pressure and are not in the True Microstructure. This is Obviously not a Well-Prepared Beryllium Specimen. Polarized Illumination. Magnification 150X.

FIGURE 7. Small Inclusions Retained by Using Method A. Bright-Field Illumination. Magnification 450X.

<u>Legend</u>		
<u>Designation</u>	<u>Areas</u>	<u>Elements</u>
Aluminum (Al)	(a)	Fe + Mn + Al + Si
Beryllium (Be)		+ amounts*
Carbon (C)		of Be, C, O, or H
Iron (Fe)	(b)	same
Hydrogen (H)	(c)	same
Manganese (Mn)	(d)	same
Oxygen (O)	(e)	same
Silicon (Si)	(f)	Al + Si + amounts
		of Be, C, O, or H
	(g)	Si + amounts
		of Be, C, O, or H
	(h)	Al + Si + amounts
		of Be, C, O, or H
	(i)	Al + amounts
		of Be, C, O, or H

* Beryllium, carbon, oxygen, and hydrogen could not be detected because of the limitations of the microprobe.

FIGURE 8. A Large Agglomeration of Inclusion Materials With Varying Amounts of Each Element. The Qualitative Analysis was Done by the Electron Microprobe. Those Areas Which have the Fine Grains Delineated by Polarized Light, Marked (h), Appear to have the Same Constituents and are Probably Beryllium-Rich. Polarized Illumination. Magnification 400X.

FIGURE 9. Unannealed Vacuum-Cast Ingot Beryllium Sheet. Subgrains are Inherent in Sheet in the Unannealed Condition. Polarized Illumination. Magnification 100X.

FIGURE 10. Fully Annealed Beryllium Specimen Showing Excellent Grain-Structure Resolution and Absence of Preparation Artifacts. Polarized Illumination. Magnification 100X.

METHOD B — The procedure involves an electrolytic swab-etch technique for the delineation of the grain structure of vacuum-cast, ingot beryllium sheet by bright-field illumination. However, inclusion retention is poor. The polishing procedure preceding swab-etching is the same as in Method A.

A hole is drilled through the rear of the potted sample for electrical contact, prior to grinding and polishing. Contact is made by tapping a brass screw into the hole or by a copper strip embedded into the hole with a low melting point alloy. The specimen then can readily be attached to the anode lead from the power supply. The swab-etch probe unit is shown in Figure 11 and in Figures 12(a) and (b). The unit becomes the cathode in a normal electro-etching cell. Figure 13 shows the operational set-up.

The electrolyte and swab-etching parameters used in Method B are tabulated in Table IV. The electrolyte is precooled by placing a beaker of the solution in an ice bath. The temperature should be below 10°C before using. The anode lead from the power supply is

attached to the specimen for electrical contact. A cotton swab is pressed over the stainless steel and of the cathode swab unit [Figure 12(b)]. The swab is dipped into the cold electrolyte and the specimen surface swabbed with a light pressure using a circular motion. Contact time should be no longer than 30 seconds. At 25 volts, there is a temperature rise at the specimen-swab interface which will cause a "burned" or stained surface. The specimen should be rinsed immediately in cold water to prevent pitting by the electrolyte. The cotton swab must be changed and again saturated with cold electrolyte.

The specimen is cleaned and dried and the swab-etching cycle repeated for an additional 30 seconds. The procedure is repeated until the desired resolution is obtained.

Figure 14 is a photomicrograph of an area under polarized illumination. Figure 15 is one of the same area under bright-field illumination after swab-etching. There is greater detail in the specimens etched by Method B than those prepared by Method A alone.

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The authors acknowledge the able assistance of D. L. Marts in developing the techniques presented in the report. Appreciation is also expressed to D. Monarchi and D. Riefenberg of the electron microprobe group for the identification of inclusions.

FIGURE 11. Cross-Sectional Drawing of the Swab-Etch Probe Unit.

FIGURE 12. The Swab-Etch Probe Unit in a Disassembled Form (a) and Assembled with Cotton Ball Pressed onto the Stainless Steel Head (b).

FIGURE 13. The Operational Set-Up of the Electrolytic Swab-Etch Unit.

TABLE IV. Electrolyte and Etching Parameters for the Swab-Etch Procedure, Method B.

Electrolyte (milliliters)	
100. phosphoric acid (H_3PO_4) (85 to 87 percent)	Temperature: below $10^{\circ}C$
30. ethanol	Current Density: 1.0 amperes per square centimeters
30. glycerol	Time: 1 to 3 minutes; 30-second cycle
2.5 sulfuric acid (H_2SO_4)

FIGURE 14. Unannealed Vacuum-Cast Ingot Sheet Prepared by Method A and Photographed under Polarized Illumination. Magnification 100X.

FIGURE 15. Identical Area as Shown in Figure 14 under Bright-Field Illumination after Electrolytic Swab-Etching, Method B. Note the Excellent Detail Compared to That Shown in Figure 14. Etch Time, 3 Minutes. Magnification 100X.

SIMPLIFIED METALLOGRAPHIC TECHNIQUE FOR BERYLLIUM

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Abstract. A simplified metallographic technique for vacuum-cast rolled ingot beryllium sheet and powder pressed beryllium has been developed. This technique is such that the beryllium metallographic specimen needs only to be ground through 600-grit (soft) silicon carbide paper and electrolytically polished. This simplified technique yields polarized light delineation of the microstructure; however, inclusions are not retained. Another technique, more precise than the simplified technique, is described for the preparation of high quality metallography of powder pressed material.

INTRODUCTION

Commercial grade S-200 beryllium made by powder metallurgy techniques, and sheet rolled from vacuum-cast ingots cast from scrap S-200 beryllium are being processed. The Metallography Laboratories are responsible for providing representative metallography of such beryllium through the various stages of fabrication.

During the fabrication of the beryllium the responsible engineers request that rapid and accurate metallography be provided so that further beryllium processing will not be impeded. Therefore, there existed a need for a simplified method to rapidly determine the grain structure characteristics. This report describes such a technique. The process will not resolve inclusions that are present in the metal, but it will provide excellent resolution of the beryllium grain structure by the use of polarized light illumination.

For beryllium specimens which must be prepared to preserve inclusions and where the photomicrographs will be included in publications, another and more precise metallographic technique must be used. Such a technique, for vacuum-cast material, is described in the report (1) "Metallographic Techniques for Vacuum-Cast Rolled Ingot Beryllium Sheet." A precise procedure for the retention of inclusions and for high quality photomicrographs for powder pressed beryllium is described in this report.

A literature search revealed a number of beryllium metallographic techniques for powder pressed material (2,3,4). At least two reports are available on techniques developed for vacuum-cast ingot beryllium sheet (1,5). These reports were used for reference in developing the procedures used in this report. However, no reported method appears to have the speed and reproducibility of this simplified electrolytic technique.

The chemical analyses of the S-200 powder pressed beryllium, and the vacuum-cast ingot-sheet beryllium, is shown in Table I.

Table I. Chemical analysis of powder-pressed beryllium and vacuum-cast ingot-sheet beryllium.

	Powder-Pressed	Vacuum-Cast Ingot Sheet
Beryllium (Be) ^a	98.6	99.29
Beryllium Oxide (BeO) ^{a,b}	1.65	0.260
Aluminum (Al)	0.090	0.075
Iron (Fe) ^a	0.150	0.170
Magnesium (Mg)	0.040	<0.002
Silicon (Si)	0.050	0.050
Carbon (C) ^a	0.080	0.070
Nitrogen (N) ^a	0.037	0.015
Manganese (Mn)	0.010	0.010
Chromium (Cr)	0.010	0.010
Copper (Cu)	0.010	0.010
Nickel (Ni)	0.020	0.025
Titanium (Ti)	0.040	0.013
Calcium (Ca)	0.010	<0.004
Cadmium (Cd)	<0.003	<0.003
Cobalt (Co)	<0.003	<0.003
Molybdenum (Mo)	<0.003	<0.003
Lead (Pb)	<0.003	0.004
Tungsten (W)	<0.006	<0.008
Zinc (Zn)	0.010	0.006

^aWet chemical analyses. All other impurities are determined by spectrographic techniques.

^bThe analyses are made by the bromine-methanol method. There is doubt in the levels reported. Neutron-activation analysis indicates that substantially less than 1000 parts per million of total oxygen is present in the ingot-sheet material with 1.5 to 2.0 percent BeO in the feed scrap.

DISCUSSION

Experimental: Three techniques are described in this report. Procedure A is the electrolytic polishing

of specimens from vacuum-cast beryllium. Procedure B describes the electrolytic polishing of powder pressed material. Procedure C describes the precise preparation technique which will preserve inclusions and resolve the grain structure, for powder pressed beryllium, so that photomicrographs, having high quality, can be obtained by the use of polarized light.

Sectioning and Mounting: The sectioning (1) of a representative area from the parent beryllium will induce mechanical deformation in the material. A carefully machined surface will have a deformation layer from 100 to 200 microns deep. A more severe cutting action, such as with a band saw, will affect deformation to a greater depth. It is therefore required that the technician remove $\frac{1}{16}$ of an inch, or more, of metal during the rough grinding of either vacuum-cast or powder pressed metallographic specimens. For ease of handling, the sample should be mounted in a suitable metallographic potting material prior to grinding (6). A hole is then drilled through the rear of the mount to the metal for the electrical contact. If the section is large, mounting may not be necessary.

Grinding: The grinding procedures for each method are tabulated in tables and the cautions which must

be taken during grinding are listed in the tables. The most important of these is the use of fresh grinding papers at all steps. A worn grinding paper tends to smear the metal, introducing an abnormally deep worked surface. There is also the danger of working the metal to such an extent that grinding furrows from the previous grit size, or grinding direction, are hidden rather than removed. An excellent example of this condition is shown in Figure 1. The 600-grit (soft) furrows appear to be unidirectional (Figure 1-a); however, after one minute of beryllium electrolytic polishing the hidden scratches, or furrows, of the prior grinding are revealed (Figure 1-b).

Mechanical polishing of a beryllium metallographic sample prepared by Procedures A or B would be time consuming and would not enhance the final electrolytic polish.

PROCEDURES

Electrolytic Polishing: Procedures A and B require the use of the laboratory electropolishing cell and power source. The Buehler (7) unit and Struers (8) Disa-Electropol unit are used in the laboratories at Rocky Flats. These units produce identical results

Figure 1. Directional scratches. Polarized light. 100X

(a) The 600-grit furrows

(b) After one-minute electrolytic polishing

When the same current density and times are applied for polishing, and identical electrolytes are used.

The composition of the electrolyte is shown in Table II. It will normally polish approximately 50 metallographic samples, each approximately one square centimeter in size, before having to be replaced.

Table II. Composition of the electrolyte used for polishing of vacuum-cast ingot beryllium sheet and powder pressed beryllium.

Composition
147 ml ethylene glycol
2 ml hydrochloric acid
1 ml nitric acid

Struers unit will require approximately 300 ml solution.
Buehler unit will require approximately 600 ml solution.

Procedure A: Electrolytic Polishing of Vacuum-Cast Rolled Ingot Beryllium Sheet.

The mechanical grinding of the vacuum-cast metallographic specimen must be done as shown in Table III.

Table III. Mechanical grinding of the vacuum-cast beryllium specimen.

Grinding Steps	Grit Size (silicon carbide paper)	Lubricant
Coarse ^{a,b,c,d}	60	water
Intermediate	180, 240, 320, 400, 600	water
Final	600 soft ^c	water

^aRemove approximately 1/16 of an inch or more.

^bGrinding papers must be fresh; change several times at each grit size.

^cAfter each grit size, etch for 10 seconds in a 10-percent sulfuric acid (H_2SO_4) aqueous solution.

^dClean the specimen thoroughly between each step.

^eBuehler (Microcut) paper; Adolph I. Buehler, Inc., Evanston, Illinois.

NOTE: Item c is important in the mechanical grinding of the vacuum-cast beryllium because the H_2SO_4 etch removes some of the worked metal-surface induced at each grinding step.

Figure 2 is a plot of the current-density and the voltage applied with the Disa-Electropol series circuit unit for vacuum-cast beryllium sheet. The data for this curve were obtained after a stabilization period of 60 seconds. The curve shows a polishing plateau at approximately 0.10 amp/cm² and between 10- and 24- volts direct current. The parameters for the electrolytic polish are shown in Table IV.

Figure 2. Current-density and direct-current voltage plot for the ethylene glycol-HCl-HNO₃ electrolyte, using the Struers Disa-Electropol circuit cell to polish vacuum-cast rolled ingot beryllium sheet specimens. Readings taken after 60 seconds hold time. Region (a) to (b) represent the polishing plateau at approximately 11- to 24-volts.

Table IV. Parameters for electrolytic polishing of vacuum-cast rolled ingot sheet.

Electrolyte	ethylene glycol-HCl-HNO ₃ solution at 27°C
Cathode	stainless steel
Voltage	20 volts/cm ²
Current	0.10 amp/cm ²
Time	6 minutes from 600-grit (soft) scratches

Figure 3 and 4 are photomicrographs taken in sequence which illustrate the removal of beryllium from the 600-grit (soft) scratches through the final 6-minute electrolytic polish cycle. The photomicrograph of the final polish (f) illustrates a scratch-free surface, free of worked metal, with a high degree of grain resolution. Figure 5 is a high magnification of the as-rolled sheet and shows the excellent grain detail resolved by this technique.

(a) 600-grit (soft)

(b) 2 minutes

(c) 3 minutes

(d) 4 minutes

(e) 5 minutes

(f) 6 minutes

Figure 3. Sequential photomicrographs of metal removal from an as-rolled vacuum-cast ingot beryllium sheet metallography sample (from the 600-grit scratches through the 6-minute electrolytic polish cycle). Note the excellent grain structure detail resolved in (f). Polarized light.

80X

Figure 4. Sequential photomicrographs of metal removal during the electrolytic polish cycle for annealed beryllium sheet from a vacuum-cast beryllium ingot. Polarized light. 160X

Figure 5. The as-rolled vacuum cast ingot sheet. Note the excellent details resolved by Procedure A. Polarized light. 160X

Based upon considerable beryllium metallography experience, I do not believe that a bright-field etch would resolve the microstructure as well as this method. Also, experience has proven that bright-field etching methods are inconsistent, are not reproducible, and are time consuming.

Procedure B: Electrolytic Polishing of Powder Pressed Beryllium.

The mechanical grinding of the powder pressed beryllium must be done as shown in Table V. The difference between this grinding method and that for vacuum-cast rolled ingot beryllium is the omission of the 10% H_2SO_4 etch between each grinding step. That etching has proven to be unnecessary for this procedure.

Table V. Mechanical grinding of the powder pressed beryllium.

Grinding Steps	Grit Size (silicon carbide paper)	Lubricant
Coarse ^{a,b,c}	60	water
Intermediate	180, 240, 320, 400, 600	water
Final	600 soft ^d	water

^aRemove approximately 1/16 of an inch or more.

^bGrinding papers must be fresh; change several times at each grit size.

^cClean the specimen thoroughly between each step.

^dBuehler (Microcut) paper; Adolph I. Buehler, Inc., Evanston, Illinois.

The current density and the voltage plot using the Disa-Electropol unit is shown in Figure 6. For this data, as in Procedure A, a stabilization period of 60 seconds was used. This curve shows a polishing plateau at approximately 0.13 amp/cm² and between 10- and 16-volts direct current. The parameters for the electrolytic polish, for the powder pressed metallographic specimen, are shown in Table VI.

Table VI. Parameters for electrolytic polishing of powder pressed beryllium.

Electrolyte	ethylene glycol-HCl-HNO ₃ solution at 27°C
Cathode	stainless steel
Voltage	13 volts/cm ²
Current	0.13 amp/cm ²
Time	6 minutes from 600-grit (soft) scratches

Figures 7 and 8 are photomicrographs taken in sequence which illustrate the metal removal from a powder pressed beryllium specimen using Procedure B. The grain resolution under polarized light is very good. Preparation time, including mounting in a thermosetting resin, and the 6-minute electrolytic

Figure 6. Current-density and direct-current voltage plot for the ethylene glycol-HCl-HNO₃ electrolyte, using the Disa-Electropol circuit cell to polish powdered pressed (S-200) beryllium. Readings taken after 60 seconds hold time. Region (a) to (b) represents a relatively narrow polishing plateau approximately 10- to 16-volts.

polish cycle, is approximately 30 minutes. The structures, Figures 7(f) and 8(b), are free of scratches and any apparent flowed surface metal. However, the inclusions have not been retained, and this tends to detract from the grain structure.

Procedure C: A Mechanical Polishing Technique for Powder Pressed Beryllium.

This method will resolve the grain structure and preserve the inclusions in powder pressed beryllium. The resulting photomicrographs will be of high quality and suitable for publications.

The grinding steps are identical to those previously tabulated for Procedure B (Table V). The mechanical polishing steps are tabulated in Table VII.

Figure 9 shows the powder pressed microstructure resolved by this procedure. There is shown a well

(a) 1 minute

(b) 2 minutes

(c) 3 minutes

(d) 4 minutes

(e) 5 minutes

(f) 6 minutes

Figure 7. Sequential photomicrographs of metal removal from a powder pressed beryllium metallography specimen through the 6-minute electrolytic polish cycle. Polarized light. 150X

Table VII. Polishing Procedure C (for automatic polishing units).^a

Polishing Steps	Cloth	Media	Lubricant	Time	Load	Revolutions Per Minute (rpm)
Rough mechanical	Nylon	6-micron diamond	water-soluble oil	15 min.	500	250
Fine mechanical	low nap	3-micron diamond	water-soluble oil	15 min.	300	150
Fine mechanical	low nap	1-micron diamond	water-soluble oil	15 min.	300	150
Fine mechanical	low nap	1/4-micron diamond	water-soluble oil	5 min.	300	150
Vibratory polish	low nap	200-cm ³ , 0.05-micron gamma-alumina	600 ml distilled water, plus 20 ml 10% chromic acid	24 hours ^b	350 mount holder	3 - 5

^a The Scandimatic 333 polishing units are used in our laboratories. Scandinavian Diamond Products, Hareskov, Copenhagen; locally represented by T. C. Jarrett Company, Denver, Colorado.

^b Additional time may be desired; and will not be injurious to the metallographic specimen.

NOTE: For hand-polishing, the technician must use a firm pressure during the first period of each polish cycle. The pressure is thereafter decreased and only a light pressure used during the final third of the cycle.

defined microstructure and the retention of the very fine inclusions in the powder pressed material. This photomicrograph is of "report quality." Figure 10 is a high magnification showing very small inclusions that are retained.

CONCLUSIONS

1. The simplified electrolytic polishing techniques described in Procedures A and B have proven to be extremely helpful in supplying quick and reliable metallography in the development and fabrication of both vacuum-cast ingot sheet and powder pressed beryllium.
2. The electrolytic polishing methods are reproducible.
3. Procedures A and B have proven to be economical methods for the metallographic preparation of beryllium.
4. Procedure C resolves the microstructure of powder pressed beryllium to a high degree and is of "report-quality."

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(a) 3 minutes

(b) 6 minutes

Figure 8. High magnification of the powder pressed beryllium metallographic specimen which was electrolytically polished. Photographed after 3 minutes of polishing and after the final 6 minutes of electrolytic polishing. Polarized light. 250X

Figure 9. Well-defined powder pressed grain structure resolved by Procedure C. Small inclusions are distributed throughout the structure. Polarized light. 160X

Figure 10. High magnification of the small inclusions throughout the powder pressed beryllium specimen. Bright field. 1000X

CATHODIC VACUUM ETCHING WITH HYDROGEN^{*}

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ABSTRACT

The use of hydrogen has been found to produce superior results in the ion-bombardment etching of carbonaceous materials for optical microscopy. It appears that atomic, rather than molecular, hydrogen species are desirable for this purpose. In addition, this procedure may have some advantages in the etching of certain metals.

^{*}Work done under the auspices of the United States Atomic Energy Commission.

INTRODUCTION

Cathodic vacuum etching with reactive gases (chemical sputtering) has received much less attention than has cathodic vacuum etching with the inert gases (physical sputtering). Although the basic phenomenon of chemical sputtering with hydrogen has been known for some time⁽¹⁾, we are unaware of its employment as a metallographic tool other than in the present work, which was reported in part elsewhere⁽²⁾.

Graphites and other carbons present special problems in etching for microscopic examination due to their low chemical reactivities, particularly when a porous structure is preserved by a plastic impregnant. For this and other reasons, cathodic vacuum etching with inert gas ions has frequently been used to remove disturbed material and develop microstructures. Attempts to develop microstructures for examination in the optical range in this way were not particularly successful, however, using a cathodic vacuum etcher built in group CMF-13 of LASL⁽³⁾.

PROCEDURE AND RESULTS

After investigating a number of gases, it was found that hydrogen as the cathodic vacuum etching medium has several advantages over the inert gases: (1) It produces an increase in optical anisotropy, whereas we have found etching with inert gas ions usually produces a decrease or no change. (2) The reflectivity of the epoxy resin impregnant is increased, facilitating its identification in pores. (3) The microstructural details in graphitic materials are more readily identified.

(4) The likelihood of redeposition of sputtered material must be very slight; whatever species are formed are quite stable, since there is no deposition of material on nearby parts of the apparatus.

It should be emphasized that the results described are obtained only when the gas discharge has the pinkish color characteristic⁽⁴⁾ of the atomic hydrogen spectrum. A hydrogen discharge with the predominantly violet color characteristic of the molecular hydrogen spectrum gives quite different and inferior results. When this was first realized, the proper operating conditions were attained by saturating the hydrogen at atmospheric pressure with water vapor before admitting it to the discharge chamber. (The presence of water vapor has long been known to promote the formation of atomic species in a hydrogen discharge⁽⁵⁾.) Later, the same results were obtained by admitting a small amount of air along with the hydrogen. Although it is possible that the best ratio of hydrogen to air may vary from one cathodic vacuum etcher to another, our equipment is adjusted to give the following approximate operating parameters: With discharge space 6 cm in diameter by 22 cm long, the hydrogen/air ratio is adjusted so that a current of 4 ma is obtained at a voltage drop of 3 kv and an operating pressure of 35 millitorr. Etching times typically range from 15 to 30 minutes.

An unexpected result was the discovery that this type of hydrogen discharge is capable of producing metallographic etches on copper, silver, and gold. A search of the literature showed, however, that some evidence for the existence of hydrides of these metals has been observed before⁽⁶⁾. It appears that this might be a useful

means of etching these, and possibly other, metals in some special cases, as, for example, where an unavoidable galvanic couple might interfere with the use of aqueous solutions.

Figures 1 through 8 illustrate some results obtained with the method.

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Fig. 1. Edge of a piece of pyrolytic graphite which has been "swivelled". The growth cone structure has been largely destroyed in bands where slip has occurred. Polarized light. 50X.

Fig. 2. Detail of previous figure containing what are, presumably, deformation twins. The grooves which have etched in this region are traces of the average basal plane. Polarized light. 1000X.

Fig. 3. Lamellar structure etched in graphitized polyfurfuryl alcohol binder residue on non-graphitic glassy carbon substrate (lower left). Epoxy resin (upper right) filling pore. Oblique bright field. 500X.

Fig. 4. Nodules in pore of a commercial graphite indicating the prior presence of metallic impurities or additions. Oblique bright field. 500X.

Fig. 5. Lamellar and scaly structures in a graphitized petroleum coke. Epoxy resin in pores. Oblique bright field. 1000X.

Fig. 6. Graphite extrusion produced from graphite flour, Thermax and polyfurfuryl alcohol. Extrusion axis vertical. Bright field. 100X.

Fig. 7. Longitudinal section through column of graphite flour particles settled in epoxy resin. Bright field. 100X.

Fig. 8. Annealed high-purity silver. Bright field. 100X.

THE QUANTIMET TELEVISION MICROSCOPE - ITS OPERATION AND EVALUATION*

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ABSTRACT

This paper describes the operation of the Quantimet Television Microscope, the results of a performance evaluation, and the application of the instrument to metallographic service work. The Quantimet is an electronic instrument which by analyzing the output from a television vidicon tube is able to rapidly measure the area and projection of images projected onto the vidicon tube from either a microscope or an epidiascope.

The evaluation of the Quantimet included grain size analysis of ASTM standard grain size charts and area analysis of known area-fraction charts. Point count and Quantimet area analyses were made from the same nickel-bakelite compact and results compared with density measurements.

The ASTM grain size number as determined by Quantimet analysis of the ASTM charts was within 0.2 of the nominal grain size numbers for ASTM grain size numbers 0 through 8. The grain size as determined by the Quantimet was found to be dependent on the magnification employed. For the same grain size, the apparent ASTM grain size number decreased (or grain size increased) as the magnification decreased. This apparent decrease in the ASTM grain size number was related to a resolution effect which caused a loss of projection near each grain boundary junction.

In the analysis of the test charts representing area fractions of 10, 20, 30, 40, and 50%, the mean values obtained were within 0.15% of the area-fraction values determined by the Gaertner measuring microscope. Volume fraction measurements of a 20 volume percent nickel-bakelite compact derived from density measurement, point count analysis, and Quantimet area analysis

*Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

were in remarkably close agreement - being within 0.15% of each other. The performance of the Quantimet in the grain size and area measurements of known standards was quite acceptable.

Examples of the application of the Quantimet included area fraction measurements of ferrite in stainless steel weld metal, of porosity in pyrolytic tungsten, of UO_2 in a stainless steel- UO_2 fuel element, and of voids in UO_2 particles.

INTRODUCTION

Quantitative metallographic techniques are often neglected in metallographic studies because of their difficult, tedious, and time-consuming nature. Over the years, various instruments have been developed to aid in making the necessary quantitative measurements. Figure 1 shows some of the instruments available for making measurements of microstructure. Figure 1a represents the conventional overlay line and grid methods employed in lineal and point count analyses. Figure 1b shows the Wentworth micrometer stage in which micrometer barrels record the total lineal traverse across selected components of the microstructure. The Zeiss particle analyzer, Fig. 1c, measures individual particles or grains from a photographic print or negative and classifies the areas measured into a size distribution. The Hurlbut counter, Fig. 1d, integrates on separate counters the lineal traverse of as many as six components. The counter is connected to the moving microscope stage by a flexible cable from the counter motor. The Swift automatic point counter, Fig. 1e, has an electrically triggered stage which allows the specimen to be moved step-wise after each count is recorded on the selected counter. The Quantimet Television Microscope, Fig. 1f, is the most advanced of the instruments and possesses speed, versatility, and ease of operation - qualities not present to the same degree in the other instruments.

The Quantimet Television Microscope (QTM), through its ability to analyze images projected onto a TV screen, significantly reduces the time required to make quantitative measurements.¹⁻³ The manufacturer, Metals Research Ltd., Melbourn Royston Herts, England, has chosen to label the instrument as the Quantimet Image Analyzing Computer, possibly to emphasize the analyzing and computer aspects. The QTM can be used in conjunction with either a microscope or an epidiastope, which is a projector required for the analysis of larger items, such as photographic prints and transparencies.

Figure 2 shows the QTM with the microscope attached to the control unit. For polished sections of metals and ceramics, incident light is supplied through a series of prisms from an incandescent lamp located in the control unit. Incident light is reflected from the specimen through the microscope objective to a beam splitting prism which projects the image simultaneously into the binocular eyepiece for direct viewing and into the television camera located in the control unit.

Figure 3 shows the QTM with the epidiascope attached to the control unit. The specimen or photographic film or print to be analyzed is placed on the stage of the epidiascope. By means of a glass diagonal and one of three objectives which screw directly onto the TV camera, the image is focussed and projected onto the TV camera.

The next two sections describe the operation of the QTM using its area, projection, and counting modes and the results of a performance evaluation of the QTM for grain size and area analysis.

OPERATION OF THE QUANTIMET

As depicted in the simplified block diagram shown in Fig. 4, the image from the microscope or the epidiascope is projected onto the TV camera tube. The output from the camera can be displayed directly on the monitor or the output can be fed into an electronic detector which responds to changes in the output voltage as the scanning spot in the tube passes over light and dark features. The threshold control can be set so that signals from features lighter or darker than the selected threshold are fed into the computing component which derives the required quantitative measurement and presents it on the meter.

Using the detected image the QTM operates in one of three modes: (1) area, (2) projection, and (3) counting. Since the QTM allows us to superimpose the detected feature directly onto the image displayed on the monitor, operation of the QTM in these three modes is best shown by observing the television monitor. To illustrate this operation we constructed a test chart made up of 14 black circles. The television image of the 14 black circles is shown in Fig. 5a. All measurements with the QTM are for a given rectangular blank frame which can be superimposed on the image. The length and height of the frame can be set for a known distance, or the length and height can be measured.

In the area mode of operation the television monitor shows the display given in Fig. 5b. The area detected is indicated by the superimposed bands. At the same time the meter gives the area fraction of the blank frame occupied by the detected feature. In this case, the QTM indicated that the black circles occupied 29% of the blank frame. The area measurement is directly related to the time spent by the television scan while traversing the area occupied by the feature.

In the projection mode of operation, shown in Fig. 5c, the forward edge of the detected feature is outlined. The meter measures the projection in terms of the number of blank frame heights. The projection is determined essentially by the instrument counting the number of intersections between the television lines and the detected feature. In this particular blank frame there are about 170 television lines, so one blank frame height would represent 170 intersections. The projection measurement furnishes a means for determining a chord distribution for the detected feature. We can determine the number of chords by multiplying the projection measurement by the number of television lines in the blank frame. By

means of a minimum chord control we can reject chords below a particular value from the projection measurement, and in this way derive a chord distribution.

In the counting mode of operation, shown in Fig. 5d, the features counted are marked by a short horizontal line which occurs at the lower right of each feature. At the same time the meter gives the number of features counted. To determine the count measurement, the projection pulses are fed into a delay line which stores the signals for one complete horizontal line. If there is a pulse from approximately the same location in the next line, the QTM recognizes the pulse as coming from the same feature. This pulse is then stored and compared with the next line, and so on. Finally, when a line passes beneath the feature without intersecting it, the stored pulse is allowed to pass to the meter integrator and one additional count is registered. Since the boundaries of individual features are generally not vertical, a special provision in the QTM must be made for this. This is done by stretching the distance over which the instrument accepts the second intercept as coming from the same feature as the first intercept. This stretch distance can be varied at will by means of the acceptance angle control.

Now, how is the minimum chord control used to obtain a size distribution? In Fig. 6 the minimum chord control has been successively set to reject particles < 0.06 mm, < 0.08 mm, < 0.10 mm, < 0.12 mm, < 0.14 mm, < 0.16 mm diam, and the television monitor shows successively 14, 9, 5, 2, 1, and 0 particles counted. Thus, there are 5 particles in the 0.06-0.08 mm range, 4 particles in the 0.08-0.10 mm range, 3 particles in the 0.10-0.12 mm range, 1 particle in the 0.12-0.14 mm range, and 1 particle in the 0.14-0.16 mm range.

Three QTM parameters (area, projection, and count) are read directly from the meter of the QTM. In addition, two other QTM parameters (the length and height of the blank frame) are required. From the QTM parameters summarized in Table 1 and the relationships given in Table 2, various quantitative measurements can be calculated. In Tables 1 and 2 one should be careful not to confuse the QTM parameters A , L , and N with the area fraction A_A , the lineal fraction L_L , the mean boundary intercept distance $\bar{L}$, and the number of intercepts per unit length N_L . One should also be careful with the meaning of N_L , that is, whether it refers to boundary or particle intercepts. To determine the volume fraction, the area measurement is sufficient since for randomly oriented microstructures, the volume fraction V_V , the area fraction A_A , and the lineal fraction L_L are equivalent.^{4,5} Other basic equations give the surface area per unit volume S_V ,⁶ the line length per unit area for a plane L_A ,⁶ and the mean intercept length for particle sections.⁴

EXPERIMENTAL EVALUATION

The experimental evaluation of the QTM involved the measurement of grain size and area fraction from known standards.

Table 1. Quantimet Measurement Parameters

Symbol	Parameter	Dimension
P	Projection	Blank frame height
PH	Projection	mm, cm, in., etc.
A	Area occupied by detected feature	Percent
N	Number of features counted	Dimensionless
L	Length of blank frame as superimposed on specimen	mm, cm, in., etc.
H	Height of blank frame as superimposed on specimen	mm, cm, in., etc.

Table 2. Relationship Between Quantimet and Quantitative Metallography Measurements

Quantitative Metallography Measurement	Boundary Projection Mode	Quantimet Measurement Dense Projection Mode	Area Mode
Volume fraction, $V_V = A_A = \frac{L_L}{L}$	----	----	$V_V = A_A = \frac{A}{100}$
Number of boundary intercepts per unit length, N_L	$N_L = \frac{P}{L}$	----	----
Mean boundary intercept distance, $\bar{L} = \frac{1}{N_L}$	$\bar{L} = \frac{L}{P}$	----	----
Number of particles intercepted per unit length, N_L	----	$N_L = \frac{P}{L}$	----
Surface area per unit volume, $S_V = 2N_L^*$	$S_V = \frac{2P}{L}$ (space filling grains)	$S_V = \frac{4P}{L}$ (separated particles)	----
Line length in a plane per unit area, $L_A = \left(\frac{\pi}{2}\right) N_L$	$L_A = \left(\frac{\pi}{2}\right) \frac{P}{L}$	----	----
Mean particle "diameter" or mean intercept length, $d = \frac{L_L}{N_L} = \frac{A_A}{N_L}$			$d = \frac{AL}{100P}$

*In this case, N_L is the number of boundary intercepts per unit length.

The term "diameter" is descriptive and is not the actual mean diameter of the particle sections. N_L is the number of particles intercepted per unit length.

Grain Size Analysis

In the QTM measurement of grain size, grain size is derived from the mean linear intercept distance, $\bar{L}$, as determined from the equation

$$\bar{L} = \frac{L}{PM}$$

where L is the length of the blank frame at the monitor, P is the projection in blank frame heights and M is the magnification at the monitor screen. The grain size as represented by the mean linear intercept distance can be converted to the ASTM grain size number, G , by means of Hilliard's formula⁷

$$G = -10.00 + 6.64 \log N_L$$

where N_L is the number of grain boundary intercepts per cm and the reciprocal of the mean linear intercept distance.

Since grain boundaries in metallographic specimens usually are not evenly etched, we chose to evaluate the QTM by using standard ASTM grain size charts which display clearly defined boundaries. Although the ASTM charts would not be expected to represent exactly their stated grain size, the charts should give an indication of the performance of the QTM instrument.

The ASTM grain size charts chosen for analysis were those given in plate I of ASTM standard E-112. Since these charts are at 100 X magnification, the epidiascope attachment was employed to project the chart image onto the TV camera tube of the QTM. Since at 100 X magnification, 1 cm is equivalent to 0.01 cm, we measured the length of the blank frame by placing a centimeter scale on the epidiascope stage and then reading each cm as if it were 0.01 cm. The number of intercepts per cm would then be

$$N_L = \frac{P}{L} \text{ cm}^{-1}$$

where P is the projection reading in blank frame heights and L is the length of the blank frame as measured by the scale on the epidiascope stage.

To measure the grain boundary projection, the threshold control on the Quantimet control unit is varied until the grain boundaries are detected as clearly as possible. Figure 7 shows the television monitor display obtained when the ASTM grain size 3 chart was analyzed. Simultaneously, the meter on the QTM would indicate the boundary projection for this particular blank frame to be about five blank frame heights.

Table 3 shows the results of the QTM analysis of the ASTM grain size charts. The standard deviations included with the average projection values reflect primarily the variations between fields measured from the ASTM charts and are not indicative of the performance of the QTM. All of the charts from ASTM numbers 0 to 8 analyzed within 0.28 ASTM grain size number of the nominal grain size number for an average deviation of ± 0.13 from the nominal grain size number.

Table 3. Quantimet Determination of Grain Size from ASTM Grain Size Charts^a

Nominal ASTM Grain Size Number G_N	Quantimet Average Projection Reading ^b $\bar{P}$ (BFH)	Number of Grain Intercepts per Unit Length $N_L = P/L^c$ (cm^{-1})	Calculated Grain Size Number ^d G	Deviation from Nominal Grain Size Number
0	2.01 ± 0.26	32.4	0.03	0.03
1	3.10 ± 0.35	50.0	1.28	0.28
2	3.78 ± 0.30	61.0	1.85	- 0.15
3	5.25 ± 0.07	84.7	2.80	- 0.20
4	2.19 ± 0.35	136.9	4.19	0.19
5	2.93 ± 0.36	183.1	5.02	0.02
6	4.00 ± 0.30	250.0	5.92	- 0.08
7	5.55 ± 0.66	346.9	6.87	- 0.13
8	7.89 ± 0.43	493.1	7.88	- 0.12
				± 0.13

^aASTM E-112, Plate I.^b1 in. focal length objective employed for grain size 0 through 3; 2.5 in. focal length objective employed for grain sizes 4 through 8.^cFor grain sizes 0 through 3, $L = 0.062$ cm; for grain sized 4 through 8, $L = 0.016$ cm.^dCalculated from Hilliard's formula.

The QTM epidiascope attachment employs three objectives - a low power, a medium power, and a high power. We might expect that we should obtain the same grain size measurement using the low power objective as the high power objective. But when the grain size 8 chart was analyzed, we obtained grain size numbers of 7.47, 7.77, and 7.85 for the low, medium, and high power objectives, respectively.

The smaller grain size number (larger grain size) obtained with the lower power objectives is due to an enhancement of a resolution effect caused by the presence of a greater number of grain boundary junctions in the blank frame at the lower magnifications. The resolution effect is best illustrated by reference to Fig. 8, which represents a grain boundary junction under analysis by the QTM. If the distance between the two converging grain boundaries is less than the resolution, r , only one intercept instead of two is counted for each television line scan. The result is a loss of projection, which in turn results in a lower total projection and a larger grain size (lower grain size number) than would be obtained if there were no resolution effect. The projection loss per junction, p , is the product of the horizontal resolution and the projection factor. The value of the projection factor depends upon the orientation of the grain boundary junction relative to the television line scan and would vary from junction to junction. To determine the mean projection loss per junction, the mean value of the projection factor must be determined. Since we did not know the precise value of the mean projection factor and were somewhat uncertain about the value of the screen resolution, we determined the value of a congruency factor, k , which would yield the smallest difference, ΔN_L , between the high and low values of N_L for the three epidiascope magnifications. The congruency factor should be equivalent to the mean projection loss per grain boundary junction. For a given blank frame, the total projection loss caused by the resolution effect is given by

$$p_t = \bar{f}rn = kn$$

where $\bar{f}$ is the mean projection factor, r is the horizontal screen resolution, n is the number of grain boundary junctions in the blank frame, and k is the congruency factor. The total projection loss reduced to 1 X magnification is then

$$p_t = \frac{kn}{100m}$$

where m is the screen magnification and the factor 100 is included because the grain size analysis was performed on a grain size chart intended for use at 100 X magnification. The total projection loss in units of blank frame heights is then

$$p_t = \frac{kn}{100mH}$$

where H is the height of the blank frame as reduced to 1 X magnification. The magnification, m , and the height of the blank frame, H , are known. From the ASTM grain size definition, each sq mm section through a specimen rated as ASTM grain size 8 should contain 1980 grains and the number

Table 4. Quantimet Data From ASTM Grain Size No. 8 Chart Corrected for Resolution Effect
(Congruency Factor, $k = 0.83$ cm)

Epidiascope Objective	Low Power 1 in. Focal Length	Medium Power 1.75 in. Focal Length	High Power 2.4 in. Focal Length
Quantimet projection (BFH), P	23.54	12.96	6.36
Length of blank frame (cm), L	0.055	0.0273	0.0130
Height of blank frame (cm), H	0.048	0.0249	0.0114
Area of superimposed blank frame (sq mm at 1 X magnification)	0.264	0.0680	0.0148
Number of grains in blank frame ^a	522.7	134.6	29.3
Number of grain boundary junctions in blank frame, n	1045.4	269.2	58.6
Screen magnification, m	4.18	8.67	18.6
Total projection loss (BFH), $P_t = k \frac{n}{100mH}$	4.32	1.03	0.23
Projection corrected (BFH), $P + p_t$	27.86	13.99	6.59
Number of grain boundary intercepts per unit length (cm ⁻¹), $N_L = \frac{P + P_t}{L}$	506.5	512.5	506.9
ASTM grain size corrected ^b	7.96	7.99	7.96
ASTM grain size uncorrected ^b	7.47	7.77	7.85

^aSince for ASTM grain size No. 8 there are 1980 grains per sq mm at 1 X, the number of grains in the blank frame equals 1980 times the area of the blank frame.

^bCalculated from Hilliard's formula.

Table 5. Summary of Corrected Quantimet Data for ASTM Grain Size No. 8 Chart^a

Epidiascope Objective	Low Power	Medium Power	High Power
Corrected projection (BFH), P	27.86 ± 0.13 ^b	13.99 ± 0.49 ^c	6.59 ± 0.39 ^d
Blank frame length (cm), L	0.055	0.0273	0.0130
Number of grain boundary intercepts per unit length, $N_L = \frac{P}{L}$	506.5 ± 2.4	512.5 ± 18.0	506.9 ± 30.0
ASTM grain size number ^e	7.96 ± 0.01	7.99 ± 0.10	7.96 ± 0.17

^aASTM designation: E-112-Plate I.

^bObtained from 10 measurements of the same field.

^cObtained from 10 measurements, two from each of 5 fields.

^dObtained from 20 measurements, two from each of 10 fields.

^eASTM grain size number calculated from Hilliard's formula.

of grain boundary junctions in each sq mm should be twice 1980. Then, since we know the area represented by the blank frame, we can determine the number of junctions in the blank frame. Thus, to determine the total projection loss, we need only the value of the congruency factor, k .

The value of the congruency factor was determined in this manner. Values of N_L were calculated for each of the three epidiascope magnifications using a selected arbitrary value of k in the equation

$$N_L = \frac{P + k \left(\frac{n}{100mH} \right)}{L} = \frac{P + p_t}{L}$$

where P is the QTM projection, p_t is the total projection loss, and L is the length of the blank frame. From the high and low values of N_L determined for each selected value of k , the difference ΔN_L was determined. The value of k at which ΔN_L was minimum was found to be about 0.083 cm, as the curve in Fig. 9 shows.

In Table 4 the QTM data has been corrected using the congruency factor 0.083 cm to give ASTM grain size numbers of 7.96, 7.99, and 7.96 for the low, medium, and high power objectives.

The corrected QTM data obtained from the ASTM grain size No. 8 chart is summarized in Table 5. The deviations given in the table are standard deviations. The deviations obtained with the low power objective are due only to variation in the values obtained by the operator, while the deviations obtained with the medium and high power objectives are due both to operator and sampling variations.

Area Analysis

We evaluated the QTM area-fraction measurement both with test charts and with a nickel-bakelite compact. The test charts represented area fractions of 10, 20, 30, 40, and 50%; and the nickel-bakelite compact was fabricated to give an area fraction of 20% nickel.

In order to reduce the amount of effort required for measuring the test charts visually with the Gaertner measuring microscope, only one test chart (A-2) was measured ten times, and only duplicate measurements were made on the other test charts. The average of ten measurements of test chart A-2 with the Gaertner measuring microscope was 30.23% with a standard deviation of $\pm 0.01\%$.

For all of the QTM measurements of the area test charts, the blank frame was set to cover an area 6.3 cm by 5.0 cm. Figure 10 shows test chart A-2 as it was displayed on the monitor when an area fraction measurement was made. The diamond shape banded area is the area detected and the meter reads 30.1%, which is the area fraction of the blank frame occupied by the detected area. In the QTM measurement of test chart A-2, two series

of area-fraction measurements were made, as given in Table 6. In the first series, the threshold control was set visually, in other words, the operator by varying the threshold control tried to superimpose as close as possible the banded area on the black diamond area. In the second series of measurements, the threshold control was set at a constant value of 480. As would be expected, the standard deviation is greater when the threshold control is set visually.

Table 6. Quantimet Analysis of Test Chart A-2

1st Series		2nd Series	
Area Fraction (%)	Threshold Control Setting	Area Fraction (%)	Threshold Control Setting
30.4	502	30.2	480
30.5	489	30.2	480
30.2	491	30.0	480
30.2	472	30.0	480
30.3	490	30.0	480
30.0	468	30.1	480
30.3	470	30.3	480
30.1	460	30.2	480
30.2	474	30.2	480
30.0	458	30.3	400
	<u>Mean</u>	<u>Variance</u>	<u>Standard Deviation</u>
1st Series	30.22	0.026	± 0.16
2nd Series	30.15	0.014	± 0.12

Table 7 presents the results of the QTM analysis of the area fraction test charts. Ten measurements were made of each test chart, and with the exception of test chart A-1, the threshold control was set at a constant value. In the analysis of test chart A-1, the threshold control was set visually and a corresponding increase in the standard deviation was observed. Out of the 60 individual area measurements represented by the data in Table 7, only three differed from the values determined by the Gaertner measuring microscope by more than 0.5% and these three were confined to measurements of chart A-1. The mean value obtained by the QTM for each of the area test charts was within 0.15% of the values measured by the Gaertner measuring microscope.

We compared measurements of the nickel-bakelite compact using the Swift automatic point counter (see Fig. 1e) with those obtained using the QTM with the microscope attachment. By using the QTM with the microscope rather than the epidiascope, we not only avoided the photographic steps but also obtained a better sampling of the microstructure.

Table 7. Quantimet Analysis of Area-Fraction Test Charts

Test Chart	Area Analysis with Gaertner Measuring Microscope			Quantimet Area Analysis		
	Area Fraction (%)	Duplicate Analysis	Standard Deviation (%)	Area Fraction (%)	Range (%)	Standard Deviation (%)
		Deviation (%)				
A-7	10.03	0.000		10.01	9.9-10.1	± 0.06
A-6	19.77	0.021		19.75	19.7-19.8	± 0.05
A-1	29.67	0.008		29.81	29.3-30.3	± 0.4
A-2	30.23	-	± 0.01	30.15	30.0-30.3	± 0.12
A-5	41.08	0.019		41.04	40.8-41.4	± 0.19
A-4	48.49	0.015		48.41	48.0-48.7	± 0.26

The nickel-bakelite compact was prepared by hot pressing a mixture of nickel and bakelite powders in a metallographic mounting press. Figure 11 shows the "microstructure" of the nickel-bakelite compact. From the weight of the compact, the volume of the compact, the compact density of bakelite, the pycnometer density of the nickel powder, and the known bulk density of nickel, the volume fraction of nickel in the compact was calculated to be 20.02%. The volume of the compact and the compact density of bakelite were determined experimentally by the immersion method.

From a total point count of 2910 points, the area fraction of the nickel in the nickel-bakelite compact was found to be 20.05%. The point count, which was made at 500 X using the Swift automatic point counter in conjunction with a Leitz microscope, required approximately one hour. The standard error, $\sigma_{\bar{x}}$, was estimated from the equation⁸

$$\sigma_{\bar{x}} = \sqrt{[p(1 - p)/n]}$$

where p is the area fraction nickel (in this case, 0.2) and n is the total number of points counted and $\sigma_{\bar{x}}$ found to be ± 0.0074 or ± 0.74%. This means that there is a 95% probability that the true value of p lies in the range 0.2005 ± 0.0148. It is assumed that the binomial distribution, for which the above formula applies, is sufficiently normal for the σ and 2 σ limits to be used for marking the 68 and 95% confidence limits.

From 96 QTM measurements of 96 fields (blank frames), which took about 1 hr, the mean area fraction occupied by the nickel was found to be 20.15% with a standard deviation of ± 5.93%. The standard error, $\sigma_{\bar{x}}$, was estimated from the equation

$$\sigma_{\bar{x}} = \frac{\sigma_x}{\sqrt{N}}$$

where σ_x is the standard deviation and N is the total number of measurements and σ_x found to be $\pm 0.61\%$. This means that there is a 95% probability that the true value of the mean area fraction lies in the range $20.15 \pm 1.22\%$.

There was remarkably good agreement between the volume fraction of nickel in the nickel-bakelite compact as determined by the three methods as summarized below:

- 20.02 As determined experimentally from density measurements.
- 20.05 ± 0.74 As determined by the point count analysis with the Swift automatic point counter. Deviation given is the standard error.
- 20.15 ± 0.61 As determined by the QTM analysis. Deviation given is the standard error.

For the point count analysis three parallel longitudinal traverses and for the QTM analysis two parallel longitudinal traverses were made down the center of the specimen so that approximately the same region of the compact was analyzed in each analysis. The close agreement between the point count and QTM analyses may be a bit fortuitous when the magnitude of the standard error is considered. In other words, if these measurements were repeated, the point count and QTM analyses would probably not be in quite as close agreement.

From the amount of time consumed (1 hr for each analysis) and the standard errors obtained the efficiency of each analysis was of the same order, the QTM analysis being somewhat more efficient time-wise than the point count analysis. Of course, if more specimens were required for measurement, operator fatigue and subsequent inaccuracy would probably be greater with the automatic point counter than with the QTM. To really pull ahead of the automatic point counter in an area analysis, the QTM requires a data handling modification. Such a modification includes an electrically controlled automatic microscope stage together with suitable accumulating registers which can be coupled to an electric typewriter or a tape punch for subsequent computer processing.

APPLICATION TO SERVICE WORK

The Quantimet Image Analyzing Computer was obtained primarily as a service tool for the Metallography Group of the Metals and Ceramics Division. While the instrument was not obtained with a particular job in mind, we hoped that it would prove beneficial to the conduct of the division's fundamental and applied research programs. Some examples of the area measurement application are presented below.

We determined the amount of ferrite in type 308 stainless steel weld metal using the QTM with the microscope attachment. To do this, we etched the specimen for 2 min in boiling alkaline ferricyanide so the ferrite was

darkened, as shown in Fig. 12. The QTM is then able to differentiate between the ferrite phase and the austenitic matrix. Measurements of 20 fields indicated the ferrite content to be 6.88%.

We have determined the amount of porosity in pyrolytic tungsten. The particular sample selected was chosen to illustrate the instrument's capability of measurement of very low area percentages. Figure 13 shows the polished microstructure of this particular pyrolytic tungsten specimen. Measurements of 20 different microscope fields indicated the amount of voids to be 0.20 area percent.

We determined the amount of UO_2 in a UO_2 -SS fuel element using the epidiastroscope attachment with the QTM. Figure 14 shows the microstructure of the UO_2 -SS fuel element. From QTM measurements of 28 fields taken from seven photomicrographs, the amount of UO_2 averaged 28.4 area percent.

We determined the void area within the UO_2 fuel particles, again using the epidiastroscope attachment. From QTM measurements of 42 fields taken from seven 500 X photomicrographs, the amount of voids in the UO_2 fuel particles averaged 15.7 area percent.

The area-fraction measurements are summarized in Table 8. The number of measurements, as given in the table, equals the number of individual fields analyzed. The values of the standard deviation and standard error are relatively high because they reflect the variation between the microstructural fields analyzed rather than the precision of the measurements. High standard deviation and standard error values indicate that a high number of measurements would be required in order to obtain an acceptable given standard error. For instance, in the area determination of the amount of UO_2 in the UO_2 -SS fuel element, 425 measurements would be required in order to have a 95% assurance that the standard error would not exceed $\pm 1\%$ of the total area. By employing a lower magnification (increasing the area of the field analyzed) the standard deviation and the standard error values could be reduced drastically and the number of measurements required for a given standard error reduced as well. Of course, a decrease in the magnification lowers the ability of the QTM to resolve microstructural detail, so a balance must be selected between the attainment of a low standard deviation and the necessity for resolving detail in the microstructure.

The area-fraction measurements presented in Table 8 include measurements made using either the microscope or the epidiastroscope attachment. Frequently, we are asked to analyze a photomicrograph when the QTM is set up with the microscope to analyze a microspecimen. To do this, we must replace the microscope with the epidiastroscope and although it requires perhaps 15 to 20 min to replace the microscope with the epidiastroscope, there is usually an alignment problem which requires the greater part of a day to solve. Because of this difficulty, there is natural reluctance to change from the microscope to the epidiastroscope (or vice versa), and this interferes with the work flow. An alternative to this difficulty is to have a television camera for each attachment so the change from one to another can be accomplished simply by turning a switch.

Table 8. Selected Quantimet Area-Fraction Determinations

Determination	Area Represented by Each Measurement (mm)	Number of Measure- ments N	Range of Measure- ments (area %)	Mean $\bar{x}$ (area %)	Variance ^a V_x (area %)	Standard Deviation ^b σ_x (area %)	Standard Error ^c $\sigma_{\bar{x}}$ (area %)
Ferrite in 308 SS weld metal	0.108 by 0.086	20	4.6 - 9.4	6.88	1.63	1.28	0.29
Porosity in pyrolytic tungsten	0.108 by 0.086	20	0.03- 0.45	0.20	0.026	0.16	0.036
UO ₂ in UO ₂ -SS fuel element	0.238 by 0.213	28	7.4 -44.0	28.40	106.4	10.31	1.95
Voids in UO ₂ particles	0.059 by 0.053	42	7.0 -25.1	15.70	117.4	4.17	0.64

$$^a \text{Variance, } V_x = \frac{1}{N-1} \sum_{i=1}^n (x_i - \bar{x})^2.$$

$$^b \text{Standard deviation, } \sigma_x = \sqrt{V_x}.$$

$$^c \text{Standard error,}$$

$$\sigma_{\bar{x}} = \frac{\sigma_x}{\sqrt{N}}.$$

CONCLUSIONS

The ASTM grain size as determined by the Quantimet Image Analyzing Computer from the ASTM charts was within 0.2 of the nominal grain size for ASTM grain size numbers 0 through 8. The average deviation from the nominal grain size numbers was ± 0.13 .

The ASTM grain size as determined by the QTM was found to be dependent on the magnification employed. For a given grain size it was found that the apparent ASTM grain size number decreased (or grain size increased) as the magnification was decreased. The smaller grain size number obtained at the lower magnifications was due to an enhancement of a resolution effect caused by the presence of a greater number of grain boundary junctions in the blank frame at the lower magnifications. The resolution effect manifests itself in a loss of projection caused by the convergence of grain boundaries at each grain boundary junction. By use of a congruency factor, k , equivalent to the product of the screen resolution and the projection factor, the deviation between the ASTM grain size numbers obtained at three different magnifications was decreased from an original deviation of 0.38 to a deviation of 0.02 ASTM grain size number.

In the area analysis of test charts setting the QTM threshold control at a constant value led to more consistent results and lower standard deviations than were obtained when the threshold control was set visually. In the analysis of test charts representing area fractions of 10, 20, 30, 40, and 50%, the mean values obtained for each of the charts was within 0.15% of the values measured by the Gaertner measuring microscope. Out of 60 individual area measurements, only three differed from the values determined by the Gaertner measuring microscope by more than 0.5%, and these were observed in a test series in which the threshold control was set visually. We can conclude from these observations that the accuracy of the QTM in performing area analysis is quite acceptable.

Measurements of the volume (area)-fraction of nickel in a nickel-bakelite compact as determined by (1) density measurements - 20.02%, (2) point count analysis - 20.05%, and (3) QTM area analysis - 20.15% were in remarkably good agreement.

Although the QTM has had considerable use in metallography service work, the instrument has not been used as extensively as hoped because of its inability to detect differences in contrast between microstructural phases. Area analyses have been performed in the determination of the amount of ferrite in type 308 stainless steel weld metal, the porosity in vapor deposited tungsten, the amount of UO_2 in a UO_2 -SS fuel element, and the amount of voids contained in UO_2 fuel particles.

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Fig. 1. Instruments Employed for Making Quantitative Metallographic Measurements

Fig. 2. Quantimet Image Analyzing Computer with Microscope Attached
Y-70921

Fig. 3. Quantimet Image Analyzing Computer with Epidiascope Attached
Y-86127

Fig. 4. Quantimet Simplified Block Diagram
Y-71779

Image

Area Mode

Projection Mode

Counting Mode

Fig. 5. Quantimet Monitor Displays

Fig. 6. Obtaining a Size Distribution with the Minimum Chord Control. The minimum chord control was successively set to reject particles. Thus, there are 5 particles in the 0.06-0.08 mm range, 4 particles in the 0.08-0.10 mm range, 3 particles in the 0.10-0.12 mm range, 1 particle in the 0.12-0.14 mm range, and 1 particle in the 0.14-0.16 mm range.

Fig. 7. Quantimet Television Monitor Display for ASTM Grain Size No. 3 Chart. Y-82962

Fig. 8. Representation of a Grain Boundary Junction. The horizontal resolution is represented by r and the projection loss for the junction is represented by p . The projection factor, f , is the ratio p/r .

Fig. 9. Congruency Factor vs the Difference Between the High and Low Calculated Values of the Number of Grain Boundary Intercepts per Unit Length.

Fig. 10. Quantimet Monitor Display of Test Chart A-2

Fig. 11. "Microstructure" of 20 Volume % Nickel-Bakelite Compact Y-85296

Fig. 12. Stainless Steel Weld Metal as Etched for Quantimet Analysis. Ferrite phase is darkened by etchant. Etched 2 min in boiling solution made up of 30 g $K_3Fe(CN)_6$, 30 g KOH, 100 ml H_2O .

Fig. 13. Chemically Vapor Deposited Nickel. Quantimet analysis indicated void fraction to be 0.20%. Y-68668

Fig. 14. UO_2 -Stainless Steel Fuel Element. Quantimet analysis of seven photomicrographs indicated 28.4% UO_2 . R-40142

EVALUATION OF THE BAUSCH & LOMB RESEARCH II METALLOGRAPH*

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ABSTRACT

The Bausch & Lomb Research II was introduced in 1965. The earlier style, the Bausch & Lomb Research I has been in use by many laboratories for over 25 years. Since the capabilities of the older style instrument is relatively well known, basic comparisons of the two instruments are presented.

The instrument was evaluated on the bases of mechanical design, convenience of operation, optical resolution, performance in all the available illumination modes (bright field, dark field, polarized light, sensitive tint, and phase contrast), and color photography. Some shortcomings were found and means of coping with some of them were devised.

The Research II metallography was found to be a superior instrument in most ways, with the promise of being even better as better lenses are developed and design and assembly bugs are worked out.

INTRODUCTION

The Bausch & Lomb Optical Company (B & L) for many years has made, as their premium line of metallurgical optical instruments, the Research I metallograph. This metallograph has been the standard of the industry in this country, primarily because of its superior performance in polarized light illumination. The Research I is not a particularly convenient instrument to operate nor pretty to look at, but it is very stable and rugged, and reasonably versatile.

The Research II prototype was unveiled at the ASM Metal Show in Detroit in 1965. Since that time consistent improvements have been made;

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

and in the past year numerous units have been delivered about the country. We at Oak Ridge National Laboratory (ORNL), Metals and Ceramics Division, received one in early April 1968. This report is an evaluation of that instrument.

The evaluation covers (1) description of the metallograph, (2) some shortcomings, and (3) performance comparison with the Research I.

DESCRIPTION

The Research II metallograph in physical appearance is very different from the Research I. It is a handsome gray desk-like console with all controls, photography, and viewing stations within easy reach. Figure 1 shows an overall view.

Figure 2 shows the instrument with an operator. Obviously much attention was given to the comfort of the operator and location of controls for his convenience.

Figure 3 is a schematic diagram of the optical system. One can see that the heart of the system is still the Foster calcite prism. Apparently, what B & L has done is fold up the Research I optical path and put it in the Research II cabinet with such added features as a zoom system, a projection station, and built-in features of exposure meter, phase contrast, and field and stereo viewing.

Figure 4 is a schematic diagram of the illumination system and the prism-objective portion of the instrument. There are two light sources, a xenon lamp and a tungsten lamp. The tungsten lamp may be moved in and out of the optical path. With the xenon lamp on, moving the tungsten light into position **automatically turns the xenon lamp off and the tungsten lamp on**. When the tungsten lamp is moved out of position, it is automatically cut off but the xenon lamp must be restarted manually.

There is a rack of filter frames for up to eight filters, which can accommodate up to 4 filters at a time in the light path. This is a great improvement over the Research I.

To achieve the desired short barrel length for each objective lens, it was necessary to fix a permanent nosepiece lens just below the objective turret. This fixed lens becomes a part of each objective as it is rotated into place, from the 5 X to the 100 X oil immersion lens.

A reticle turret is also in the system to provide a micrometer for parfocalizing the system. There are six positions in the turret for whatever reticles are desired. Available are the micrometer, twinned and untwinned grain size, graphite flakes, and dirt reticles.

Figure 1 (overall view of the Research II metallograph) shows the location of most of the controls. Figures 5 through 8 show some specific

groups of controls. In Fig. 5 the lamp controls are pointed out. There are off-on switches for the main power, lamps and accessory circuits. In addition, there are rheostats for voltage control for both lamps and a starter button for the xenon lamp. The xenon lamp centering controls move the bulb in x and y directions for centering the filaments relative to a fixed spherical mirror behind the bulb. The xenon focus knob moves the condenser system to fill the field with light. The tungsten lamp selector knob is a push-pull control that moves the tungsten lamp in and out of position. It also turns to focus the lamp.

Figure 6 shows the illumination selector controls and is labelled to be self-explanatory.

The specimen stage on the Research II is mechanically identical to the Research I stage. Figure 7 shows the stage with the stage plate removed, revealing an objective and the index wheel. The stage must be elevated with the lever at the upper left in order to change objectives. The index wheel is numbered 1 through 5 and is matched to objectives, usually ascending numbers corresponding to higher magnifications.

Figure 8 shows the controls on the right side of the instrument and is appropriately labelled. The shutter controls provide for selecting the exposure time, shutter cocking, shutter release and for opening the shutter for viewing without the necessity of resetting the shutter speed to time.

The Research II exposure meter is a photometer with four levels of sensitivity, each succeeding level ten times more sensitive than the preceding one. For the selected sensitivity range, the light level is read out on a linear scale meter on the right side of the instrument and the exposure determined by use of a circular slide rule calculator, as shown in Fig. 9. One sets the film speed on the inner scale, then rotates the proper range index to the meter reading and reads exposure time opposite the long pointer.

When the exposure meter is in the optical path, exactly half the light reaches the film plane. It is, therefore, possible to reduce an inordinately long exposure by half by switching to the projection position after the normal exposure time is determined. This might certainly be desirable in the cases of dark field or polarized light photography.

BUGS AND HOW TO EXTERMINATE THEM

As in any new piece of equipment, there are shortcomings and bugs that it seems only the customer can find. The Research II is no exception.

The first small handicap that we encountered was in the dust cover. It is made of polyethylene and is tailored to fit over the stage only. There is a hole in one side to accommodate the phase illumination annulus and the space between the annulus and filter rack is too small to allow easy access with the cover. This was overcome by simply cutting through

one side of the hole in the cover. Now, it slips on and off quickly and still provides as much protection as ever.

Dust seems to be a particular problem in the Research II. We found considerable dust in the projection system that apparently had been shaken loose in shipping. The B & L service man was able to clear up the problem by disassembling the lenses and cleaning them.

Dust can also show up on the cover glass over the calcite prism. This can be reached by removing one of the objective lenses and blowing the dust away with freon or compressed air. One must be very careful about touching some of the glass surfaces not normally available for cleaning. They have soft coatings that are easily scratched.

The xenon and tungsten lamps are dust traps, also, and large particles show up as shadows in the field. Figure 10 shows the effect of dust on the xenon bulb. To clean the bulb it must be turned off and allowed to cool for at least ten minutes before opening the cabinet. Then the bulb may be wiped off with a brush or a suitable sized wire loop covered with lens tissue. A freon can is useful to blow away loose dust. Safety goggles are provided with the metallograph and should be worn. Xenon bulbs are under considerable pressure and have been known to explode with devastating effect. They must be handled with gloved hands.

The xenon light source on our metallograph was not quite centered and caused uneven lighting over a 5" x 7" field. When the light source is properly centered, the image of the bulb filaments should close down concentrically about the center of the ground glass as one moves the lamp condenser system. Figure 11 shows the position of our filaments before any effort was made at centering.

Centering the light spot is done by moving the condenser lens behind the aperture diaphragm. Figure 12 shows this lens with the diaphragm assembly removed. This unit is held in place by three small screws spaced 120° apart with one always at the bottom. The arrow indicates one of the screws. The upper screw at the back is extremely difficult to get at and requires a special Allen wrench and a dental mirror. Very little movement of the screws is required to properly align the light spot.

During the evaluation, the bright field retardation plate loosened and turned, giving polarized light at the bright field position. By removing one of the objective lenses, one can get at the plate with a sharp probe and move it in its mount. The plate was rotated until maximum brightness was obtained and a dab of cement applied to the edge. No more difficulty has been experienced.

None of the objective lenses except the 20 X are the exact magnification marked on the barrel. This means you cannot multiply the zoom control setting by the objective magnification for an exact magnification at the photographic station. The discrepancy is small and most of the time insignificant, but is worth knowing about. The instrument must be calibrated for exact magnifications. Table 1 shows the variation of our metallograph at some standard magnifications.

All of the objectives are achromat flat field* and a 5" x 7" field is covered in good focus to the corners, except for the aforementioned 100 X oil immersion lens. Combined with wide field eyepieces one gets almost too much field. It becomes almost like watching a cinemascope movie.

The negative amplifier projection system gives a slightly increased magnification at the field edges but it is not bothersome. The extent of this varies from one instrument to another.

The optical resolution of the Research II was compared to the Research I at several magnifications and found to be generally superior.

Figure 15 compares resolution at 200 X and 400 X using a eutectoid steel. The resolution of the pearlite lamellae is a bit sharper on the Research II.

The Research II has a continuous magnification range of 25 to 3000 X through the use of six available objectives and the built-in zoom system. Some loss of resolution results in using the zoom system and is illustrated in Fig. 16. At 750 X it is necessary to use the 40 X objective with a zoom setting of 18.75 and the resolution is about the same as on the Research I. At 800 X the Research II uses the 80 X dry objective with a zoom setting of 10 and the resolution is better than on the Research I using the same lenses as for 750 X but with a slightly longer bellows draw. This difference in resolution is due not to the increased bellows draw on the Research I but to the fact that an objective of higher numerical aperture is used on the Research II. One should always use the highest power objective possible and the lowest possible zoom setting.

Figure 17 illustrates the resolution using oil immersion lenses on both metallographs.

Polarized light performance of the Research II is superior, at least for viewing. The difference does not appear as great in photography. Figure 18 compares Research I and II using a specimen of anodized Zircaloy-2. There does appear to be more snap in the photomicrograph made on the Research II. Better resolution is obtained because one is able to operate at the optimum aperture diaphragm setting instead of stopped down completely.

It is possible to achieve rotatable sensitive tint¹ on the Research II, but in an awkward manner. If this feature is desired, B & L will leave the sensitive tint plate free to turn in the turret. By removing an objective opposite to the one to be used and reaching in the hole with a pointed steel probe, the place can be nudged around to any desired position. Figure 19 shows a close-up of how this is accomplished.

Since rotatable sensitive tint usually results in rather spectacular colored microstructures, at this point color photomicrography will be discussed.

*Apochromat objectives are reported to be available in the near future.

Table 1. Research II Magnification Chart

Indicated	Actual
50	51
100	102
150	156
250	250
500	530
750	790
1000	1025 (oil)
1500	1560 (oil)

Our 5 X objective has some bad internal reflections that cause a washed out image, especially of dark materials such as graphite. This effect is easily corrected by placing a $\frac{1}{4}$ -wave cap over the nose of the objective lens. This cap was provided by B & L. Figure 13 shows the results of photographing graphite through an uncorrected and corrected lens. To use the cap, the illumination turret is set at the polarized light position, the cap rotated to maximum brightness and the aperture diaphragm opened completely. If the diaphragm is not opened fully, dust on the $\frac{1}{4}$ -wave plate will show up. Bausch & Lomb makes a specially coated objective lens that corrects the reflection almost as well as the cap.

Although the 100 X oil immersion lens is called a flat field objective, it is not, actually. At 100 X the edges of a 5" x 7" field are out of focus, as can be seen in Fig. 14.

Most of the shortcomings mentioned are minor annoyances or can be tolerated. However, the very short vertical stage travel ($\sim \frac{1}{4}$ ") does restrict one somewhat. This feature combined with the fixed nosepiece lens makes it impossible to use low power objectives, such as the Zeiss macro lenses,¹ for low magnification work as one can on the Research I. This limits the utility of the metallograph.

PERFORMANCE COMPARISON

As has been mentioned, the Research II was designed with the metallographer in mind and is very easy to operate. All controls are within easy reach and, with the stage controls at waist level, prolonged examinations are not fatiguing.

¹R. S. Crouse, "Bausch & Lomb Research Metallograph Modifications," Advances in Metallography, Technical Papers of the Twentieth Metallographic Conference, Dow Chemical Co., Rocky Flats Div., Golden, Colorado, RFP-658.

The xenon light source on the Research II is rated at 6500°K which should be suitable for daylight color film. All exposures on Ektachrome Daylight Type film were too green and we were unable to compensate by filtration. Ektachrome Type B film, which is balanced for 3200°K light, gave a slightly overall blue exposure which could be corrected by using an 81EF filter or a 25% underexposure.

Tungsten light gave a somewhat warmer toned transparency than did xenon but the appearance was quite close to what one sees through the eyepiece. Tungsten exposures were on Ektachrome Type B without filters.

Color results with the Research II are just as good as on the Research I and somewhat easier to obtain. One needs only to underexpose or add a single filter for xenon light or photograph directly with tungsten. A water cell or an infra red cut-off filter is not needed as on the Research I.

Phase contrast is built into the Research II and is quite easy to operate. By comparison with the Nomarski system on the Reichert metallograph, it leaves something to be desired, especially at magnifications above 250 X. Below 250 X, the Research II gives better contrast than the Reichert. Figure 20 shows a comparison at 400 X.

Dark field illumination is seldom used but does on occasion have its uses. Here, again, the Research II is not only easier to convert than the Research I but does a superior job. Figure 21 is a comparison.

SUMMARY AND CONCLUSIONS

Bausch & Lomb has taken the heart of the Research I metallograph - the Foster calcite prism - and built around it an excellent new optical instrument. They have engineered it to cater to the comfort of the metallographer. All controls are extremely accessible and easy to operate. Every type of illumination one could possibly want is built right in. New light sources and lenses give superior optical performance.

The instrument is not perfect, however. The major difficulty lies in the tendency for various glass surfaces to collect dust, which then shows up in the photomicrographs. The xenon light source must be critically centered about the center of the photographic station for most even illumination. It seems that a different condenser system might give more even illumination. Even if it resulted in less intensity, this would be preferable since there is more light than is really needed.

Very short stage travel and the fixed nosepiece lens eliminates the possibility of low magnification work using the Zeiss macro lens.

Overall, the Research II is an excellent metallograph, somewhat improved over the Research I, with promise of being even better when further improved lenses are available. Quality inspection at the manufacturer's plant could definitely be improved; however, they were most

cooperative in solving our difficulties. If the 5 X and 100 X oil immersion lenses are brought up to a par with the other lenses, the phase contrast and the xenon light source improved, it will be, in the authors' opinion, the best metallograph we have had the pleasure to operate.

Fig. 1. Overall View of Research II Metallograph
Y-87701

Photo Courtesy of Bausch & Lomb

Fig. 2. Research II Metallograph with Operator

Fig. 3. Diagram of Optical System Y-87600
Courtesy of Bausch & Lomb

Fig. 4. Diagram of Illumination System Y-87601
Courtesy of Bausch & Lomb

Fig. 5. Research II Metallograph Emphasizing
Light Source Controls Y-87702
Courtesy of Bausch & Lomb

Fig. 6. Illumination System Controls Y-87703
Courtesy of Bausch & Lomb

Fig. 7. Stage with Plate Removed

Y-87704

Courtesy of Bausch & Lomb

Fig. 8. Controls on Right Side of Instrument

Y-87707

Courtesy of Bausch & Lomb

Fig. 9. Exposure Calculator Y-87699

After Cleaning Xenon Lamp

Dust on Xenon Lamp

Fig. 10. Effect of Dust Spots on the Xenon Bulb

Fig. 11. Position of Xenon Lamp Filaments on ORNL Metallograph Before Centering Y-87709

Fig. 12. Condenser Lens Behind Aperture Diaphragm. Arrow indicates one of three screws for centering. Y-87280

Without Cap

With Cap

Fig. 13. Comparison of 5X Objective Without and With $\frac{1}{4}$ -Wave Cap

Fig. 14. Hypoeutectoid Steel at 1000 X Using
100 X Oil Immersion Objective Y-87644

Research I

Research II

Fig. 15. Comparison of Resolution at 200 and 400 X

Research I

Research II

Fig. 16. Comparison of Resolution at 750 and 800 X

Research I

Research II

Fig. 17. Comparison of Resolution at 1000 X Using Oil Immersion

Research I
Research II
Fig. 18. Comparison of Polarized Light Performance. Specimen is anodized Zircaloy-2.

Fig. 19. Close-Up of Rotatable Sensitive Tint Arrangement
Y-85803

Reichert

Research II

Fig. 20. Comparison of Reichert Phase Contrast (Nomarski) with Research II

Research I

Research II

Fig. 21. Comparison of Dark Field Performance

AN ORBITAL GRINDER-POLISHER FOR PREPARATION OF IRRADIATED
METALLOGRAPHY SPECIMENS IN HOT CELLS.*

by

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Abstract

A unique orbital grinder-polisher was developed, fabricated, and installed in hot cells for preparation of irradiated metallography specimens. The compact unit occupies approximately 0.2 cu. ft. of cell space. It was specifically designed to provide the capabilities of commercially available vibratory polishers without their large space requirements. Units have been in operation about two years. The design of the grinder-polisher is described, operating experience is discussed, and illustrations of results are presented.

* Developed under Contract AT(45-1)-1830 between the United States Atomic Energy Commission and Battelle Memorial Institute.

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INTRODUCTION

One phase of metallographic preparation that is essential for the modern metallography laboratory is "vibratory" polishing.

In the Battelle-Northwest Radiometallurgy Laboratory at Richland, Washington, large numbers of irradiated samples are prepared for metallographic examination with remotized equipment in hot cells. Samples processed cover nearly the entire spectrum of metals, alloys, ceramics, and cermets utilized in the nuclear industry. Providing "vibratory" polishing capabilities for the metallography hot cells using commercially available equipment posed insurmountable problems. Commercial units in general had one or more of three shortcomings that made them unsuitable for our use. They required too much cell space; they were too complex to operate and maintain in cell with manipulators; or the cost to remotize them for use in hot cells was too great.

The problem was solved by designing a simple, compact, and relatively inexpensive polishing unit that satisfied our requirements but did not have shortcomings of commercially available equipment. About two years ago the first unit was fabricated and installed in a hot cell for evaluation.

The unit was so successful, that since that time, additional units have replaced most of the rotary type equipment. Although the Orbital was primarily designed as a polisher it was found that it also made an excellent grinder and now the bulk of both grinding and polishing in our laboratory is done on Orbital units.

DESIGN

The Orbital grinder-polisher^(a) assembly is shown in Figure I.

The drive consists of a 1:1 ratio angle gear^(b) which is mounted on a cell plug. Drive linkage extends through the plug to the exterior of the cell wall where it is belt driven by a vari-speed 1/4 H.P. electric motor. A plate thrust bearing built into the bottom of the pan holder assembly is attached to the in-cell end of the angle gear shaft. The end of the shaft that fits into the thrust bearing is machined .093 inch eccentric,

(a) Contact W. J. Gruber for detailed information or design drawings.

(b) Boston Gear R320.

which imparts a 3/16 inch diameter orbital motion to the pan holder when the motor is actuated. The stainless steel pans are 1 inch deep by 6-3/4 inches diameter and are held in the pan holder by a thumb screw that can be tightened or released with a manipulator. A disposable plastic disc^(c) 1/16 inch thick covers the bottom of the pan. Abrasive papers for grinding and cloths for polishing are glued to plastic discs prior to insertion into the hot cell. The desired grinding or polishing step is accomplished by selection of the proper abrasive paper or cloth covered disc and placing it in the pan. To prevent the disc from slipping in the pan during operation a small dowel was welded in a vertical position to the inside edge of each pan. On the periphery of each disc a notch is cut. When a disc is placed in a pan the notch is matched with the dowel. The tolerance is such that a disc will not fit into the pan properly unless the notch and dowel are matched.

The sample holder assembly consists of a plate with cut outs for standard sample mounts. Sample holder assemblies are made to accommodate three sample mount sizes. Clearance around the sample mounts is .015 to .020 inch. A right angle bar is welded to the plate and extends to a mount on the cell plug. A second plate is welded to the bar about 2-1/2 inches above and parallel to the sample plate to provide sample weight guides. The sample weight guide plate is drilled and 1/2 inch long tubing is inserted and welded directly above the center of each cut out in the sample holder plate. One-fourth inch diameter pins are inserted through the guide plate and rest on the mounted samples. The weights are lead cylinders drilled axially to fit over the 1/4 inch diameter pins. The pins are flanged above the guide plate to prevent the weights from contacting the plate so that all applied weight is imparted to the samples. Weight sizes are 100, 200, and 400 grams and the pins are long enough to accommodate three 400 gram weights.

The sample holder assembly is held rigidly in place during operation by a tapered, dove-tailed joint at the cell plug. The insert is welded to the right angle bar and a matching slot is machined in a block bolted to the plug. The slot for the insert is machined sufficiently wide to allow easy insertion or removal in the vertical direction. It is tightened to a rigid position by the sample holder

(c) Manufactured by Fabricators Inc., Seattle, Washington.

clamp. The sample holder clamp is a threaded rod which extends through the cell plug and is operated from the exterior of the cell. When tightened, the rod forces the matching dove tails together, rigidly positioning and supporting the sample holder assembly.

Rotation of the pan is supplied by an adjustable rod through the cell plug in line with the edge of the pan above the pan holder. A polyvinyl chloride plug is fitted over the in-cell end of the rod. The rod is adjusted so that the tip lightly contacts the edge of the pan in its position nearest the rod. The pan contacts the polyvinyl chloride tip once during each orbital motion causing the pan to rotate slowly in the direction opposite the orbital movement.

The in-cell portion of the unit occupies only about 0.2 cu. ft. With the sample holder assembly and pan removed the unit can be removed from the cell for maintenance or repair without disrupting other in-cell operations.

OPERATION

The sequence for operation of the orbital unit is as follows:

1. A clean pan is clamped into the pan holder and an abrasive paper or cloth covered plastic disc is placed in the pan.
2. The disc is covered with 1/16 to 1/8 inch of lubricating fluid for grinding steps or a thin abrasive slurry for polishing steps.
3. The sample holder assembly is mounted and clamped in place.
4. Samples are placed in the holder and weighted. Normally weights range between 400 and 800 grams per sample.
5. The motor is actuated and operated normally at 1725 r.p.m.

In operation, the pan makes 3/16 inch diameter orbital motions at the rate of 1725 per minute beneath rigidly held samples. Energy from contact with the pan results in a slow rotation of the samples in the same direction as the orbital motion while the pan slowly rotates in the direction opposite the orbital motion. These three simultaneous motions produce samples with flat, nondirectional, planar surfaces and extremely sharp edges.

EXPERIENCE WITH THE ORBITAL

We have had considerable success with the Orbital units, and, as previously mentioned, replaced most of the rotary type units with Orbital units. Sample surfaces produced by the Orbital are at least equal to those produced on conventional vibratory units, however, sample processing time is only about one-fourth of that required for conventional units. The Orbital is particularly effective where extremely flat surfaces are required, edge and inclusion retention is a necessity⁽¹⁾, or low relief is necessary in specimens consisting of two or more materials with extreme hardness variations.

The Orbital has been used successfully to prepare nearly all metals, alloys, ceramics, and cermets utilized in the nuclear industry. As is the case with most preparation equipment, extremely soft materials, such as lead and annealed low alloy aluminum, are the most difficult to properly prepare with the Orbital.

The motor speed of 1725 r.p.m. is used for preparing nearly all materials. Obviously, the highest speed possible utilizes the capabilities of the Orbital most efficiently. During testing it was found that samples began to bounce, reducing efficiency, as the motor speed approached 1800 r.p.m. and that the optimum speed was just below that for all materials with very few exceptions. Lower motor speeds were required only with extremely soft or fragile materials. Because there was little need for motor speed adjustment, all additional units put into operation were equipped with less expensive, constant speed, 1725 r.p.m. motors, and the few samples requiring lower speeds are processed on the unit with the vari-speed motor.

Because of the simple design, initial cost is low and the units are virtually maintenance free. Break downs are extremely rare and maintenance is limited to lubrication of the drive train.

Results with irradiated materials prepared on Orbitals in-cell are shown in Figures 2, 3, 4, and 5. The samples illustrated are representative of specimen types that can be very difficult to prepare for metallography.

DISCUSSION

The design described in this paper is tailored for the requirements of our laboratory, however, possibilities for design modifications to utilize it in other surroundings are unlimited. The heart of the unit is the unique eccentric drive that imparts the orbital motion to the pan, but the size of the unit and the power train can vary widely to suit particular needs. Some possibilities are: pans may be enlarged to accommodate more samples; a straight line drive may be utilized for glove boxes with the motor located underneath and the drive shaft sealed where it enters the enclosure; or a compact unit without an extended drive train may be used in a preparation facility with limited space.

SUMMARY

A compact, inexpensive unit was developed to provide "vibratory" polishing capabilities for our hot cells where it was impractical to use commercially available equipment. The unique orbital motion produces sample surfaces of the same quality as commercial "vibratory" polishers but requires only about one-fourth of the time. The design is simple and, with variations in either the power train or size, the Orbital can be adapted to any surroundings.

Orbitals have been in use for about two years. During that time a wide range of reactor fuels and structural materials have been prepared successfully. It was found that the Orbital did an excellent job of grinding as well as polishing and the units now serve a dual purpose. These units have proved particularly effective where extreme flatness or edge and inclusion retention is necessary, and they provide low relief in specimens consisting of two or more materials with extreme hardness variations. The simple design makes the in-cell functions easy to perform with manipulators and the units have been virtually maintenance free. The Orbital performed so well that it has replaced most of the rotary equipment in our laboratory and the bulk of metallography sample preparation is done on these units.

REFERENCES

1. W. J. Gruber, F. M. Smith, and E. C. Watts, RFP-658, Technical Papers of the Twentieth Metallographic Conference, 1966, p. 106.

ORBITAL GRINDER - POLISHER

FIGURE 1

250X

FIGURE 2
6063 Al Alloy Showing Oxide
Layer Formed During
Irradiation

500X

FIGURE 3
Porosity in 1100 Al Alloy
Weld. Etched to Show
Microstructure.

1000X

FIGURE 4
Zircaloy-2 Corrosion Coupon
with Badly Fragmented Oxide
Layer. Specimen was Electro-
less Nickel Plated to Preserve
Oxide During Preparation.
Shown as Polished.

250X

FIGURE 5
 PuO_2 -Stainless Steel Cermet.
Stainless Steel has been
Etched to Show Phases Pre-
cipitated During Irradiation.

AN ALPHA METALLOGRAPHY LABORATORY AT OAK RIDGE NATIONAL LABORATORY*

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ABSTRACT

An alpha metallography glove-box line has been fabricated and installed at Oak Ridge National Laboratory. The installation is designed primarily for the handling of plutonium and its alloys, and the operating discipline is complete containment for all processes. A negative air pressure is maintained for normal operations or, if required, argon can be substituted as the internal atmosphere. The various operations in the eight glove boxes are as follows: (1) cutting, grinding, and mounting; (2) mechanical polishing; (3) vacuum deposition etching; (4) microscopic inspection; (5) vacuum cathodic etching; (6) chemical and electrolytic etching; (7) replication and minor repairs of equipment; and (8) microscopy and photomicrography.

Grinding of specimens is by a lapping method; and the mechanical polishing is done on a conventional 8-in. motor-driven wheel, as well as vibratory polishing units. The inspection microscope is a modified Leitz Metallux. The metallograph is a highly modified Bausch & Lomb Research I instrument which has been sectioned so the inverted microscope is within the glove box. Illumination, visual examination, and photomicrography are coupled with the microscope through three optical relays.

In addition to the eight glove boxes in a line, two glove boxes are isolated. One box is utilized for microhardness testing and mensuration, and the other box is equipped for photomacrography and mensuration.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

INTRODUCTION

There has been an increase in the interest in high temperature fuels work at Oak Ridge National Laboratory (ORNL). The ORNL sol-gel process,¹ in particular, provides a variety of fuel materials for different fabrication schemes. Mixed oxides and nitrides of plutonium-uranium are strong candidate fuels for liquid metal cooled fast breeder reactors. The need for high quality metallography in evaluating the various processes for these fuels is imperative. In this paper, we describe the various equipment and techniques for specimen preparation, etching, and photomicrography as well as microhardness, mensuration, and photomacrography, which are all performed in glove boxes. Photographs of all the glove boxes described in this paper were taken prior to the installation of gloves so there would be less restriction in viewing the interior.

DESIGN AND OPERATING PHILOSOPHY

Complete containment for all the preparation and microscopic examination steps, microhardness, and photography has been followed. The three glove boxes for the more basic steps - cutting, mounting, and grinding; hand and vibratory polishing; and chemical and electrolytic etching - follow a more conventional design of a glove box, which is 6' long and 30 $\frac{1}{2}$ " deep with slanting fronts. All boxes were fabricated from series 300 stainless steel. The floor of each box is $\frac{1}{4}$ " thick and the sides and top are 11 gauge (0.125"). One exception is the metallograph box which has a $\frac{3}{8}$ " thick floor. The transparent fronts are polished safety glass ($\frac{1}{4}$ " thick) or $\frac{1}{4}$ " or $\frac{1}{2}$ " thick Plexiglas.* One important feature in the fabrication is all side and bottom joints have 5/8" radius bends to expedite cleaning.

The integrity of the boxes was tested with internal positive and negative pressures of 8.0" water gauge (W.G.) relative to the room. Leak rate tests were made with 4.0" W.G. positive pressure. Leaks were limited to 0.006-0.012% of box volume/in./hr. The boxes normally operate at -0.5 to -1.0" W.G. with either air or argon atmosphere as dictated by the specimen requirements.

The alpha glove boxes for microhardness, photomacrography and the metallograph were designed by building full size cardboard mock-up boxes around a microhardness tester, macrocamera, and metallograph prior to making the drawings for fabrication.

OPERATIONAL STEPS

There are ten glove boxes for preparation, examination, and hardness measurements of metallographic specimens. Eight boxes are in a continuous

¹R. G. Wymer, Laboratory and Engineering Studies of Sol-Gel Processes at Oak Ridge National Laboratory, ORNL-TM-2205, May 1968.

*Rohm-Haas Type SE-3 or equal.

line and two boxes are isolated - one for microhardness testing and the other for photomacrography (Fig. 1). The functions of these boxes are shown in Table 1 in the order of specimen preparation and examination.

Table 1. Function of Each Glove Box

Operation	Box
A-1 Cut metallographic specimen from larger piece of material	16
A-2 Mount specimen in epoxy resin plastic (vacuum mounting is available if required)	16
A-3 Grind mounted specimen to desired depth	16
B-1 Polish specimen on motor-driven wheel or by vibratory polishing	17
B-2 Ultrasonic cleaning of specimen	17
C-1 Vacuum coating of specimen	20L
D-1 Microscopic inspection	18
E-1 Vacuum cathodic etching	20R
F-1 Electrolytic polishing and etching	19
F-2 Chemical etching	19
F-3 Ultrasonic cleaning	19
G-1 Specimen replication	21A
G-2 Metallograph maintenance	21A
G-3 Microscopy and photomicrography	21B
H-1 Photomacrography and mensuration	22
I-1 Microhardness and mensuration	23

The continuous glove box line 16 through 21 is shown in Fig. 2.

Specimen Preparation Box 16

The box, shown in Fig. 3, is 72" long x 27" high x 30 $\frac{1}{2}$ " deep. Metallographic specimens are cut, mounted, and ground in this box. The box contains a sink (12" x 12" x 6" deep) to which is attached an external drain and valve. At the present time, this sink drain is not connected to a drain line for radioactive waste; but such a connection can be made at a later date with little difficulty. All solid waste is bagged out and decanted liquid waste is transferred to box 17, which is connected to a radioactive waste drain. The procedure for depositing liquid waste will be described under box 17.

Fig. 1. Alpha Metallography Laboratory. Arrows and numbers indicate camera angle and figure number. Y-88422

Fig. 2. Alpha Metallography Laboratory. The continuous line of glove boxes 16 to 21 are limitations required the line to assume a "U" shape.

Fig. 3. Glove Box 16 for Cutting, Mounting, and Grinding of Specimens. Grinding is done on the lapping machine shown on the left. Cut-off saw is shown behind the third glove port. Vacuum mounting of specimens in epoxy resin is done in chamber between third and fourth glove ports. The argon drying line is above the third glove port.

Y-87512

Specimen Cutting

Sample cutting for metallographic specimens is accomplished with a saw fabricated at ORNL following a design developed at Argonne National Laboratory. This saw, shown in Fig. 4, is powered by a small Bodine electric motor with gear reduction which results in a no-load speed of 170 rpm on the blade spindle. The blades being utilized are aluminum oxide and silicon carbide abrasive blades and diamond-impregnated metal blades. All blades are $4\frac{1}{2}$ " diam and are available in thicknesses from 0.008 to 0.030". The low rpm of this saw prevents slinging of particles and dust from the sample, and if the saw blade should break, the fragments will not be hazardous. The saw blade travels through a sponge wetted with a suitable coolant (silicone oil, tetradecane, or water) to minimize air borne contamination during the cutting operation. The sponge is changed periodically to reduce the quantity of contaminated dust and small particles which are collected. The saw is operated by an on-off switch outside the box. The sample is clamped in a vise and applied to the wheel by manual control.

Specimen Mounting

Specimens are mounted in a room-temperature-setting epoxy resin.* Precast blank right cylinder mounts $1\frac{1}{4}$ " diam x 1" high of epoxy resin with $\frac{1}{4}$ " and $\frac{1}{2}$ " center holes are used for small specimens. The specimen is inserted into the hole and the cavity filled with the same epoxy resin. Larger specimens are mounted in a full $1\frac{1}{4}$ " diam mold.

Flamability tests have been performed on the epoxy resin and hardener. These materials burn only if supported by an open flame. A solvent for dissolving the specimen from a cured mount also was tested, and was found to burn only in a supported flame.

A $5\frac{1}{2}$ " diam chamber is in the box for vacuum mounting. Specimens with surface-connected voids can be mounted by this method to fill these areas with the epoxy resin. The vacuum chamber is connected to a mechanical vacuum pump outside the box through a cannister CWF filter. The exhaust from the pump is connected back to the glove box with another CWF filter and an oil mist filter in the return line.

Specimen Grinding

Specimens are ground on a Speed Lap Model G, Style B grinder** (Fig. 5) using 600 grit alumina abrasive and a suitable vehicle (silicone oil, tetradecane or water). This machine uses a $4\frac{1}{2}$ " diam sample-holding turret for four standard $1\frac{1}{4}$ " diam mounts. The turret with the four specimens revolves

*Araldite 502 and hardener 951 (10 to 1 mixture by weight), Ciba Products Co., Summitt, New Jersey.

**Speed Fam Corp., 3620 Oakton St., Skokie, Illinois 60076.

Fig. 4. Cut-Off Saw Used in Glove Box 16. The hand wheel on top controls the cutting depth. Note the sponge for wiping the cutting wheel. Y-84852

(a)

(b)

Fig. 5. Abrasive Grinder for Glove Box 16. The grinder shown above was installed with the control panel outside the box and the Archimedes screw was altered so the unit was separate from the grinder. The conical plate to confine the drainage to the outer part of the sink is shown in (b).
(a) Y-83169 (b) Y-83170

on the 12" diam cast iron grinding or lapping wheel. The speed of the grinding wheel is 87 rpm. A modification was made to the as-purchased grinder by adding a conical insert under the lapping wheel (Fig. 5a). This insert limits abrasive and particulates, which run off the wheel into the sink directly below, to the outer part of the sink where the agitator will prevent caking. Also, the drain line was increased from 3/8" to 1". The Archimedes-type slurry pump, shown in Fig. 5a, was fastened on top the grinder (see Fig. 3) to expedite repair or complete replacement.

Specimens are cleaned in an ultrasonic cleaner with water (if the specimen is compatible with water), washed with ethynol (see Appendix) and dried by a jet of compressed argon from a hand held plastic line from the back of the box (see Fig. 3). If there is a need for a potentially explosive solvent, such as acetone, special measures are exercised (see Appendix). Water is added to the box from a two gallon supply bottle on top of the box. An external valve and an internal valve must be opened before the water will flow by gravity into the box.

Polishing Box 17

This glove box, shown in Fig. 6, is 72" long x 27" high x 30 $\frac{1}{2}$ " deep. Operations performed in this box are limited to specimen polishing with a conventional 8" motor-driven polishing wheel or by vibratory polishing in a 10" bowl.* The box also contains an ultrasonic cleaner.

The 8" diam polishing wheel is motor driven at 125 rpm. Various cloths can be attached to the horizontal wheel and the specimen is held in contact with the revolving cloth while a suitable vehicle (silicone oil, tetradecane, or water) and abrasive are added. The specimen can be inserted in a clamp and held by the gloved hand. The clamp prevents damage to the glove. The usual practice is to use a specimen holder such as an Automet or a guiding device which moves the specimen across the polishing wheel.

The two 10" vibratory bowl units are identical in size and design. Various cloths, abrasives, and vehicles are used as needed. Cloths generally are limited to Pellon** (PAN W) and Microcloth.*** Abrasives are alumina^Δ (Linde A,B,C) and diamond^{ΔΔ} and the vehicle is water or silicone oil.^{ΔΔΔ} The standard 1 $\frac{1}{2}$ " mounted specimen is clamped into a 350 gram stainless steel cap and placed into the bowl with the polishing face down.

*Normally, the vibratory polisher is designed for a 12" bowl. This reduction to 10" was required for entry to and exit from the boxes.

**Pellon Corp., 1120 Avenue of Americas, New York, New York.

***Buehler Ltd., 2120 Greenwood St., Evanston, Illinois.

^ΔLinde Co., Crystal Products Dept., 4120 Kennedy Ave., East Chicago, Illinois.

^{ΔΔ}Elgin National Watch Co., Abrasive Division, Elgin, Illinois.

^{ΔΔΔ}Dow Corning 702 Fluid, Dow Corning Corp., Midland, Michigan.

Fig. 6. Glove Box 17 for Hand and Vibratory Polishing of Specimens. Note the stereozoom microscope shown in use in Fig. 7. The argon drying hose is above the right glove port. Y-87611

Fig. 7. Stereozoom Microscope. The microscope can be suspended from a bracket on glove boxes 16, 17 and 19. Y-87612

An ultrasonic cleaner is available for cleaning the specimen between or after the polishing steps.

A stereozoom microscope with a magnification range of 10.5 to 60 X is attached outside the box for viewing the specimen (Fig. 7). A ring light is attached to the microscope for illuminating the specimen. This microscope can be attached to boxes 16, 17, and 19.

This specimen polishing box is equipped with a hot drain for the disposal of liquid waste. The liquid waste is always made alkaline* before disposal and all solids are allowed to settle prior to disposal. The solids then are removed by bag-out procedure. Two valves are in the drain before the major drain line. One of these two valves is always closed to reduce the possibility of a back contamination into the glove box from fumes which might be present in the major drain line. A water flushing line is connected to the drain just under the sink drain valve. After the liquid waste is deposited it is diluted with this water and the drain line flushed.

The use of solvents, the washing and drying of specimens, and the introduction of water into the box follows the procedures previously described for box 16.

Angle Transfer Box 20L (Left Side)

The room size necessitated the formation of the glove box line into a "U" shape; consequently, there are two angle boxes. This angle box is ~ 33" x 20" x 21" (Fig. 8). Although only one glove port is available on the front of the box, there are two glove ports on the back. This box does not contain equipment at present; vacuum deposition apparatus² will be installed soon.

Inspection Microscope Box 18

This box is 36" x 20" x 30" (Fig. 8). cursory examinations of the progress in polishing and etching the metallographic specimens are done in this box. The microscope is a Leitz Metallux equipped with an optical

*The liquid waste line is stainless steel and the drain is connected to a "tank farm" which has storage tanks of stainless steel. The tank contents are chemically processed to recover desirable elements. It is most important that waste products be compatible with the stainless steel; hence, a pH above 7, as measured by litmus paper, is required. Alkalinity or neutralization is obtained by the addition of a strong base such as NaOH.

²J. O. Stiegler and R. J. Gray, "Phase Identification by Deposition of Surface Films," Technical Papers of the 20th AEC Metallographic Group Meeting held May 18-20, 1966, at Dow Chemical Company, Rocky Flats Div., Golden, Colorado, RFP-658.

Fig. 8. Angle Boxes 20L and 20R and Inspection Microscope Box 18
Y-87513

relay* to extend the tube length of the microscope. Containment is accomplished with "O" ring seals in positioning the lenses in the relay. A Leitz Aristophot stand was extended to correspond with the extension of the optical relay. A camera is supported above the box in the event photomicrographs are required; however, photomicrography generally is done with the metallograph in glove box 20. This inspection box is equipped with a sphincter valve like the one shown in Fig. 9. The sphincter valve consists of ten circular sheets of 6" diam x 1/16" thick neoprene, each containing 3" I.D. holes. The circular sheets are spaced by 1/2" Plexiglas pieces which are circular with the same outer diameter as the neoprene sheets but with 4 1/4" I.D. holes. The neoprene sheets and Plexiglas are cemented and bolted together. Specimens which have been encapsulated or bagged are placed into a cylindrical (ice cream) carton, which is 3 5/8" diam, and pushed through the neoprene openings. The wiping action of the multiple layers of neoprene serves as a seal. One carton always remains in the sphincter valve and the next carton merely pushes the previous carton through the opening into the box. When not in use, additional protection is afforded by a hinged door with an "O" ring gasket.

Angle Transfer Box 20R (Right Side)

This box is identical in design and size (~33" x 20" x 21") to 20L (Fig. 8). Vacuum cathodic etching equipment is being fabricated and will be installed in this box. Only the vacuum chamber will be within the box. The vacuum pump and power supply will be connected through the box wall to the vacuum chamber.

Specimen Etching Box 19

This box is 72" x 27" x 30 1/2" and is shown in Fig. 10. Because of the potential corrosive nature of the etchants in the box, the internal stainless steel surface is protected with a fiberglass coating plus an Amercote layer. Chemical etching is performed in an etching hood which is provided with a neutralizing, internal exhaust system. The fumes generated by the etchants are drawn through two Drierite bottles by means of a small fan - all within the glove box. In this manner the negative pressure of the box is undisturbed. The etching hood was designed for complete assembly or disassembly within the box.

*An optical relay is a system of lenses which transports an image from one location in an optical system (microscope) to another location with a minimum change in magnification, resolution or aberration. The optical relay may be 2 or 3" long or several inches or several feet long as required for the installation. The optical relay is developed by the use of optical physics to determine the proper lens combinations and their spacings or a microscope is attached to an optical bench and various lens combinations are placed in the optical path to transfer the image at the microscope eyepiece to another designated location on the optical bench.

Fig. 9. Sphincter Valve for Entering Specimens Into Glove Box. External view (a) shows multiple neoprene sheets and outer door. The carton is not shown in place. Internal view (b) shows transfer carton in place.

(a) Y-88256 (b) Y-88255

Fig. 10. Electropolishing and Chemical Etching Box 19. Electro-
polishing and etching power supply is shown on lower shelf. Y-87610

This box is equipped with a hot waste drain for liquid. The disposal procedure follows the steps described for box 17.

The electropolisher is operated with the electrical controls and power supply outside the box. Spent electrolytes are disposed of through the sink drain after following the standard neutralizing procedures described previously for chemical etchants.

An ultrasonic cleaner is available for removing the etchants or electrolytes from the specimen surface prior to microscopic examination.

The use of solvents, the washing and drying of specimens, and the introduction of water follow the procedures previously described for box 16.

Metallograph Enclosure Box 21

This enclosure consists of two separate glove boxes. Box 21A is 36" x 30 $\frac{1}{2}$ " x 30", and box 21B is 30 $\frac{1}{2}$ " x 30 $\frac{1}{2}$ " x 30" (see Figs. 11 and 12). Box 21A is intended as a clean area for replication purposes, for the maintenance and repair of the metallograph, or the in-box repairs of other equipment, and for other miscellaneous operations requiring a relatively clean area.

In transferring a specimen from the specimen etching box 19 to the microscopy box 21A, the bung in box 19 is removed and the specimen is placed in the pass-through port. The bung is replaced so the specimen is between this bung and the adjacent bung in box 21A. This in-between area is evacuated and flushed with argon, then the bung in box 21A is removed and the specimen transferred through boxes 21A and 21B and placed on the metallograph stage. Such care is exercised to minimize the transfer of fumes from the etching box to the metallograph.

A Bausch & Lomb Research I metallograph is located in box 21B. The supporting stand for the glove box is $\frac{1}{2}$ " thick steel plate on a 1" grating; in addition, the floor of box 21B is a $\frac{1}{2}$ " plate. This stand then serves as the optical alignment for the metallograph. The box is firmly secured to the $\frac{1}{2}$ " steel plate of the stand. The original optical bench of the metallograph was cut into three sections so the camera, inverted microscope, and carbon arc lamp are separated (Figs. 11b and 12). The inverted microscope is enclosed in the glove box and the camera and carbon arc lamp are outside the box on the left and right sides, respectively. Three optical relays are required.

The carbon arc lamp is unaltered. The optical relay for the lamp consists of two aspheric lenses sealed in an aluminum tube (Fig. 13). The internal surface of the tube is coated with a black epoxy resin to reduce internal reflections, and the space between the two lenses is filled with water. The water serves as a coolant of the light beam before it enters the microscope, and the higher refractive index of the water changes the light path advantageously in filling the aperture of the microscope.

Fig. 11. Alpha Metallograph Glove Boxes 21A and 21B. The bag-out port is above the camera. Box 21A (a) is undesignated for equipment. The remote control for focussing the microscope can be seen below the camera in (b).

(a) Y-87664 (b) Y-87508

Fig. 12. Alpha Metallograph Glove Box 21B. The carbon arc illuminator is on the right and the sphincter valve is above the illuminator. A lamp for back lighting the specimen is above the microscope stage. Y-87507

Fig. 13. Optical Relay for Illumination. The optical relay is an aluminum tube with two aspheric lenses sealed in place. The space between the lenses is filled with water. The filler tube (top) and drain can be seen. Y-85098

The optical relays for the camera and for binocular viewing are alike. Each relay is made of two tubes which are telescopic in design so the overall length of the two tubes can be reduced if there is a need to remove the metallograph from its base for servicing. The lens systems within the tubes are sealed in place with "O" rings.

When the metallograph is in use for binocular viewing, the operator has command of x-y movements of the stage, coarse and fine focussing, selection of filters and all normal controls of the metallograph by the gloved hands. After the field is selected and there is a desire to make a photograph, the image is changed to the camera ground glass. Although it is not shown in the photographs, a mirror is positioned so the projected field can be observed and aligned as desired. Fine focussing while viewing the image on the ground glass is accomplished with a step-motor* (Fig. 14) and the adjustable speed drive* (Fig. 15). This motor is designed so the stepping increments of rotation are 1.8° in both directions. Positive movement of the focussing shaft of the metallograph is by a PIC** positive drive belt and matching geared pulleys. With this controlled movement, the 1.8° rotation is equivalent to $\frac{1}{25}$ micron vertical movement of the stage. This fine focussing control is equal or better than the normal movement done by an experienced microscopist by hand.

The box is equipped with an overhead lamp which can be used for back-lighting of the specimen (Fig. 12). An example of this use to produce contrast between the specimen and the mounting medium is shown in Fig. 16. Other examples of the quality of the optics of the metallograph are shown in Fig. 17. Plutonium-dioxide spheres prepared in the glove box line and photographed with the metallograph are shown in Fig. 18.

The sphincter valve for box 21B can be seen in Fig. 12. This valve is identical to the one described previously (see Fig. 9).

Macrocamera Box 22

This box is 37" wide (lower half) and 28" wide (upper half) x 24" high x 27" deep (lower half) and 21" deep (upper half), as shown in Fig. 19. This box is isolated, so all specimens are received through a sphincter valve similar to Fig. 9 and exit through a bag-out port. Electronic flash lamps are positioned on each side. The power supply for the flash units provides a selection of 25, 50, 100 and 200 watt sec. During exposure, the entire inner box is illuminated and the interior surface of the stainless steel box serves as a reflector for uniform illumination. A small lamp is located within the box to aid in focussing.

The camera has double cylindrical bellows; a tapered bellows inside the box and a straight cylindrical bellows outside the box. Each bellows

*Slo-Syn Motor Type SS50-1008 and Adjustable Speed Drive Type ST1800BV, The Superior Electric Co., Bristol, Conn. 06010.

**PIC Design Corp., East Rockaway, Long Island, New York 11518.

Fig. 14. Close-Up Views of Alpha Metallograph and Focussing Motor. The optical relays for the camera and binocular viewing can be seen in (a). The step-motor for focussing is shown in (b).

(a) Y-87509 (b) Y-87666

Fig. 15. Adjustable Speed Drive and Remote Control for Focussing Motor. The adjustable speed drive controls the motor speed for continuous movement in either direction. The small remote control box can be carried by hand. The toggle switch controls the direction of rotation of the motor shaft and a single push of the button rotates the shaft 1.8° . The adjustable speed drive and remote control can be seen in Fig. 2.

Y-87665

Fig. 16. Pyrolytic-Carbon Coated Coke Spheres Photographed with the Alpha Metallograph. (a) Shows normal bright field illumination; (b) shows polarized light; and (c) shows polarized light with back lighting. Note the edge sharpness in (c). (a) Y-87596 (b) Y-87597 (c) Y-87598

Fig. 17. Photomicrographs Made with Alpha Metallograph. The copper-phosphorus eutectic structure was selected because of the demands on the optical system. Flatness of field and resolution qualities can be seen.

(a) Y-87594 (b) Y-87595

Fig. 18. Plutonium Oxide ($^{239}\text{PuO}_2$) Microspheres Prepared and Photographed in Alpha Metallography Laboratory. Y-88034

Fig. 19. Alpha Macrocamera in Box 22. Electronic flash lamps are supported outside the box for illumination. A sphincter valve is evident in (b). Both bellows (inside and outside the box) are extended and contracted via a rack and pinion gear.

(a) Y-87515 (b) Y-87613

is adjustable by a rack and pinion. Continuation of the alpha containment within the camera box is accomplished with a glass plate located about midway in the bellows chamber. With the glass plate in this position, there is minimum image interference caused by reflection, dust, etc. (since this plane is out of focus). The glass plate is protected by a steel plate which slides into position except when the camera is in use, Fig. 20. An example of a photomicrograph made with this camera is shown in Fig. 21. The specimen stage is a motor-driven scissors jack that can be raised or lowered by a switch inside the box or an identical switch outside the box.

Microhardness Box 23

This box is 36" wide x 30" high x 30" deep (Fig. 22). This box also is isolated from the glove box line. Encapsulated or bagged specimens enter the box through a sphincter valve, shown in Fig. 9. Specimens are removed from the box by a conventional bag-out procedure. A commercial microhardness tester* is positioned in the box and an optical relay extends the microscope image outside the box. Since this relay must move up and down with the focussing of the microscope, containment is maintained in passing the optical relay through the top of the box with a double boot (one inside and one outside the box). Containment within the optical relay is with "O" seals for the lenses. A counter load is attached to the optical relay outside and above the microscope to compensate for the weight of the optical relay.

Loads ranging from 1 to 1000 grams on the indenter are applied to the pan attached to the beam. For heavier loads, up to 10,000 grams, a cross beam is balanced on the standard load pan. This cross beam, shown in Fig. 22, has two pans (one on each side of the hardness tester). Equal loads are applied to each pan.

In addition to hardness testing, this glove box can be used for x and y mensuration of specimens up to one inch. The x-y stage can be replaced with a traveling stage which provides 4" of travel with accuracy of 0.0005".

CONCLUSIONS

A metallography glove box facility has been designed and fabricated for use with alpha emitting specimens. The boxes are designed for negative pressures with air or argon atmospheres. The philosophy is complete containment for all metallographic operations, including photomicrography, and microhardness testing. The results of these procedures have been equivalent to the same results in a standard metallography laboratory from non-radioactive materials. Plutonium specimens have been prepared and photomicrographs made.

*Service-Diamond Microhardness Tester.

Fig. 20. Close-Up of Bellows with Rod (A) for Inserting or retracting protective steel plate over glass plate in the bellows. The steel plate is retracted into the envelope (B) when the camera is in use. Y-88257

Fig. 21. Example of Photomicrograph Made with the Alpha Macrocamera. Y-86598

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Fig. 22. Macrohardness Tester in Box 23. Optical relay for viewing and mensuration and the sphincter valve can be seen in (b). Note the balanced weight pans for increased loads. (a) Y-87616 (b) Y-87614

APPENDIX

Use of Alcohol in Alpha Metallography Glove Box

Metallography specimens must be dried properly. This drying action must be rapid and thorough. Water, polishing vehicle, or etchants must be removed from the minute interstices of the specimen. If these liquids are not removed, they can creep to the polished surface, develop stains and often confuse the microscopist in the interpretation of the microstructure. In the normal laboratory these liquids are removed by a thorough washing in hot water or in an ultrasonic cleaner followed by a rinse with absolute (200 proof) ethynol and a quick dry with a hot air blast. In the normal laboratory there is no reasonable limitation on the use of alcohol; however, in the glove box this freedom cannot be exercised. The cleaning procedure and the subsequent use of alcohol in the glove box are as follows:

The specimen is cleaned in water in the ultrasonic cleaner and rinsed with absolute ethynol. Prior to rinsing the specimen with alcohol, all electrical equipment in the box is turned off. We realize this move does not remove all possible means of initiating a fire explosion. (A spark due to static electricity from the movement of the gloves is a potential danger.) Two plastic bottles of absolute alcohol are in each box. One bottle holds one liter and serves as an alcohol supply for filling a squirt bottle which is limited to 50 ml. The liter supply bottle is capped except when filling the smaller squirt bottle. This supply bottle prevents bagging in 50 ml of alcohol for each rinsing sequence. Each specimen is rinsed with 2-5 ml of alcohol from the squirt bottle and dried by directing a stream of argon gas onto the specimen surface. During this rinsing operation, the specimen is held over a one liter stainless steel or plastic beaker containing a minimum of 200 ml of water. The alcohol is directed against the specimen and the excess alcohol drains into the beaker. The beaker is covered with a recessed conical plate (which has a $\frac{1}{2}$ -in. center hole so it resembles a funnel with the spout cut off) that extends beyond the diameter of the beaker. This plate minimizes the evaporation of alcohol from the alcohol-water solution and aids in catching the alcohol drippings from the specimen during the rinse.

We have established a limit of 8 specimens/batch to be exposed to the alcohol rinsing operation within a 30 min period. We have selected this number because (1) the exhaust flow in each box is equivalent to three atmosphere changes per hour (we realize, however, some areas in the box do not receive this change of air), and (2) it has been calculated* that it would take 55.7 ml of alcohol that had been allowed to evaporate in a static atmosphere to create an explosive mixture in a glove box of this size.

It may be necessary to have more than 50 ml of alcohol exposed in the box at one time. A specimen may be incompatible with water and, to

*Handbook of Chemistry and Physics, 48th Edition, 1967-68, p D-57.

prevent hydrolysis, alcohol may be used in the ultrasonic cleaner. If this excess alcohol is necessary, the box is flushed with argon or nitrogen and the inert atmosphere is maintained during the entire rinsing period and for 30 min after the alcohol is removed from the box. After this period the electrical equipment can be operated. This operation requires the installation of box-end-bungs to isolate the particular box from the line.

Alcohol and alcohol-water solutions are removed from the boxes via the sink drain which is connected to a radioactive waste line. The lines are flushed with water after each drainage.

Use of Acetone in Alpha Metallography Box

Acetone is used occasionally for cleaning purposes when other solvents do not perform satisfactorily. The use of acetone is very limited and lately we have been able to substitute other nonflammable solvents where possible. An example is the removal of adhesive from vibratory polishing bowls. Some polishing cloths have an adhesive backing for sticking the cloth to a bowl. Our normal practice in a laboratory is to dissolve the adhesive from the bowl with acetone. We have found a substitute for acetone in the glove box for this purpose by using an epoxy resin solvent.* This solvent has a chloroform base (its composition is proprietary information) and we have found this nonflammable solvent to be very satisfactory in removing this adhesive. We are aware of the reported** potential danger of a violent reaction of plutonium with chlorinated degreasing agents; however, the polishing bowls do not contain plutonium, so this danger should not exist. If acetone must be used, it is limited to < 25 ml and all electrical equipment is turned off. The box is purged with argon or nitrogen for 30 min before the acetone is opened in the box. After the work is completed with the acetone and the solvent and solvent-saturated wipes are removed, the box is purged for another 30 min before the electrical equipment is operated.

*Dissolver, AC-4079 Water White, Hysol Division, the Dexter Corporation, Olean, New York 14760.

**Staff of Factory Mutual Research Corporation, Glove Box Fire Safety, TID 24236 (1967).

"The New Y-12 Dry Room for the Metallography of Hygroscopic Materials"

by

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Introduction

Within the past year, a dry room facility for preparing metallographic specimens of hygroscopic materials has been added to the Metallurgical Services Laboratory of the Y-12 Plant. Due to the low humidity of this room, which is approximately 3%, it has been possible to prepare specimens for photomicrography or microprobe study without any appreciable oxidation of the specimens.

Description of Dry Room

The new dry room, which has an area of approximately 350 square feet, is located next to the metallography laboratory and can be conveniently entered through an air lock from an adjoining hallway.

For regulating the temperature and maintaining a relative humidity which is approximately 3% in this room, there is an environmental control system which consists of: (1) a dehumidifier for reducing the moisture content of the circulating air, (2) a refrigeration system for maintaining the desired temperature, and (3) an air distribution system for permitting maximum recirculation of air without contamination. Makeup air to the room for ventilation control is provided by the use of dry, clean instrument air. The air is circulated through filters by an exhaust hood in the room.

To minimize the amount of moisture coming into this room, after construction of the room, all cracks and openings around pipes in the

ceilings and walls were carefully calked and sealed. Then the room was painted twice with a special moisture proof paint.

Equipment in Dry Room

The dry room houses a large stainless steel dry box and other metallographic processing equipment. Along the walls of the room, there is ample counter space and storage room.

The large stainless steel dry box with its interlock, vacuum pump, polishing wheel, and inert gas supply can be used for the metallographic preparation of specimens in an ultra dry atmosphere of less than 100 ppm moisture. A calibrated moisture monitor is connected to the dry box.

Metallographic processing equipment in the dry room includes (1) a Simplimet press for mounting specimens, (2) two Buehler polishing wheels with Automet and Whirlimet attachments, (3) an ultrasonic specimen cleaner, (4) A Bausch and Lomb Research Metallograph #1, (5) a Bausch and Lomb Dynazoom metallograph, (6) a Bausch and Lomb model L camera, and (7) a Wilson Tukon microhardness tester.

Operation of Dry Room

After eliminating the usual startup difficulties that accompany a new operation, the dry room was made available for processing specimens in August 1967. Since then, many mixtures of various hygroscopic materials have been metallographically prepared for photomicrography or microprobe studies.

The basic technique used for the metallographic preparation of these hygroscopic mixtures is as follows:

1. The specimens are received in the Metallurgical Services Laboratory sealed under an inert atmosphere. (These are always small enough and require no cutting.)
2. The specimens are mounted in black bakelite in a one-inch mount. The bakelite has been dried prior to this time by exposure to the dry room.
3. The specimens are ground with 320, 400, and 600 grit silicon carbide paper using Dow 702 diffusion oil as a lubricant. This work is done with a polishing wheel using a Whirlimet attachment (with three weights). Dry cyclohexane is used to clean the specimen. (For porous materials, the ultrasonic cleaner is used.) Dry air is not necessary for drying the specimen since the cyclohexane evaporates immediately.
4. The specimens are rough polished with a nylon cloth on the polishing wheel using 3 micron diamond paste and Dow 702 diffusion oil. The Whirlimet attachment, with 3 weights, is used. Dry cyclohexane is used to clean the specimen.
5. The specimens are given a final polish with 1/4" micron diamond paste and a microcloth on the polishing wheel. Again, a Whirlimet attachment with 3 weights is used and Dow 702 diffusion oil is the lubricant. Dry cyclohexane is used to clean off the specimen.
6. The specimens are etched with a mixture of 25% pure ethyl alcohol and 75% dry cyclohexane. The strength of the alcohol determines the etching rate.
7. The specimens are photomicrographed with a Bausch and Lomb Research Metallograph #1.
8. Specimens that are to be used for microprobe analysis are repolished and sealed immediately under argon.

Photographs. Figure 1 and 2 each show one side of dry room. Figure 3 is mounting press and microhardness tester. Figure 4 is polishing table and Figure 5 is stainless steel dry box. Research metallograph and macro camera are in Figure 6; Dynazoom camera, ultrasonic cleaner and ventilation hood in Figure 7.

Photomicrographs of Various Hygroscopic Materials

Figures 8-13 are photomicrographs of various unidentified mixtures of hygroscopic materials that have been prepared in the dry room by the method described above. The different structures seen in these photomicrographs reflect the variety of binary mixtures studied. However, all of these photomicrographs are similar in one respect; they show the absence of appreciable oxidation due to the low humidity environment in which the specimens were prepared.

Summary

The Metallurgical Services Laboratory of the Y-12 Plant now has a special dry room facility for preparing metallographic specimens of hygroscopic materials and is now engaged in this type of metallography.

Future plans for this room include a remote control metallograph to be connected to the stainless steel dry box and a scanning electron microscope be installed in this area. We also hope to have the use of an electron microprobe to use in conjunction with the above work.

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1. Mason A. Butner, Jr. did the metallography
2. P. J. Breman did the engineering for the environmental control.
3. The photomicrographs were taken of hygroscopic mixtures sent to the laboratory by Dr. J. R. McIntyre.

Figure 1 Photograph of one side of dry room.

Figure 2 Photograph of other side of dry room

Figure 3 Mounting press and microhardness tester.

Figure 4 Polishing table

Figure 5 Stainless steel dry box.

Figure 6 Research metallograph and macro camera.

Figure 7 Dynazoom camera, ultrasonic cleaner and ventilation hood

Figure 8 500X

Figure 9 1000X

Figure 10 250X

Figure 11 250X

Figure 12 500X

Figure 13 100X

TECHNIQUES FOR THE PREPARATION OF TRANSMISSION ELECTRON
MICROSCOPY SPECIMENS FROM TUBING*

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ABSTRACT

The application of transmission electron microscopy to engineering materials requires techniques for preparing specimens from intricate structures. Suitable flat tabs can be cut or ground from massive pieces and thinned using standard techniques, but small-diameter, thin-wall tubing presents special problems that cannot be handled in this way. Modifications to the ORNL jet polishing technique that enable good specimens to be rapidly and reliably prepared from tubing using a minimum of material are described. Special features of a glove-box facility for thinning alpha-contaminated materials are also described.

I. INTRODUCTION

A demand for the application of transmission electron microscopy to complex, engineering materials has led to the development of sophisticated techniques for the preparation of specimens from irregularly shaped sections. In the case of massive pieces, wafers or thin discs can be cut by mechanical or chemical¹⁻³ means or by electrodischarge machining.⁴ Such pieces then are thinned for electron microscopy by electrolytic techniques often involving jet polishing⁵⁻¹² to localize the removal of material and telescopes¹³⁻²⁰ or photocell detectors²¹⁻²⁴ to signal perforation. Tubing presents special problems, however, since it is usually thin in one dimension in addition to being curved. Owens and Aqua²⁵ have devised a technique in which flat tabs are ground from tubing by standard metallographic procedures. This technique is time consuming, particularly for radioactive specimens, and requires fairly large diameter tubing having an appreciable wall thickness to give large enough tabs for thinning by conventional techniques.

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In this paper we will describe a procedure based on the ORNL jet polishing system²¹ that is suitable for the preparation of specimens from thin-wall, small-diameter tubing which is both rapid and economical in its consumption of material. We will first consider a method for rough sectioning of the tubing into pieces small enough to be accommodated in the electron microscope and then modifications to the jet polishing technique⁵ for the preparation of suitable thin areas. We will also describe the adaptation of the equipment to glove box operation for handling alpha-contaminated materials.

II. PRELIMINARY CUTTING

In general, electron microscopy specimens must be less than about 0.2 in. in diameter in order to fit into the microscope holder. Fuel pins, in the form of small-diameter thin-walled tubing, required development of specialized rough-cutting techniques to provide such specimens without deforming them.²⁶ Since thermal and flux gradients are often quite pronounced over relatively short distances in the fuel pins, it is necessary to be able to pinpoint the location of a microscope specimen relative to the bulk tube, not only to correlate the structure with prior history, but also to compensate for differences in thinning characteristics caused by the various thermal or neutron exposure histories.

We have developed the fixture illustrated in Fig. 1 to meet these needs. The tube is first inserted over the mandrel rod (a) chosen to give a snug fit. A slitting saw is used to make longitudinal cuts about 1/8 in. apart, slit (b). The indexing wheel (c) is provided to rotate the rod, the proper amount between cuts. A band about 1/4-in. long is left unslit at the end of the tube to keep the tubing attached to the rod. The tubing-rod composite is then sliced into 1/8-in. lengths to produce curved sections of the tubing roughly 1/8-in. square as follows. The tubing-rod composite is cut at slit (d) which is located 1/8 in. from the end of the block. The composite is then advanced to the end of the block and a second cut is made at the slit 1/8-in. from the first. The pieces of tubing usually cling to the rod (e) in Fig. 1. These sections can be identified and stored separately until the individual pieces are removed as shown at (f).

Disposable mandrel rods are provided for each piece of tubing to be sectioned and suitable indexing wheels must be made for each diameter tubing to be used. The rod provides a firm enough foundation that the tube is not deformed or bent during cutting and also allows location of individual sections to be identified.

III. JET POLISHING

In jet polishing a fine stream of electrolyte is directed against a specimen to confine material removal to a specific area of the specimen. Construction of the glass jet polishing unit is shown in Fig. 2. Previous work has shown that on flat specimens the shape of the polished regions can be controlled by means of the voltage applied to the system, as shown in Fig. 3 in which the inserts describe the cross section of the jet polished region. Notice that at low voltages the depression is dish shaped, at high voltages it is crowned, and at intermediate voltages it is relatively flat. A similar diagram for tubing specimens is shown in Fig. 4. Cross sections illustrating the depressions at the outer and inner diameters are shown above and below the current voltage curve, respectively. Again, fairly large, flat depressions or dimples can be produced in an appropriate voltage range. This is better demonstrated in the enlargements shown in Fig. 5. Optimum conditions are shown in Fig. 5(c) and (d). Sections transverse and parallel to the axis of the rod are shown in Fig. 6 and a photomacrograph of a dimple in Fig. 7.

Jet polishing is halted before a hole forms to prevent mechanical damage to the specimen. Jet polishing is a preliminary operation in which a portion of the larger piece is selectively thinned to produce a smooth area of nearly constant thickness that can then be thinned further by conventional means until perforation occurs. Material removal rates are high in jet polishing—several mils per minute—so the procedure is rapid. In addition, through control of the polishing voltage, the shape of the dimple bottom can be managed. If the dimpled region possesses flat, parallel faces, continued uniform removal of material, by conventional electropolishing for example, will result in large electron-transparent areas adjacent to holes that ultimately form.

IV. FINAL POLISHING

In practice the thin areas are limited because the surfaces are not precisely parallel or polishing is not truly uniform. It is necessary, therefore, to stop the final polish as soon as the hole appears. This has been accomplished by use of a telescope to allow visual examination of the surface during polishing with the voltage cut off as soon as the operator

sees a hole or by a system in which a phototransistor detects a beam of light transmitted by the specimen when the hole forms. The latter system, developed at ORNL, is shown in Fig. 8. Since we are concerned with radioactive materials, we use the latter system to minimize exposure to the operator.

The arrangement in this system is shown in Fig. 9. Light is transmitted to the polishing cell through a fiber optics system (a), a lens system (b), at the end of the entrance tube focuses the beam onto the specimen (c) held by platinum-tipped tweezers. When the initial perforation is made, the light is picked up by a second fiber optics system (d) and transmitted to a phototransistor, actuating a control circuit which switches off the voltage to the specimen and sounds an alarm. We have found that cathode design and location is not critical as long as the cathode is large with respect to the specimen.²⁷ Details of the construction and operation of this system are given in Ref. 21. Electrolytes and polishing conditions for various tubing materials that we have examined are given in the appendix.

V. PREPARATION OF SPECIMENS OF ALPHA-CONTAMINATED MATERIALS

The failure of transuranium element target rods in the High Flux Isotope Reactor (HFIR) resulted in contamination of the reactor coolant system and led to a request to examine sections of the target hex-sheaths to determine the cause of the failure. The sheaths were also contaminated requiring location of the thinning equipment in a glove box. In order to use the procedure described earlier, several modifications were required to accommodate the equipment in a glove box.

Because of limited space and a high level of contamination in the box, all electrical equipment is located outside the box as shown in Fig. 10. Electrical connections are made through the bulkhead with insulated "banana" plugs. A quick disconnect plug is used to supply compressed air to the jet polisher; the control valve is outside the box. The fiber optics lines are potted in Tygon tubing using RTV rubber. This allows them to be inserted through the bulkhead using a universal vacuum seal with a regular "O" ring. The rubber potting allows the fiber optics bundle to be clamped in the seal and also prevents contamination from leaving the box through the bundle.

Cooling of the electrolyte presents a special problem since it is inconvenient and difficult to transfer ice into the box several times daily. The regular polishing dish with lens (light) ports is encased in a larger dish having openings for the inflow and discharge of cooling liquid as illustrated in Fig. 11. In our system water is pumped through the cooling dish by a vibratory pump (a) attached to a rubber hose at the discharge port. The rubber hose on the other side of the pump is attached to a copper line which goes through the bulkhead to a cooling coil immersed in a dewar flask outside the glove box. A line from the coil enters the box and is attached to the cooling dish by a short length of rubber tubing. A constant electrolyte temperature of 7°C can be maintained for several hours by filling the flask with ice.

Specimens and electrolytes are transferred into and out of the box by standard bagging procedure. Since the original alpha contamination of the material was only on the surface, the polished specimens can be handled outside the glove box with only the usual precautions for β - γ radiation.

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Material	Jet Polishing			Photo-Cell Polishing		
	Solution	Current ¹ (ma)	Temp. (°C)	Solution	Current ¹ (ma)	Temp. (°C)
<u>Aluminum</u>						
Unirradiated	700 ml ethanol 120 ml H ₂ O	100	RT	{ 5% HClO ₄ in ethanol ²	400	0
Irradiated	100 ml butyl cellosolve 78 ml HClO ₄	75	RT	{ 1% HClO ₄ in ethanol ²	80	7
<u>Stainless Steel</u>						
Unirradiated		175	100	{ 60% H ₃ PO ₄ 40% H ₂ SO ₄	30	60
Irradiated	{ 60% H ₃ PO ₄ 40% H ₂ SO ₄	175	100	{ 5% HClO ₄ in ethanol	300	12
<u>Vanadium</u>						
Unirradiated	900 ml methanol 100 ml H ₂ O	220	RT		170	RT
Irradiated	60 ml H ₂ SO ₄ 15 ml HF	220	RT	{ 20% H ₂ SO ₄ 80% methanol	170	RT

¹For 3 mm² specimen and 35 mil jet orifice.

²Methanol will not polish.

Fig. 1. Tube Slitting Jig. (a) Mandrel, (b) Longitudinal cutting slit, (c) Indexing wheel, (d) Transverse cutting slit 1/8-in. from end, (e) Cut pieces of tubing and mandrel, (f) Pieces removed from mandrel.

Fig. 2. Construction of Jet Polishing Rig.

Fig. 3. The Effect of Current Changes on the Shape of the Dimple for Flat Specimens.

Fig. 4. The Effect of Current Changes on the Shape of the Dimple for Curved Specimens.

Fig. 5. Cross Section of Tubing Illustrating the Dimple Shape with Current Changes.

(a) 250 ma on the O.D. and (b) I.D., (c) 175 ma on the O.D. and (d) I.D., (e) 60 ma on the O.D. and (f) I.D., optimum conditions are (c) and (d).

Fig. 6. Sections Transverse and Parallel to the Axis of the Tube.

Fig. 7. Macrograph of a Dimple on the Surface of Tubing.

Fig. 8. Polishing Cell and Phototransistor Controller. (a) Leads to direct-current power supply, (b) Relay box, (c) Controller, (d) Field-Effect transistor, (e) Fiber-optic bundle, and (f) Polishing cell.

Fig. 9. Polishing Cell. Light is transmitted to the polishing cell through a fiber optics system. (a) A lens system, (b) At the end focuses the beam onto the specimen, (c) A second fiber optics system, (d) Transmits to the phototransistor. Insert shows light beam striking the specimen during operation.

Fig. 10. Thinning Equipment in a Glove Box. (a) D.C. power supplies, (b) Jet polisher, (c) Valve for compressed air to jet polisher, (d) Photocell controller, (e) Bulkhead penetration for fiber optics, (f) Polishing cell-cooling dish, (g) Vibratory pump, (h) Bulkhead penetration for cooling water, (i) Cooling coil and dewar flask, and (j) Light source for photocell.

Fig. 11. Polishing Cell Inside Glove Box, Showing Cooling Dish and Vibratory Pump (a), Fiber Optics are Shown at (b) and (c).

ON PREPARING ZIRCONIUM ALLOYS FOR TRANSMISSION ELECTRON MICROSCOPY

by

C. M. Owens and R. J. Davies

ABSTRACT

A technique has been developed to prepare Zirconium Alloys for transmission electron microscopy. Foils of high quality can be obtained consistently from relatively small test sections. The technique is described and typical micrographs are shown of results obtained on Zircaloy-4 (pre-and post-irradiated) and several of the common alloys of Zirconium.

PROCEDURE

The thinning procedure normally consists of three distinct steps, viz, bulk preparation, chemical pre-thinning and finally, electropolishing. The bulk material is initially prepared to provide a microscope size specimen (i.e., a punch out). Thin wall tubular stock, which is quite common in the nuclear field, and a difficult form, is prepared as described in the paper by Owens and Aqua⁽¹⁾. Basically, a small sheet form (4-5 mils thick) is produced by grinding on successively finer SiC papers. In this manner punch out stock is obtained without tube straightening.

Generally speaking, it is desirable to electropolish a specimen in as thin a section as possible. To this end, the second step in this technique is to

chemically polish the punch out to approximately two mils. The punch outs are dipped for a few seconds in a solution of 45 parts HNO_3 , 45 parts H_2O and 10 parts HF . A small stainless steel basket is used which provides for simultaneous thinning of a number of samples.

The final preparation step, electropolishing, is carried out in a Fisher-Szirmae⁽²⁾ polishing unit (Figure 1) using a 5% Perchloric-Methanol electrolyte. This unit is operated with stainless steel point cathodes at 12 volts using vigorous stirring at a temperature of 15°C . A dielectric "stop off" is used to mask the specimen and the cathodes (only the tips are left bare). The anode-to-cathode distance is maintained at about $1/8"$. Specimens 2-3 mils thick will perforate after polishing for about 20 seconds under these conditions.

At perforation, the power is shut off and the specimen is immersed in a methanol bath where the lacquer is removed. Clean tweezers and a fresh methanol bath are used to accomplish the final washing. The specimen is dried in still air and placed in the microscope specimen holder.

RESULTS

The described procedure has consistently produced quality foils over the past year. Figures 2, 3 and 4 contain micrographs typical of results obtained on annealed Zr-4, irradiated and annealed Zr-4 and annealed Zr-Nb-Cu respectively. Figure 5 represents the annealed microstructure of a Zr-Nb-Sn alloy.

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Figure 1. Fisher-Szirmae Electropolisher

Figure 2a.

16,000X

Figure 2b.

20,000X

Figure 2. Annealed Zircaloy-4

Figure 3a.

27,000X

Figure 3b.

37,000X

Figure 3. Irradiated-Annealed Zircaloy-4

Figure 4. Annealed Zr-2.5Nb-0.5Cu 20,000X

Figure 5a.

12,000X

Figure 5b.

12,000X

Figure 5. Annealed Zr-3Nb-1Sn

ELECTRON MICROSCOPE-MICROPROBE ANALYSIS OF PRECIPITATION*

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ABSTRACT

Understanding the role of microstructure on mechanical and physical properties of alloy systems necessitates the identification of precipitated phases occurring in these materials. Usually, combinations of techniques available to the metallurgist, such as optical metallography, electron microscopy of thin foils and extraction replicas, electron and x-ray diffraction of extracted precipitates, and conventional electron microprobe analysis of precipitates in the bulk specimen, are used to identify and characterize precipitates. However, it is often impossible to identify specific precipitate particles and morphologies because of limitations of these techniques.

We have found that an electron probe microanalyzer accessory to the electron microscope, used in conjunction with standard electron microscope specimens, provides the means for obtaining a quick and reliable analysis of individual precipitates. The uniqueness of this tool is most apparent when using extraction replicas, permitting chemical analysis without matrix interference along with usual electron microscopy and diffraction of individual particles (a) in the same spatial distribution as the bulk material, (b) of the thin dendritic morphology often present in grain boundaries, (c) of a size or distribution too fine to be resolved by conventional microprobe techniques, and (d) in quantities not detectable by x-ray diffraction analysis of extraction residues.

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In applying this tool to our research problems, we have made observations which would not have been possible without the use of this type of microanalyzer. For example, the fine carbide-type precipitates in grain boundaries of Hastelloy N on aging are of a different type from those which are present in the matrix, although the lattice parameters of both of these M_6C types are indistinguishable. Of more significance, silicon appears to play a major role in the formation of precipitate particles commonly identified as carbides. We have also identified precipitates containing elements having a deleterious effect on properties, such as sulfides. Other applications of this instrument will be discussed, as well as the limitations associated with its use.

INTRODUCTION

Microstructural evaluations of engineering alloys are often complicated by the presence of complex phases which precipitate as a result of mechanical processing and various heat treatments. Certain types of precipitates are common to a given alloy system and different microconstituents can often be identified by the usual metallographic techniques. However, many of the nickel-base alloys and stainless steels have complex forms of carbides which may have different compositions and morphologies but similar crystallographic identity. Mechanical and physical properties may be influenced by precipitate behavior which, in turn, may be attributable to a particular element in a complex carbide, for example. Although a combination of conventional techniques is often sufficient to identify a type of precipitate present, subtle differences are difficult, if not impossible, to detect for various morphologies.

Optical and transmission electron microscopy are effective in determining the type of microstructure and the presence of various

precipitates although the true precipitate morphology, particularly for grain boundary types, can best be determined by extraction replicas. With the latter technique, electron diffraction from thin particles or films provides information for structure identification. X-ray diffraction from extracted residues gives accurate values for d-spacings and, when used in conjunction with electron diffraction data from particles on extraction replicas, provides for good identification of various phases or morphologies provided they have different lattice parameters.

Unfortunately, complex precipitates often contain minor amounts of elements which would not necessarily be expected and which could affect precipitate behavior and properties of the material and can also expand or contract the lattice constants reported in the ASTM powder diffraction file for a given type of precipitate. Problems arise when several unidentified complex phases are present in an alloy. Conventional electron microprobe analyses can supply information regarding the composition of large inclusions, but matrix dilution effects prohibit the analysis of small particle or grain boundary films in the bulk specimen. Resolution of phases and selection of areas for analysis are impossible for fine precipitates on extraction replicas using conventional microprobe equipment and replicas are often torn or severely distorted by the electron beam.

DESCRIPTION

To overcome these difficulties of providing chemical analysis of small particles and films, we have added a microanalyzer attachment to one of our electron microscopes. This accessory replaces the standard specimen stage and permits analysis of specific particles concurrently with electron diffraction and usual electron microscopy. Figure 1 shows the Hitachi HU-11 microscope with the microanalyzer and related electronics. Figure 2 shows the construction of the microanalyzer specimen stage and x-ray path. For this particular instrument, a Hitachi HXA-1,

an x-ray take-off angle of 30 deg is used, which provides a minimum of interference from the supporting grid. The x rays are diffracted from a semifocusing mica crystal and detected by a gas-flow proportional counter. The signal is passed through a preamplifier, amplifier, pulse height analyzer, and count-rate meter with the resulting intensities plotted on a time-base strip-chart recorder for determination of peak position and intensity. These intensities are then compared with those from standards, usually in the form of a grid or a polished strip of material. Specimen current is also measured.

APPLICATIONS

This instrument is useful for analysis and identification of various types of particles, particularly those on extraction replicas. X-ray diffraction from extraction residues of Hastelloy N shows that only one form of an M_6C -type carbide is present after relatively short exposures to elevated temperature. However, extraction replication clearly reveals several different grain boundary morphologies in addition to large globular particles. Figure 3 is an extraction replica containing one grain boundary morphology and a globular phase. Conventional microprobe analysis of the blocky precipitates in bulk material indicates that they are near the Ni_3Mo_3C composition, with some chromium and about 2.5% Si present. The microanalyzer attachment provides results which are in good agreement with the above but shows that the grain boundary morphologies are more nearly of the Ni_2Mo_4C type. In addition, this phase appears to be even richer in silicon than the globular particles. Without the microanalyzer accessory, the second M_6C type would not have been identified. When several precipitate phases are found by x-ray diffraction from extracted residues, identification of a particular type of particle may easily be made.

Small particles which are too fine to be analyzed in the conventional microprobe, existing in quantities which are undetectable by x-ray

analysis and too thick to give good electron diffraction patterns have been identified. Figure 4 is a transmission micrograph of titanium-modified type 304L stainless steel exhibiting a precipitate seldom observed. Analysis of this type of inclusion on an extraction replica showed it to be a titanium sulfide. Electron diffraction from the associated needles confirmed this with positive identification as the tau phase, Ti_2S .

Analysis of oxidation and corrosion products is also simplified. The oxidation behavior of Hastelloy N is dependent upon silicon concentration, with increased silicon greatly retarding spalling.¹ Oxide films can often be easily removed by standard electrolytic extraction technique. Figure 5 shows one of these oxide films with associated carbides. Electron diffraction and microanalyzer data indicate that the film is a spinel of Cr, Mn, and Si.

We have also run spectral scans to identify corrosion products, such as the copper sulfides reported earlier at this conference by Japnell Braun.² Analyses of this type are rapid and do not require the extensive specimen preparation needed for conventional microprobe analysis. Individual particles may be examined with high resolution in the selection of areas for analysis.

We will also be using the microanalyzer for determining the thickness of transmission samples, utilizing either x-ray intensity or specimen current. By calibrating either measurement to specimens of known thickness (determined by interferometry) we will be able to obtain better results for calculations of void, bubble, or precipitate densities in transmission specimens.

LIMITATIONS

The microanalyzer accessory does have limitations on its use, and these must be recognized in interpreting results. It does not have the high precision found in conventional microprobes and a greater spread exists in series of data taken from a given area. The semifocusing mica crystal does not provide optimum x-ray intensities. The electron beam is larger than most particles analyzed and thin films are often quite transparent to a 50-kv beam. Peak separation is not extremely great with a mica crystal and often nonideal lines must be used for analysis.

The count rate is quite low for small particles and thin films, and it is not unusual for thin films to have a total x-ray intensity of 1%. Thus, intensity ratios must be normalized. Also, ideal specimens would have flat surfaces, whereas extracted precipitates usually are not flat.

Correction factors are difficult to apply for several reasons. First, the high accelerating voltages used in electron microscopy make x-ray absorption a particular problem for particles thicker than about 2000 Å. The intensity fractions obtained from films less than 2000 Å may be normalized without being corrected for absorption or atomic number effects. We have found this to be justifiable by analyzing transmission samples of alloys with known composition. However, thick particles must be corrected, particularly when x rays of widely different wavelengths are analyzed. We find that analyses of thick precipitates correlate well with those analyzed with conventional microprobe techniques if corrections are applied. We are presently modifying the electron microscope to obtain lower accelerating voltages of 25 and 35 kv in addition to the higher voltages normally used.

Recognizing the problems inherent in this microprobe analyzer, we feel that at worst, our data should not be in error more than 10%. It has proved to be extremely valuable as a qualitative and semiquantitative tool and is showing promise for quantitative work. As more laboratories make use of the equipment, modification and improvements will probably be made to the microanalyzer to increase the accuracy and improve resolution. It has proved capable of meeting our needs for analyses of various types.

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Fig. 1. Electron Microscope with Electron-Probe Microanalyzer Accessory Replacing Standard Specimen Stage. Associated electronics are conveniently placed on wheeled cart.

Fig. 2. Diagram of Microanalyzer Accessory. Courtesy of Hitachi, Ltd., Japan.

Fig. 3. Direct Carbon Extraction Replica from Hastelloy N Showing Dendritic Grain Boundary and Massive Globular M_6C -Type Precipitates. 1000X.

Fig. 4. Transmission Electron Micrograph of Titanium Sulfide Inclusion (Ti_2S) Identified by Microanalyzer. 10,000X.

Fig. 5. Surface Oxidation Product and Associated Carbides Electrolytically Stripped from Bulk Specimen. The microanalyzer accessory permits rapid determination of metallic constituents in the oxide film and the carbides. 4000X.

TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION OF
HAYNES ALLOY No. 25 AND ELECTRON BEAM WELDS
IN THIS ALLOY

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ABSTRACT

A method for preparing thin specimens of Haynes alloy No. 25 for transmission studies is discussed. The technique retains most of the usual inclusions in the alloy. The substructure of the alloy is shown and discussed.

INTRODUCTION

The current use of cobalt-based superalloys as high temperature encapsulation material requires that the structural properties be carefully studied. Haynes alloy No. 25 is presently being used to encapsulate heat sources at Mound Laboratory. Since many of these containers are sealed using electron beam welds, the structures of both the Haynes alloy No. 25 and of electron beam welds in this alloy are being studied. Several other investigators have worked on this alloy; however, no thin film transmission studies have been reported in the literature. The work of Wlodek¹ has been used as the main reference for previous work on this alloy. In

*Mound Laboratory is operated by Monsanto Research Corporation for the Atomic Energy Commission under contract AT-33-1-GEN-53.

this investigation optical microscopy, electron microprobe, extraction replication and transmission electron microscopy techniques were used. Since there are no other known studies of weld structures of alloys reported in the literature, these structures will be compared with the weld structures of 304L stainless steel, reported last year.

PROCEDURE

Samples were obtained for the parent metal studies from 3/8-in. Haynes 25 rod, which had been annealed. Weld samples were obtained from two 1/4-in. plates which had been placed together and welded, perpendicularly to their interface, with approximately 80% penetration. The chemical composition of the welded Haynes 25 sample is shown in Figure 1.

Extraction replicas of the weld samples were obtained by etching a polished sample in concentrated HCl and H₂O₂ and making a cellulose acetate replica of this surface. The tape removed most of the precipitates from the surface. A Pt-Pd shadowed carbon replica was then made from the tape replica for observation in the electron microscope.

Specimens for transmission electron microscopy were obtained by thin sectioning 6-8-mil slices from the samples and grinding these on 600 grit SiC to 3-4 mils. The slices were then thinned using a Dual-Jet Thinner with 10% HClO₄ in butyl cellosolve and alcohol at 4-5°C. The polishing plateau for this solution is an extended range of about 14 V, from 12 to 26 V, with a current density of about 50 mA/cm². Thin specimens for observation were obtained by cutting around the thinned area with a scalpel; however, this cutting was found to be

difficult and resulted in bending and tearing of the thin foil and rapid dulling of the scalpel blade. Better techniques for removing the thinned areas are currently under investigation.

RESULTS

I. Parent Metal An optical micrograph of the parent metal is shown in Figure 2. This micrograph shows the highly twinned structure of the Haynes 25, as well as circular precipitates, probably carbides, and square precipitates identified as a Zr(CN). A transmission electron micrograph of a twinned grain containing two of the circular type precipitates is shown in Figure 3. Many of the long dislocations visible are restrained from free movement; since there are no visible precipitates at the pinning point, this is probably due to a stress field around a solute atom. There are also large numbers of stacking faults, extended dislocations, and dislocation nodes. The stacking fault energy of this alloy could be calculated from the radius of curvature of the partial dislocations making up the nodes in an area like the one indicated by an arrow in Figure 3. The twin boundary in the upper left corner of this figure is observed to be curved due to the stress field around the precipitate. Figure 4 shows another area in which there are overlapping stacking faults, dislocation slip traces, and a number of small precipitates. The faulting structure around a large precipitate is shown in Figure 5.

The presence of a possible second phase, which may be hcp Co, is seen as a needle-like precipitate extending from the larger carbide particle.

II. Weld A low magnification optical micrograph of the weld sample

is shown in Figure 6. The difference in the grain size and shape and in the "cell" size and shape from the outside edge of the weld to the center is visible. The intragranular cell structure is due to segregation of alloy components. The cell structure can be seen more clearly in Figure 7, an optical micrograph of the weld at 500X. The darker areas are the cell boundaries and the lighter areas are the interior. Note that the precipitates are predominantly in the grain and cell boundaries.

Electron microprobe analysis of an area similar to that shown in Figure 8 shows that the concentration of Co and Ni are higher in the cell interior than in the cell boundaries, and the W, Cr, Mn and Fe concentrations are higher in the cell boundaries. This effect is similar to that observed in 304L stainless steel welds reported last year.

The cell structure from an area near the edge of the weld as seen by transmission is shown in Figure 9. The dislocations and sub-boundaries indicate a "creep" structure due to thermal stresses arising during cooling of the weld. This substructure is shown more clearly in Figure 10, which shows a sub-boundary due to thermal stresses on the weld. This feature along with a grain boundary precipitate is visible in Figure 11. The "creep" structure of these welds is similar to that observed in 304L stainless steel, except that the sub-grain boundaries are not as well developed. A comparison is shown in Figure 12 (2900X), which is a transmission micrograph of a 304L fusion weld.

The decreased development of the creep structure in Haynes 25 is explained by the presence of smaller precipitates in the weld and the lower stacking fault energy of this cobalt-based superalloy. This latter property is demonstrated by the occurrence of stacking faults in the Haynes 25 welds which were not observed in 304L stainless welds (Figure 13). These faults are seen more clearly in Figure 14. Note that in several areas dislocations have separated into partials, with a stacking fault between them. In some cases these are quite extended -- note in particular the extended node near the small precipitate in the upper right area of the micrograph closes in as it approaches the precipitate. There are also nodes and shorter extended dislocations present. The weld-parent metal interface is shown in Figure 15. The precipitates in the weld occur predominantly at the cell and grain boundaries. These precipitates are shown more clearly in the extraction replica of the weld-parent metal interface, Figure 16. The precipitates in the extraction replica of the weld area are shown in Figure 17. An electron diffraction pattern from this area was completely indexed based on the $M_{23}C_6$ carbide. The carbides shown at higher magnification in Figure 18 have a "tree-like" form typical of the $M_{23}C_6$ carbides observed in other alloys.

Some rather interesting precipitates observed in thin foils of the weld are shown in the next four slides. Figure 19 shows a needle-like grain boundary precipitate and a circular precipitate. The needle-like precipitate appears to be a Co_3W_2Si supposed Laves phase. A precipitate similar to the circular one is seen in Figure 20. The fringes observed may be Moire fringes or may be due to a dislocation

network between the precipitate and the matrix or another crystal slightly misoriented but of the same crystal structure as the precipitate. The fringe symmetry in some areas is more like what would be expected from an interface dislocation network. One particle containing these fringes appears to have a $M_{23}C_6$ carbide attached to it and is shown in Figure 21. This small precipitate has tentatively been identified as the M_7C_3 carbide, which usually is not stable and is reported to transform to $M_{23}C_6$.²

The structures of Haynes 25 and electron beam welds in Haynes 25 are similar to the fusion welds observed in 304L stainless steel. The main differences are:

1. A smaller grain size and "cell" size and shape due to the more rapid process of welding using electron beam techniques;
2. A smaller number of sub-boundaries and the presence of stacking faults in the Haynes 25;
3. In 304L the major precipitating phases are δ -ferrite and $M_{23}C_6$ usually associated with the δ -ferrite. However, in the Haynes 25 welds $M_{23}C_6$ is the predominant precipitate, and small amounts of M_7C_3 and Co_3W_2Si are observed instead of the M_6C usually found in such alloys.³ These precipitates occur as expected in the W-Cr-rich cell boundaries in the weld.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Gordon Powell of Ohio State University for his assistance as consultant on this work. He also thanks Dale Roesch for doing the electron microprobe analysis and R. C. McWilliams for technical assistance.

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CHEMICAL ANALYSIS OF WELDED HAYNES 25 ALLOY

Element	Weight Per Cent
Chromium	19.9
Tungsten	15.3
Nickel	9.9
Iron	1.32
Manganese	1.18
Silicon	0.9
Zirconium	0.03
Titanium	0.003
Carbon	0.086
Cobalt, balance	51.4

Figure 1 - Chemical analysis of Haynes alloy No. 25.

Figure 2 - Optical micrograph of parent metal (500X).

Figure 3 - Parent metal substructure, transmission electron micrograph (6000X):

Figure 4 - Parent metal, slip traces and stacking faults (9000X).

Figure 5 - Parent metal, faulting structure around precipitate (22,700X).

Figure 6 - Optical micrograph, weld (50X).

Figure 7 - Intragranular cell structure, weld (500X).

Figure 8 - Electron microprobe analysis results, cell area in weld (200X).

Figure 9 - Weld cell structure shown by transmission (3000X).

Figure 10 - Creep substructure in weld (18,000X).

Figure 11 - Weld substructure and grain boundary precipitate (9000X).

Figure 12 - Creep structure as observed in 304L stainless steel fusion weld (2900X).

Figure 13 - Weld structure showing stacking faults (4500X).

Figure 14 - Weld structure, stacking faults (10,600X).

Figure 15 - Optical micrograph, weld-parent metal interface (500X).

Figure 16 - Extraction replica, weld-parent metal interface (1800X).

Figure 17 - Extraction replica of weld showing precipitates (1800X).

Figure 18 - Carbide precipitate in weld (18,000X).

Figure 19 - Needle-like precipitate in thin foil, weld (90000X).

Figure 20 - Circular precipitate in thin foil of weld (35,000X).

Figure 21 - Mixed carbide precipitate, thin foil of weld (35,000X).

PREPARATION OF BERYLLIUM FOILS FOR
TRANSMISSION ELECTRON
MICROSCOPY

V. K. GROTZKY & F. J. FRAIKOR

ABSTRACT

Transmission electron microscopy investigations of the effect of various heat treatments on lattice defects in beryllium ingot sheet require thin foils which are representative of the bulk material. However, beryllium ingot sheet which has been annealed at elevated temperatures is particularly susceptible to damage by preparation techniques such as diamond saw cutting, spark cutting, etc. Therefore a chemical saw has been devised and constructed to provide strain-free cutting of coupons from the bulk ingot sheet. The saw consists essentially of an acid-soaked thread which moves across the specimen through the action of an eccentrically mounted pulley. Thin slices of 0.030 in. to 0.050 in. thick can easily be obtained from the heat-treated beryllium sheet. These specimens are chemically thinned to approximately 0.015 in. thick and subsequently electrolytically thinned by a dual-jet technique.

Several representative photomicrographs will be shown of precipitate and dislocation structures in beryllium foils obtained from tested tensile specimens, electron beam welds, and quenched and aged ingot sheet.

An apparatus for cutting beryllium thin-specimens for transmission electron microscopy has been designed and implemented at Rocky Flats. It provides for strain free cutting of thin coupons so that structure studies may be accomplished without deformation from the use of mechanical cutting tools and polishing equipment.¹

The unit is similar to one designed by McGuire and Fiore,² however, it has been modified to produce much thinner specimen slices which would be subsequently electropolished for transmission electron microscopy studies.

Figure 1 is a schematic diagram of the chemical saw which, in principle, consists of a weighted thread traversing across a specimen held in position by a polyethylene vise. A movable jaw on the vise permits handling of samples with a maximum diameter of one inch. The amount of stroke for the saw can be governed by positioning the motor at varying distances from the center of the pulley. Experimental results for cutting through beryllium specimens 3/16 inch thick by 3/8 inch wide were best achieved by operating the Barber Coleman motor at 40 RPM with a 4 inch stroke on the thread. Several chemicals and saw thread combinations were used before the desired results were obtained. Currently a solution of 75% HCl and distilled H₂O is being utilized

with an 0.005 in. diameter Saran cutting thread which has extremely good wear characteristics. This thread is 9.5% vinyl-chloride and 90.5% vinylidene chloride or "Saran" manufactured by the Dow Chemical Company. The raw material is extruded into thread ranging in size from 0.002 in. to 0.015 in. by National Plastics Products Company, Odenton, Maryland. The Saran can be utilized in various solutions, such as HCl, H₂SO₄, HF, HNO₃ or aqua regia. A water bath to prolong the life of the thread is not necessary as is the case for many other chemical saw materials.³

A slice from a beryllium tensile specimen, 3/16 inch thick by 3/8 inch wide can be obtained in approximately 1-1/2 hours. Thin slices of 0.030-0.050 in. thick are easily obtained. Any surplus of chemical on the thread which makes the saw cut too wide can be removed by placing a tissue lightly against the thread as it comes out of the chemical reservoir. The entire saw with the exception of the motor is constructed from polyethylene so that it will not react with most solutions. A polyethylene graduate makes an excellent reservoir in that the chemicals may be readily measured and mixed in the graduate and a minimum amount of solution is required.

To prepare the thin beryllium specimens for transmission electron microscopy, the coupon, as it comes from the saw, is suspended in

a solution of 200 ml of H_2O , 100 ml of HNO_3 and 9 ml of HF where it is further thinned to approximately 0.015 in. thick. This step will take nearly 30 minutes, depending on the initial thickness of the coupon. Preferential attack may be obtained by using lacquer as a mask.

The final phase of specimen preparation consists of electrolyte thinning in a Glenn Dual Jet unit⁴ or a Fischione Disk unit.⁵ The electrolyte is a solution of:

400 ml ethylene glycol
40 ml nitric acid
8 ml hydrochloric acid
8 ml sulphuric acid

The polishing plateau for this particular electrolyte appears to be reached at 36 to 40 volts. The solution is kept at 10-15°C during the thinning operation by a circulating ice water bath. Figure 2 shows a disk specimen of an aluminum-beryllium electron beam braze weld. This specimen was thinned in the Fischione unit and the desired thin areas are located around the hole in the center of the disk.

Figure 3 is an electron transmission photomicrograph taken from the outer edge of the heat effected zone of beryllium sheet which

has been electron beam welded. The photomicrograph shows that while complete recrystallization did not occur in this area, enough thermal energy was provided to polygonize the as-rolled micro-structure.

Figure 4 is another photomicrograph at higher magnification from the same zone and shows a precipitate particle (probably AlFeBe_4), impeding the motion of the dislocations to the metastable array of polygonized sub-boundaries.

These results are indicative of the photomicrographs which can be obtained using these procedures for specimen preparation.

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FIGURE 1. SCHEMATIC DRAWING OF CHEMICAL SAW

FIGURE 2. ALUMINUM-BERYLLIUM ELECTRON BEAM BRAZE WELD 10X

FIGURE 3. TRANSMISSION PHOTOMICROGRAPH OF POLYGONIZED MICROSTRUCTURE IN THE HEAT-EFFECTED ZONE OF ELECTRON BEAM WELDED BERYLLIUM.

FIGURE 4. HIGHER MAGNIFICATION OF POLYGONIZED AREA OF FIGURE 3 SHOWING A PRECIPITATE, (PROBABLY AlFeBe_4), IMPEDING DISLOCATION MOTION.

REPLICATION OF IRRADIATED MATERIALS FOR ELECTRON MICROSCOPY*

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ABSTRACT

Various replicating techniques have been used to examine highly-radioactive materials by electron microscopy. Heretofore, obtaining replicas of good quality and acceptable activity levels have required either costly sophisticated equipment or tedious time-consuming techniques. Described here is a good, two-stage technique for obtaining high quality replicas.

Examples of electron micrographs from polished, etched and fractured materials are presented with comments on the merits of carbon and metallic replicas.

INTRODUCTION

Examination of radioactive materials at the High Radiation Level Examination Laboratory involves both optical metallography and electron microscopy. Because activity levels of some materials are so high, electron microscopy examination can be performed only by using replicas. Various replica methods for radioactive materials have been described in the literature¹⁻³ but all require either space-consuming equipment or are tedious and time consuming. Since hot cell space is limited and tedious operations should be avoided whenever possible, a quick, simple and reproducible replica method was needed.

We have adopted a two-stage plastic/carbon technique that meets these requirements.

In many instances the plastic/carbon replica was unsatisfactory because of carbon drift and pile-up. This was a particularly troublesome problem

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when very small gas holes were to be measured. The piled-up carbon made measurement of the hole diameter practically impossible. Accurate measurement of gas holes could be made using chromium metal replicas.

PROCEDURE AND DISCUSSION

Procuring the replicas involve an in-cell and out-of-cell procedure. In the in-cell procedure, samples which have been prepared for metallographic examination are wet thoroughly with acetone, after which a short piece of cellulose acetate is softened on one side with acetone and placed onto the wet sample surface. A rubber stopper is used to press the acetate firmly onto the surface to assure penetration of the plastic into every feature. (See Fig. 1) The plastic is allowed to dry about 10 min before removing from the sample. The first three replicas are discarded, their function being to remove any loose sample material and to insure a perfectly clean surface. Three replicas are then made for the examination, placed in clean plastic bags and removed from the cells.

Five- to six-mil acetate was used because it was thick enough to allow one side to be softened sufficiently to form a good replica and at the same time remain strong enough to prevent distortion or damage when stripped from the sample by the manipulators. In addition, acetate of this thickness was easily dissolved in subsequent steps. The procedure for replicating fractured surfaces is identical to the above except a small vise is used to hold the sample during replication. We have successfully replicated materials with activity levels as high as 30,000 roentgens. The activity levels of the replicas removed from the cells ranged from only about 50 milliroentgens to 10 roentgens. Most of the activity resulted from contamination of the plastic surrounding the replicas. When removed from very active samples in less than 10 min, no detrimental effect to the plastic is observed.

In the out-of-cell procedure, the plastic replica is examined for quality and those acceptable are placed on glass microscope slides in an evaporator, shadowed with chromium and re-replicated with carbon or chromium metal.

Metal secondary replicas formed from vapor-deposited chromium portray more distinct details since the problem of drifting and pile-up encountered with carbon does not exist. The metal replicas have approximately the same thickness as carbon secondary replicas but because of the density difference have higher contrast. Most replicas are more suitable for polished and etched samples than for relatively rough fractured surfaces because the metal is much more brittle than carbon and consequently cannot withstand the stresses involved when the plastic is removed. (See Figs. 2 and 3)

Removal of the plastic is accomplished by dissolution in acetone. During dissolution the acetate expands to about one and one-half times its original dimensions, which results in a large strain on the secondary

replica, often tearing it into small pieces. A method of limiting this strain and obtaining a complete section of replica is to place the secondary replica next to the specimen screen, then as the acetate expands the screen lends support to the secondary replica. (See Fig. 4) Also, allowing the acetate to dissolve slowly in the manner shown in Fig. 4 helps to prevent breaking of the secondary replica. After approximately 15 min in the first solution bath, most of the cellulose acetate has been dissolved. The specimen screen containing the secondary replica is placed on a cold finger in a reflux condenser containing acetone and washed approximately one and one-half hours to remove the remaining acetate.

Upon removal from the reflux condenser the activity level of the samples normally range from 0 to 1 milliroentgen. In some instances, the activity may be 20 milliroentgens as a result of extracted particles that were not removed by washing. The fact that these particles remain on the replica will permit the identification of the material by electron diffraction.

CONCLUSIONS

The method described here for the replication of radioactive sample surfaces allows routine examination of these materials by electron microscopy. The simplicity of the operation, the lack of further sample preparation and limited need for equipment allow for a minimum in cost for such an examination. The accuracy of replication of the surfaces with cellulose acetate tape and the subsequent re-replication can produce resolutions of 60 Å.

The use of metal replicas, specifically chromium, alleviates the problem of drift and pile-up encountered in carbon replicas. However, the best application of metal replicas is on polished and etched samples, not on fractured surfaces.

Workable activity levels can be attained by using the replicating tape to extract and clean the surfaces of the radioactive samples. The subsequent re-replication and wash of the secondary replicas result in activities of the order of 0 to 360 disintegrations per minute (alpha) and less than 1 milliroentgen for beta gamma.

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APPENDIX A

Examples of electron micrographs obtained using this replication technique:

1. Fig. A-1. Comparison of optical metallography and electron micrography.
2. A study of tensile specimens of unirradiated and irradiated ASTM A-212 Grade B steels by electron microscopy. Fig. A-2. Fractography. Fig. A-3. Polished and etched.
3. Fig. A-4. Crystallographic hole in irradiated zirconium carbide-carbon secondary replica.
4. Fig. A-5. Micrographs of a polished microsphere of uranium dioxide.
 - a. Electron micrograph of a fabrication hole, as polished.
 - b. Electron micrograph of a fabrication hole, etched.
 - c. Optical micrograph of sphere.
5. Fig. A-6. Electron micrograph of $\text{PuO}_2\text{-UO}_2$ showing growth steps on the surface of the microsphere.

REPLICATION OF POLISHED AND ETCHED SPECIMEN

REPLICATION OF A FRACTURED SPECIMEN

Fig. 1 (R-44106). In-Cell Replication Technique

CHROMIUM REPLICA **CARBON REPLICA**

Fig. 2 (R-44107). Comparison of Chromium Replica with a Carbon Replica of ASTM A-212 Grade B Steel.

CHROMIUM REPLICA **CARBON REPLICA**

Fig. 3 (R-44108). Comparison of a Chromium Replica with a Carbon Replica.
Fractographs of Irradiated ASTM A-212 Grade B Steel.

Fig. 4 (R-44109). Dissolution of the Cellulose Acetate Replica.

**METALLOGRAPHIC SECTION
(LIGHT OPTICS)**

**FRACTOGRAPHIC SECTION
(ELECTRON OPTICS)**

Fig. A-1 (R-41616). Fission-Gas Bubbles in a Nuclear Fuel as Revealed by Standard Metallography and Electron Microscopy.

UNIRRADIATED

($T_t = 77^\circ\text{K}$)

IRRADIATED

$\Phi = 1.0 \times 10^{19} \text{ n/cm}^2 \text{ AT } 60^\circ\text{C}$

($T_t = 34^\circ\text{K}$)

Fig. A-2 (R-42800). Fractographs of Tensile Specimen of ASTM A-212-B Steel.

UNIRRADIATED

($T_t = 50^\circ \text{K}$)

3 μ

IRRADIATED

$\Phi = 1.0 \times 10^{19} \text{ n/cm}^2$ AT 60°C

($T_t = 34^\circ \text{K}$)

Fig. A-3 (R-42801). Electron Micrographs of Tensile Specimens of ASTM-A-212-B Steel, Longitudinal Section Near Fracture Surface.

CARBON REPLICA

Fig. A-4 (R-44110). Crystallographic Hole in Irradiated Zirconium Carbide.

ELECTRON MICROGRAPHS

OPTICAL MICROGRAPH

Fig. A-5 (R-44111). Fabrication Holes in Unirradiated Uranium Dioxide Microspheres.

Fig. A-6 (R-44112). Replica of 20% PuO₂-UO₂ Microsphere Surface.

A TECHNIQUE FOR REPLICATING $^{238}\text{PuO}_2$ FOR
ELECTRON MICROSCOPE STUDIES

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ABSTRACT

Cross-sectioned and polished specimens of $^{238}\text{PuO}_2$ microspheres have been replicated for electron microscope studies by a technique which produces replicas that are free of radioactive contamination. The microspheres are thoroughly decontaminated by ultrasonic cleansing in ethanol which removes all loose particulates. Proper cleansing of the microspheres and the use of an uncontaminated die prevent contamination of the amber Bakelite resin during mounting. Following metallographic preparation the mount is decontaminated ultrasonically; cellulose acetate tape is softened with acetone and applied firmly to the surface.

*Operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

When the dried tape is stripped from the surface, it retains the particulates which did not adhere to the microsphere surfaces and which contaminate the replica. The radioactive contamination on the replica is determined by alpha counting; then a series of successive replications is made until all the loose surface material is removed and the count on the final replica is below the background level. High quality metallographic preparation of the specimen reduces the number of replications required by minimizing "micro-plucking," which results from surface damage.

INTRODUCTION

A technique was developed for preparing nonradioactive replicas of $^{238}\text{PuO}_2$ microspheres for electron microscope studies. This work was prompted by the requirement for electron microscope studies in the investigation of the helium retention characteristics of $^{238}\text{PuO}_2$ microspheres. The development of the technique was carried out without benefit of prior experience at Mound Laboratory in the replication of highly radioactive materials. Uncontaminated replicas were required to enable handling and

observation in a nonradioactive area.

The plasma-fired microsphere of PuO_2 is a unique particle because of its contamination-free nature. Unlike any other form of PuO_2 , it can contact other surfaces without transferring radioactive contamination. This property was demonstrated earlier for microspheres of $^{239}\text{PuO}_2$.¹ Although the specific activity is nearly 300 times greater for ^{238}Pu than for ^{239}Pu , the same contamination-free nature has been observed for $^{238}\text{PuO}_2$ microspheres. All plasma-fired PuO_2 microspheres possess clean surfaces when they are formed. However, exposure and handling inside a radioactive glovebox result in contamination of the microspheres, and they must be decontaminated for applications requiring clean particles. Decontamination is achieved by rinsing in ethyl alcohol with ultrasonic agitation. As many as 10 to 15 separate steps may be required for a highly contaminated specimen. The progress of the decontamination can be checked by immersion of an alpha survey wipe into the alcohol followed by drying and counting. After the final rinse, the dry microspheres should not transmit detectable contamination when they are rolled on a clean surface.

A technique for cross-sectioning and metallographic preparation

of PuO_2 microspheres was developed previously.² These procedures were employed in the first attempt to prepare the microspheres for replication. A specimen of decontaminated microspheres was passed into the plutonium metallography glovebox and mounted in a press employing amber Bakelite. The specimen was first ground on 600 grit silicon carbide paper with carbon tetrachloride as a lubricant. After being ultrasonically cleaned in carbon tetrachloride the specimen was rough polished with six micron diamond paste on Politex Pre-PS paper using olive oil as a lubricant. This polishing step was continued until the spheres were sectioned to a point near their centers. After additional ultrasonic cleaning the specimen was fine polished employing three micron diamond. The specimen was cleaned and then passed from the glovebox to a fumehood where ultrasonic decontamination was continued in several stages. At this stage the specimens were handled with rubber gloves due to the wipeable contamination, but no contamination was released into the air.

It was reasoned that the first replica would trap the remaining loosely adherent radioactive material, cleansing the surface of the mount. Subsequent replicas would then be relatively contamination free.

Cellulose acetate replicating tape and acetone were employed in the first replication of the surface, and the replica gave a direct reading of greater than 2,000,000 counts per minute. After 20 successive replications the replica still gave a reading of 500,000 counts per minute, which was not acceptable for a nonradioactive area. It was concluded that the contamination was being released from the amber Bakelite mount. The supply of amber Bakelite in the glovebox was probably contaminated, and the die of the mounting press was known to be contaminated. Attack of the mount during replication by the acetone plus the loosely bonded condition of the radioactive contamination in the Bakelite apparently resulted in a gradual release of the contamination.

To avoid contamination within the mount the spheres were next mounted in an uncontaminated mounting press outside the glovebox. The die of this mounting press remained contamination free after preparation of the mount.

The sample was ground and polished as before in the metallography glovebox and decontaminated for 15 minutes in ethyl alcohol employing ultrasonic agitation. Alpha counts of the first replica read 12,000 counts per minute, and subsequent replicas

read 2000, 1200, 500, 150, and 9 counts per minute. The decrease in the contamination of the replica was due to the removal of the loose surface material.

The replicas were made employing a Fullam No. 2200 EFFA general grid with Fullam No. 1134 replicating tape. A photograph of one of the replicas in transmitted light is shown in Figure 1.

After the preparation and cold replication of a specimen in the as-polished condition, the specimen was chemically etched by immersion for four hours in a solution of 50 parts HF, 50 parts HCl, and 2 parts HNO_3 . After being washed in water and ultrasonically decontaminated in ethyl alcohol, the first replica gave a direct reading of 10,000 counts per minute. Subsequent replicas read 5000, 2000, 500, 126, and 12 counts per minute.

The need for replication of $^{238}\text{PuO}_2$ microspheres was not confined to cross-sectioned and polished surfaces. Replicas were also required of the outer surfaces of the microspheres where considerable structural detail appeared. Figure 2 is a reflected light photograph of the outer surface of a microsphere showing what appear to be colonies of fine radially oriented grains. A spot near the center of each colony appears

to be the original nucleation site, and a prominent boundary occurs between the colonies where they were blocked during solidification. Figure 3 is a similar photograph of a microsphere which had experienced long-term exposure at high temperature. Each colony in this particle appears to be comprised of platelets. Annealing has resulted in a broadening and sharper definition of the boundaries.

The preparation of the microspheres for outer surface replication was made in the following manner. After ultrasonic cleaning the spheres were placed on a flat piece of soft glass and heated in an electric furnace. After the glass had softened, the specimen was held in the furnace just long enough for the spheres to sink a distance of two-thirds of their diameters into the glass.

This process took five minutes at 875°C.

Figure 4 is a photograph of a glass specimen containing embedded microspheres. The same group of microspheres is shown in Figure 5 at higher magnification. The glass is completely invisible in this photograph, but the interface where the microsphere protrudes from the glass can be detected by light reflections on several of the spheres. The glass mount retained the microspheres, enabling successful replication of the surfaces.

) The first replica gave a direct reading of 10,000 counts per minute, and subsequent replicas read 6000, 2000, 500 and 0 counts per minute.

It was considered desirable to examine internal surfaces of broken microspheres for comparison with ground and polished surfaces. However, mounting small fragments with an exposed surface for replication was complicated by the minute size of the specimen. A suitable specimen was prepared with microspheres partially submerged in glass as in Figures 4 and 5. The protruding caps of the microspheres were cleaved off with a micro-chisel leaving many flat fragments on the surface. However, there were also many minute chips and particles, and over 25 replications were required to remove all the loosely held pieces before a cold replica was obtained.

SUMMARY

Uncontaminated replicas of $^{238}\text{PuO}_2$ can be produced for electron microscope studies. The specimen is mounted, after thorough cleaning, with a cold mounting press and contamination-free resin. After being sectioned and polished, the specimen is decontaminated ultrasonically in ethyl alcohol. Acetone softened cellulose acetate replicating tape is employed to further remove surface contamination. After several replicating steps the replica obtained is sufficiently free of radioactive contamination that it can be handled in a nonradioactive area. Contamination-free replicas of minute specimens which do not have flat surfaces can be obtained in a similar manner with the specimens partially embedded in soft glass.

REFERENCES

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2. M. D. Kelly and P. A. Tucker, "Metallographic Examination of Plutonium Dioxide Microspheres," Proceedings of the 21st AEC Metallography Group Meeting, May 1967.

Figure 1 - Cellulose acetate replica with grid
(50X, enlarged 3X).

Figure 2 - External surface of $^{238}\text{PuO}_2$ Microsphere
(250X, enlarged 4X).

Figure 3 - External surface of annealed $^{238}\text{PuO}_2$ microsphere (250X, enlarged 4X).

Figure 4 - $^{238}\text{PuO}_2$ microspheres embedded in glass.

Figure 5 - $^{238}\text{PuO}_2$ microspheres embedded in glass
(60X, enlarged 2X).

ELECTRON MICROSCOPY INVESTIGATION OF
STRUCTURAL FEATURES IN $^{238}\text{PuO}_2$

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ABSTRACT

A technique for obtaining nonradioactive replicas of $^{238}\text{PuO}_2$ has been developed. The results of observations on freshly prepared, aged, and high temperature annealed microspheres will be presented.

INTRODUCTION

Plutonium-238 dioxide is currently being used as a fuel for heat sources. In the radioactive decay of ^{238}Pu helium is produced. In the case of nonporous oxides, such as plasma-fired $^{238}\text{PuO}_2$ microspheres, most of that helium is retained in the spheres. It was recently shown that 66% of the theoretical trapped helium is still retained after the microspheres had been heated for one week at 810°C . A study was initiated at Mound Laboratory by Dr. E. W. Johnson, R. Zielinski and P. Bonnell to investigate this helium retention. This presentation is part of preliminary investigations to determine if the presence of helium can be

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observed by replica techniques, and to evaluate the effects on helium retention of annealing at different temperatures. It was necessary first to determine if cold (i.e., nonradioactive) replicas could readily be obtained for $^{238}\text{PuO}_2$ microspheres and to develop the techniques best suited to provide the information.

PROCEDURE

Plasma-fired $^{238}\text{PuO}_2$ microspheres from freshly prepared and from eight-month old batches were obtained for investigation. Part of the eight-month old batch was subsequently heated at 1100°C for 52 hr, and samples from this aged, heat-treated material were also obtained. The samples were mounted and prepared for replication by M. Kelly as discussed in a concurrent paper.

The technique for obtaining good replicas was first developed using ZrO_2 microspheres. The usual cellulose acetate tape technique was unsuitable for replicating these spheres because shadowed carbon replicas of the plastic broke and curled no matter what thickness of carbon was deposited. Probably the flat surfaces provided so little irregularity in the carbon film that swelling of the plastic replica during dissolution caused the carbon to crack. To alleviate this situation a copper grid was placed over the sample area; then the acetate tape was softened and pressed through the grid onto the sample. The grid provided sufficient relief in the replica to allow the carbon to expand during the dissolution; thus good replicas were obtained.

Replicas of the freshly prepared $^{238}\text{PuO}_2$ and of ZrO_2 were made for comparison with aged and with aged, heat-treated samples of $^{238}\text{PuO}_2$ so micro-pores or voids, which might be characteristic of the plasma forming process, could be distinguished from bubbles due to helium. Samples of as-polished, of etched, and of outer surfaces of the spheres were replicated. The initial samples were shadowed with gold at 45° , but the formation of large gold nuclei reduced the high magnification resolution. Chromium was tried, but was found to crack making it also unsuitable as a shadowing material. All subsequent replicas were made using platinum-palladium shadowing.

RESULTS

The as-polished surface of a ZrO_2 microsphere as observed in a gold shadowed carbon replica is shown in Figure 1. In this slide cleavage surfaces from plucked areas of the microsphere are visible. In general these cleavage surfaces were areas of major interest since they should contain fewer polishing artifacts.

The as-polished surface of freshly prepared $^{238}\text{PuO}_2$ is shown in Figure 2. In this micrograph a plucked area and several geometrically shaped raised areas are visible. These raised areas are possibly due to the presence of a second phase [Pu_2O_3 or $(\text{FeCr})_2\text{O}_3$]. Figure 3 is a micrograph of a fairly large void probably

arising in the forming process. Figure 4 shows a cleavage area with what appear to be large numbers of small bubbles or micro-voids.

These micro-voids appeared in only a couple of the observed microspheres and only in isolated areas. These micro-voids are shown more clearly at higher magnification in Figure 5, and may be due to the presence of gas bubbles in the rapidly solidified microspheres.

The surfaces of the microspheres were replicated using the same techniques followed for the polished spheres. The mounting technique is the same as described by M. Kelly. (Cerium dioxide microspheres were used to develop the technique for replicating the surfaces of the spheres.) An example of the surface appearance of CeO_2 plasma-fired microspheres is shown in Figure 6. The large boundaries are believed to be associated with grain boundaries or possibly "cell" boundaries. The appearance of the surface of the freshly prepared PuO_2 is shown in Figure 7. A similar "cell-like" structure is observed along with what appears to be a fine needle-like structure. This needle-like structure is similar to that frequently seen on the surface of rapidly solidified alloys. This appearance is shown more clearly in Figure 8; the cell-like structure also is shown prominently.

The as-polished surface of an aged (but not heat-treated) microsphere is shown in Figure 9. Cleavage steps are visible in this plucked area, but no micro-pores are visible.

Voids were observed in some of the aged material as shown in Figure 10 at 3000X. These voids are about $1\ \mu$ in diameter. Some smaller voids, approximately $0.04\ \mu$, are also present but are somewhat obscured due to the size of the gold nuclei. These smaller voids are shown more clearly in Figure 11.

The as-polished appearance of the (aged) microspheres after heat-treating to eliminate helium is shown in Figure 12. The micro-voids in this slide are $1\text{-}1.5\ \mu$ in diameter, which is similar to the size of those observed in the aged, but not heat-treated samples, although there seem to be more of them. The same area, at higher magnification, is shown in Figure 13.

An interesting feature of a $7.5\ \mu$ micro-void is shown in Figure 14. The surface of the void has what appear to be concentric circular steps. These may be growth steps associated with the formation of the microsphere in the plasma or they may be deformation steps. These steps may be seen more clearly in Figure 15. This micrograph is from a second replica of the same sample and is of the same void.

The aged, unheated sample was etched and the structure of the etched surface is shown in Figure 16. The grain boundaries, a second phase in the boundaries and some geometrically shaped etch pits are visible in this slide. The large etch pit is shown in

Figure 17. A model of this etch pit based on the structure of PuO_2 shows that the pentagonal faces are parallel to (111) planes and the square faces are parallel to (100) planes; the basal plane for this etch pit should be the (110) plane. One of the spheres from this sample is apparently a single crystal. This sphere is shown in Figure 18. The aligned etch pits are believed to follow sub-boundaries in the crystal. The evidence that this is a single crystal is the alignment of the edges of the geometrically shaped etch pits across the sub-boundaries and the lack of any defined grains on the replica.

DISCUSSION

These preliminary results indicate that cold replicas can be obtained. The best areas for locating micro-pores are cleaved surfaces (which may be obtained by fracturing the microspheres) or plucked areas of the sectioned and polished spheres. A technique for studying these fractured surfaces of microspheres is currently being developed. The polished and etched surfaces, although interesting, do not represent good surfaces for observing micro-porosity because the surface is disturbed in an uncontrolled manner by sample preparation.

Micro-pores were present in some areas of the freshly prepared microspheres but not in others. Micropores were also present that were indistinguishable from porosity formed in the aged,

heat-treated samples. Consequently, a large area of good surface must be studied to obtain unambiguous results.

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Figure 1 - Fresh ZrO_2 (2400X).

Figure 2 - $^{238}\text{PuO}_2$, as-polished (6000X).

Figure 3 - $^{238}\text{PuO}_2$, as-polished (12,000X).

Figure 4 - $^{238}\text{PuO}_2$, as-polished (80,000X).

Figure 5 - $^{238}\text{PuO}_2$, as-polished (24,000X).

Figure 6 - Plasma-fired CeO_2 microspheres (8000X).

Figure 7 - Freshly prepared $^{238}\text{PuO}_2$
microsphere surface (2400X).

Figure 8 - Freshly prepared $^{238}\text{PuO}_2$
microsphere surface (4000X).

Figure 9 - Aged (not heat-treated) $^{238}\text{PuO}_2$ microsphere, as polished (9000X).

Figure 10 - Aged (not heat-treated) $^{238}\text{PuO}_2$ microsphere, as polished (3000X).

Figure 11 - Aged (not heat-treated) $^{238}\text{PuO}_2$ microsphere, as polished (24,000X)
The arrows indicate rows of smaller voids.

Figure 12 - Aged, heat-treated $^{238}\text{PuO}_2$ as-polished (2400X).

Figure 13 - Aged, heat-treated $^{238}\text{PuO}_2$
as-polished (6000X).

Figure 14 - Aged, heat-treated $^{238}\text{PuO}_2$
as-polished (12,000X).

Figure 15 - Aged, heat-treated $^{238}\text{PuO}_2$
as-polished (12,000X).

Figure 16 - Aged (not heat-treated) $^{238}\text{PuO}_2$ etched
(2400X).

Figure 17 - Aged (not heat-treated) $^{238}\text{PuO}_2$ etched (8000X).

Figure 18 - Aged (not heat-treated) $^{238}\text{PuO}_2$ etched (2400X).

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