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Technical Papers of the

21st

**METALLOGRAPHIC
GROUP MEETING**

held May 10-12, 1967

Brookhaven National

Laboratory

Upton, New York

United States Atomic Energy Commission
Division of Technical Information

P3406

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✓ A TECHNIQUE FOR POLISHING
AND ETCHING BERYLLIUM

G. A. Wheeler and C. W. Price

ABSTRACT

A metallographic technique is described for beryllium that produces both a satisfactory polish and an excellent bright-field etch. An electrolyte of hydrochloric, nitric, and perchloric acids in ethylene glycol is used. Examples of polishes and etches that can be achieved with this technique are given.

INTRODUCTION

The major difficulties encountered in the metallographic preparation of beryllium are the severe surface deformation that is encountered during mechanical polishing and the lack of a suitable bright field etchant. The technique presented in this paper overcomes these difficulties and has the additional advantages of excellent reproducibility, rapidity, and ease of polishing and etching. This technique was derived from an electrolytic lapping technique that was developed for beryllium (1). The electrolyte used for the electrolytic lapping was modified so that it could be used for both conventional electrolytic polishing and electrolytic etching techniques. The use of this electrolyte forms the basis for the present technique.

EXPERIMENTAL TECHNIQUE

Specimen Preparation. Beryllium specimens may be either mounted or unmounted for the use of this technique, and the size of the specimens is not important. Specimens with surface areas up to 4 cm² have been electrolytically polished and etched successfully with this technique. As in all electrolytic techniques, the most important requirement is to provide a good electrical contact to the specimens, preferably on the back of the specimens. When specimens are mounted, a hole is drilled through the back of the mount so that the specimen can be contacted with a probe.

Conventional metallographic grinding techniques are used to prepare the specimens for electrolytic polishing. The specimens are ground on silicon carbide papers. Grinding through the usual series of papers down to the 600-grit paper is recommended to minimize the electro-polishing time, although successful electrolytic polishes and etches have been obtained

by grinding only through the coarser papers. A continuous flow of water is used during grinding to provide lubrication and to minimize contamination. Mechanical polishing is not required because high rates of material removal are achieved with the electrolytic polishing.

Polishing. Most of the results reported in this paper were obtained with a "Disa-Electropol", manufactured by Struers Scientific Instruments of Copenhagen, Denmark. Satisfactory results have also been obtained with the conventional beaker technique of electrolytic polishing, and a schematic diagram of the experimental set-up used for the beaker technique is shown in Figure 1. Conditions applicable to both the Disa unit and the beaker technique will be described.

Stainless steel cathodes are used in both techniques. In the beaker technique, a flat cathode with an area at least twice that of the specimen is used, and the specimen is held parallel to the cathode. The distance between the specimen and the cathode affects the quality of the electropolish. This distance is set at about 7 mm in the Disa unit; the same distance produces the best results in the beaker technique. Specimen-cathode distances greater than about 20 mm produce considerable relief, while distances less than 7 mm cause high current densities that are difficult to control.

An electrolyte of 2 percent HCl, 2 percent HNO₃, and 2 percent HClO₄ in ethylene glycol gives the most satisfactory results for both electrolytic polishing and etching. This electrolyte was developed by altering the composition of a similar electrolyte used for electrolytic lapping⁽¹⁾ and adding HClO₄ to improve the etching characteristics of the electrolyte. Variations from 0.25 percent to as much as 5 percent of each of the acids do not significantly affect the results, but the greatest amount of control and reproducibility can be obtained with the composition of 2 percent of each acid. Generally, lesser amounts of the acids produce lower polishing and etching rates, while greater amounts of acids cause high current densities that are difficult to control.

The temperature of the electrolyte is not critical for electropolishing, although increased temperatures do produce some difficulty in etching, as will be discussed below. The electrolyte is usually used at or near room temperature, but satisfactory polishes have been obtained with electrolyte temperatures as high as 40 C.

One of the distinct advantages of this electrolyte is that the current density-voltage plateau, the region of optimum polishing, is quite broad and can be found quite easily. Figure 2 shows a typical current density-voltage plot for the electrolyte at a temperature of 27 C. When the electrolyte is used at or near room temperature, the plateau occurs at about 0.1 amp/cm². An increase in the electrolyte temperature increases the current density at which the plateau is obtained, decreases the voltage at which the plateau begins, and decreases the width of the plateau. The voltage for polishing is selected from near the beginning of the plateau to eliminate any extraneous effects of high voltage. At room temperature, the voltage is usually in a range from 10 to 16 volts.

The quality of the electropolish is not noticeably affected by electrolyte flow rates. Since the flow rate does affect the uniformity of the etch, the flow rate for polishing is usually dictated by the requirements for etching. Usually, a flow-rate setting of 3-1/2 on the Disa unit is used. This corresponds to a moderate stirring rate in the beaker technique. The quality of the electropolish is also unaffected by the time of polishing, although a few seconds are required to establish the necessary electrolytic conditions to initiate polishing. The electropolishing time is governed by the amount of polishing required to remove the deformation introduced by grinding. This amounts to about 2-1/2 min. for specimens that have been ground through the 600-grit paper.

Etching. The specimens are etched in the electropolishing cell immediately after electropolishing by merely reducing the voltage. Satisfactory etches are usually obtained with the etching voltage selector of the Disa set at step 5, which corresponds to a potential of about 5 volts. Optimum etches are usually obtained in 5 to 7 sec. The most essential part of the etching technique is that the current must not be interrupted between the polishing and the etching cycles. This is done automatically on the Disa unit. Satisfactory etches are also achieved with the beaker technique if the current is not interrupted when changing from the polishing voltage to the etching voltage.

The extent of etching across a specimen is usually uniform once the proper etching conditions are found. Occasionally, a gradient of etching occurs across specimens etched on the Disa unit. This condition can often be controlled by adjusting the flow rate. The most satisfactory flow rate for etching was found at a setting of 3-1/2 on the Disa unit, as already mentioned. When extreme etching gradients are encountered, a decrease in etching voltage and an increase in etching time are also helpful in eliminating the gradient.

Another factor that does affect the reproducibility of etching is the electrolyte temperature. As the temperature increases, the plateau of the current density-voltage plot shifts to lower voltages and higher current densities, and the voltage has to be decreased to obtain satisfactory etching.

Electron Microscopy. Electron microscopy examinations using both replica and transmission techniques were conducted on some of the specimens to show more clearly the sharpness of the grain boundary delineation, the retention of the inclusions and constituent particles, and the correlation between structures revealed by the etching technique and structures revealed in transmission electron microscopy specimens. The specimens were replicated with the conventional two-stage cellulose acetate-carbon technique, and the replicas were shadowed from an angle of 30° with platinum-carbon. The specimens were prepared for transmission electron microscopy by first using a jet-indenting technique similar to the ones reported by Stickler and Engle⁽²⁾ and Blankenburgs and Wheeler⁽³⁾ and then using a final thinning technique similar to the one reported by Glenn and Raley⁽⁴⁾. An electrolyte of 10 percent HNO₃ was used for the jet indenting, and an electrolyte of 2 percent HNO₃ and 1 percent HCl in ethylene glycol was used for the final thinning. The electrolyte used for the final thinning was the same as that recommended for electrolytic lapping⁽¹⁾.

RESULTS

An example of the quality of the electropolish that can be achieved with the technique outlined in this paper is shown in Figure 3. This figure was taken from a vacuum-hot-pressed specimen which contained the usual distribution of fine oxides. This figure shows the excellent retention of these oxides, and it also shows the retention and delineation of some of the other inclusions and constituent particles. Preferential attack can be seen around some of the larger inclusions and constituent particles. Some of these particles undoubtedly were removed from the specimen, but most of the particles were retained. This was verified when the specimen was examined at high magnifications, particularly by electron microscopy.

The quality of the results that can be obtained with the etching technique are shown in Figures 4 and 5. Figure 4 was taken at the same magnification as Figure 3 to show the clear delineation of the grain boundaries, and Figure 5 was taken at a relatively low magnification to show that the grain boundary delineation is not distorted at these magnifications by the slight amount of preferential attack that usually occurs along grain boundaries when specimens are prepared electrolytically. The sharpness of the grain boundary delineation is shown in the electron micrographs of Figures 6 and 7. These electron micrographs were obtained from replicas of the vacuum-hot-pressed specimen. Figures 6 and 7 also show the excellent retention of inclusions and constituent particles--Figure 6 shows a large inclusion that was retained, and Figure 7 shows fine inclusions and constituent particles that were retained. Several of the fine particles that appeared to be oxides were extracted by the replicas.

The only questionable effect of this electrolytic technique was the preferential attack around some of the larger inclusions and constituent particles that was encountered during electropolishing. This caused an exaggeration of the size of these particles at low magnifications, and this is the reason for the appearance of the large black spots in Figure 5. This condition is definitely not detrimental to metallographic examinations of beryllium at low magnifications. Since many of these particles are not visible in mechanically polished specimens, evaluations of the distribution of these particles are more realistic in electropolished specimens than they are in mechanically polished specimens even though the size of the preferentially attacked particles is exaggerated in the electropolished specimens.

The relation between the oxide dispersion and the structure of the vacuum-hot-pressed specimen can be seen in Figures 4 through 7. Some of the oxides appeared to have been clustered along the grain boundaries, while others appeared to be in positions of prior boundaries. Therefore, the specimens were examined by transmission electron microscopy to determine if the structure revealed by etching technique corresponded to the structure revealed by transmission studies. Figure 8 shows an area where a grain boundary appears to have migrated away from the original boundary along which the oxides had formed. Tilting experiments verified that a grain boundary was no longer present along the oxides. Figure 9 shows an area where most of the oxides were along boundaries. A fairly high density of fine particles that could be oxides can be seen within one of the grains shown in Figure 9.

This could be an area where a grain boundary approximately parallel to the plane of the foil was intersected by one of the foil surfaces. These figures show that a direct correspondence was obtained between the structure revealed by the etching technique and the structures revealed by transmission electron microscopy.

The sharp delineation of the grain boundaries that is obtained with this etching technique could be enhanced by decoration effects such as grain-boundary precipitation or segregation, but evidence was obtained from a high-purity vacuum-distilled beryllium specimen in the as-deposited condition that showed that decoration effects are not necessary to achieve the sharp delineation. The etched structure of this specimen is shown in Figure 10. Large twins were formed in this specimen when it was fractured. These twins can be seen in the figure, and their sharp delineation is obviously not related to decoration effects. The specimen also had a columnar structure, and most of the grain appeared to have a basal orientation approximately parallel to the plane of deposition. Close orientation relations between adjacent grains made many of the grain boundaries difficult to detect under polarized light, but most of these boundaries were sharply delineated when the specimen was electrolytically polished and etched.

Examples of the quality of the etch that can be obtained from rolled sheets of both vacuum-cast material and powder-pressed material are shown in Figures 11 through 16. Figure 11 was taken from a rolled vacuum-cast specimen with a low oxide content. The equiaxed grain structure of this specimen indicates that it recrystallized after rolling, but definite evidence of sub-boundary formation can be seen throughout the structure. The fine particles that are suspected to be oxides appeared to be retained, although they were too small to be clearly resolved. Some preferential attack occurred around some of the larger particles, but most of these particles still appeared to be present. An electron micrograph from a replica of this specimen is shown in Figure 12. The sharp delineation of the grain boundaries and the excellent retention of the fine inclusions and constituent particles can be seen in this figure. Sub-boundaries appear to be delineated by changes in the orientation of the directional texturing that resembles faceting. Although this directional texturing is an etching effect that is obviously orientation dependent, the origin of this texturing is not known.

Figure 13 is from a rolled vacuum-cast sheet that appeared to show definite evidence of partial recrystallization. This was indicated by the presence of sub-boundaries in the relatively large grains and the formation of small, sharply delineated grains in between the larger grains. The same field in Figure 13 is shown in Figure 14 under polarized light. Figure 14 also indicates that the small grains were formed by recrystallization, although this specimen was not particularly susceptible to analysis by polarized light because of the high degree of preferred orientation.

A rolled specimen from powder-pressed material with an oxide content of approximately 1.8 percent is shown in Figure 15. The rolled texture of this specimen is clearly evident, and many of the grains appear to be elongated even though the structure does appear to have been recrystallized. No evidence of the formation of sub-boundaries was found in this specimen. The excellent

retention of the inclusions and constituent particles is again demonstrated in this specimen, and this is shown more clearly in Fig. 16 which is an electron micrograph taken from a replica of the specimen. Some of the particles in Fig. 16 appear to have been extracted by the replica, but these particles were not abundant enough to obtain useful selected-area electron diffraction patterns to identify the particles.

The results shown above demonstrate that the technique presented in this paper does provide a means for obtaining high quality etches in beryllium. Much of the structure in beryllium specimens that is revealed by electrolytic etching is usually not detected in polarized light examinations of mechanically polished specimens. This is particularly true of sub-boundaries and other fine structures such as precipitates. This emphasizes the desirability and, actually, the necessity of examining beryllium specimens in the etched condition.

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FIGURE 1. SCHEMATIC DIAGRAM OF THE SETUP USED FOR CONVENTIONAL BEAKER ELECTROLYTIC POLISHING AND ETCHING

FIGURE 2. PLOT OF CURRENT DENSITY VERSUS VOLTAGE FOR 2% HCl, 2% HNO₃, 2% HClO₄ IN ETHYLENE GLYCOL AT 20 C

FIGURE 3. A VACUUM-HOT-PRESSED SPECIMEN IN THE ELECTROPOLISHED CONDITION, 500X

FIGURE 4. THE STRUCTURE REVEALED IN THE VACUUM-HOT-PRESSED SPECIMEN BY ETCHING, 500X

FIGURE 5. THE QUALITY OF THE ETCH ON THE VACUUM-HOT-PRESSED SPECIMEN AT LOW MAGNIFICATION, 100X

FIGURE 6. AN ELECTRON MICROGRAPH FROM A REPLICA OF THE VACUUM-HOT-PRESSED SPECIMEN SHOWING THE SHARP GRAIN-BOUNDARY DELINEATION AND RETENTION OF A LARGE INCLUSION, 4500X

FIGURE 7. ANOTHER ELECTRON MICROGRAPH FROM THE VACUUM-HOT-PRESSED SPECIMEN SHOWING THE SHARP GRAIN-BOUNDARY DELINEATION AND RETENTION OF FINE INCLUSIONS AND CONSTITUENT PARTICLES, 4500X

FIGURE 8. TRANSMISSION ELECTRON MICROGRAPH FROM THE VACUUM-HOT-PRESSED SPECIMEN SHOWING AN AREA WHERE A GRAIN BOUNDARY APPEARS TO HAVE MIGRATED AWAY FROM THE ORIGINAL BOUNDARY ALONG WHICH THE OXIDES HAD FORMED 12,500X

FIGURE 9. ANOTHER TRANSMISSION ELECTRON MICROGRAPH OF THE VACUUM-HOT-PRESSED SPECIMEN SHOWING THE PRESENCE OF OXIDES ALONG MOST OF THE BOUNDARIES, 12,500X

FIGURE 10. TWINS AND GRAIN BOUNDARIES REVEALED IN A HIGH-PURITY VACUUM-DISTILLED SPECIMEN BY ETCHING, 250X

FIGURE 11. STRUCTURE OF A ROLLED-VACUUM-CAST SPECIMEN WITH A LOW OXIDE CONTENT, 250X

FIGURE 12. AN ELECTRON MICROGRAPH FROM A REPLICA OF THE SPECIMEN SHOWN IN FIG. 11, 4,500X

FIGURE 13. A ROLLED-VACUUM-CAST SHEET THAT SHOWS EVIDENCE OF PARTIAL RECRYSTALLIZATION, 250X

FIGURE 14. THE SAME FIELD SHOWN IN FIG. 13 UNDER POLARIZED LIGHT, 250X

FIGURE 15. STRUCTURE OF A ROLLED-POWDER-PRESSED SPECIMAN WITH A HIGH OXIDE CONTENT, 500X

FIGURE 16. AN ELECTRON MICROGRAPH FROM A REPLICA OF THE SPECIMEN SHOWN IN FIG. 15, 4,500X

✓ METALLOGRAPHIC PROCESSING OF OXIDE SPECIMENS

by

James R. Dvorak* & Robert F. Domagala**

ABSTRACT

Metallographic examination of annealed and quenched specimens was required during the course of a study of phase relations in the zirconia-scandia system. Although polishing was accomplished using rather conventional techniques, the somewhat inert properties of the oxides caused some problems. When a satisfactory etchant (hot phosphoric acid) was found, a suitable mounting material was needed to withstand the vigorous attack of the highly oxidizing reagent. Mineral-filled diallyl phthalate proved to withstand the etchant better than any of the other mounting materials which were examined.

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INTRODUCTION

During the course of study of phase realtions in the zirconia-scandia system it was desirable to examine metallographic specimens which had undergone various heat treatments. The specimens were polished using standard conventional preparation techniques. The etchant which proved to be most suitable was hot phosphoric acid. It was then necessary to find a mounting material which would withstand the vigorous attack of the etch.

PROCEDURES AND RESULTS

The specimens were polished using the Automet. The initial polishing was performed on 120 and 400 grit silicon carbide papers, using water as a lubricant. The next step consisted of polishing on a nylon cloth with 9 micron size diamond paste as the abrasive; a commercial diamond lubricant was used. The next step involved polishing on Texmet with 1 micron diamond paste with the same lubricant. Final polishing was accomplished on microcloth using Linde B alumina as the abrasive and distilled water as the lubricant.

Because these oxides are rather inert, the etching had to be quite severe. The etchant which proved to be most successful was hot (200°C) concentrated phosphoric acid. Etching times varied from 1 to 2 minutes for the scandia-rich specimens to 60 minutes or longer for the zirconia-rich compositions.

Various mounting materials were subjected to an etching cycle in order to find one which would hold up best during etching. Table I lists several mounting materials and the effect of the etch upon them. The material most suitable for this work was diallyl phthalate. Figures 1 to 4 show typical structures prepared using the above technique.

Since these materials are somewhat transparent, it is difficult to resolve structures at higher optical magnifications. A thin coating (~ 100 Å) of aluminum was vapor-deposited on the surface to improve the reflective properties of the sample. Figure 5 is an example of a specimen which was aluminum coated. Figure 6 shows the same specimen and area, photographed using polarized light. The aluminum coating was thick enough to reflect the light but thin enough not to interfere with the reaction to polarized light.

CONCLUSIONS

Other metallurgical tools, x-ray, and chemical analysis will be used in addition to the metallographic studies. These photomicrographs are only the results of initial investigations, but the technique appears to work well. These ceramic materials respond well to established metallographic procedures with certain precautions, principally in the choice of mounting material. The same techniques can also be applied to other hard and brittle materials.

ACKNOWLEDGMENTS

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TABLE I
EFFECT OF 30-MINUTE EXPOSURE TO HOT (200°C) ACID
ON VARIOUS MOUNTING MATERIALS

Type of Mounting Material	Manufacturer		Effect of Etchant
	Name	Catalog No.	
Epoxy	Buehler Ltd.	20-8130 resin 20-8132 hardner	Dissolved, became tacky and soft.
Epoxy	Marblette Co.	655 resin 553 hardner	Dissolved, became tacky and soft.
Acrylic	Vernon-Benshoff & Co.	Koldmount	Swelled and became porous.
Polyester	Buehler Ltd.	20-8124 plastic 20-8126 hardner	Swelled and surface cracked.
Melamine	American Cynamid	1077S-SS	Dissolved
Bakelite	Buehler Ltd.	20-3200	Swelled, surface burned and cracked.
Diallyl phthalate	Buehler Ltd.	20-3330	Slight color change with no other change.

X200

Fig. 1

Single-phase structure of the as-cast 100% scandia specimen. Etched for 5 minutes.

X200

Fig. 2

A zirconia-70 w/o scandia composition as cast; note typical dendritic growth. Etched for 10 minutes.

X300

Fig. 3

A zirconia-65 w/o scandia composition; note lamellar structure. Etched for 10 minutes.

X500

Fig. 4

A zirconia-75 w/o scandia specimen, which exhibits a lamellar structure. Etched for 10 minutes.

X500

Fig. 5

The structure of the zirconia-15 w/o scandia composition. The specimen was etched for 60 minutes and vapor-deposited with a thin film of aluminum to improve resolution.

X500 PL

Fig. 6

The same specimen and area as in Fig. 5

21: 43681

Paper 7

✓ METALLOGRAPHIC PREPARATION OF CERIUM CARBIDES*

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ABSTRACT

Special procedures were required to prepare cerium carbides metallographically because of their strong reactivity with moisture. A chemical, an electrolytic, and a protective-oil method were developed for preparing these carbides for examination. In both the chemical and electrolytic methods a stainless steel screw served as a contact with the CeC_2 .

Cerium dicarbide is either chemically polished or passivated by immersion in equal parts acetic, lactic, and nitric acids depending upon whether the mount is partially or totally immersed. If the CeC_2 specimen is partially immersed so that the stainless steel screw does not contact the solution, only chemical polishing takes place. If the mounted specimen is totally immersed, a galvanic cell is created such that CeC_2 is the anode and stainless steel is the cathode. The emf developed by this cell provides the necessary potential for passivation of the CeC_2 .

In the electrolytic method the CeC_2 was anodized at 5 v for 10 sec in equal parts acetic, lactic, and sulfuric acids.

In the protective-oil method CeC_2 was chemically polished in acetic-lactic-nitric acids and then washed with ethyl alcohol. Silicone oil was added to displace the ethyl alcohol, and a cover glass was placed on the CeC_2 specimen. For two-phase specimens containing CeC_2 and Ce_2Ca , the protective-oil procedure was followed but with the exception that chemical polishing was not employed.

INTRODUCTION

Cerium carbides are of general interest to the nuclear energy program because of the chemical similarity of lanthanide and actinide compounds.

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

An investigation of the chemical properties of cerium carbides may give us an insight to the chemical properties of plutonium carbides. Metallography serves as one means of characterizing the purity of arc-melted cerium carbides used in such an investigation.

In only one instance¹ have photomicrographs of the microstructure of cerium carbides been found in the scientific literature. This may result from a lack of awareness of the value of metallography as an investigatory adjunct or it may result from the difficulties encountered in the metallographic preparation of cerium carbides. Cerium carbides are difficult to prepare metallographically, mainly because they react strongly with moisture either in the room air or in the polishing media.

At Oak Ridge National Laboratory (ORNL) we have had considerable success in the metallographic preparation of thorium-uranium carbides and thorium carbides, which are also moisture reactive.^{2,3} The method devised for these carbides is to immerse the specimens in nitric acid solutions to give the polished surface sufficient passivity so they do not react with moisture contained in the room air. Simple immersion in a nitric acid solution was not effective for cerium carbides since the surface was etched rather than rendered passive. We, therefore, resorted to other methods for preparing these carbides metallographically. We developed what might be termed an electrolytic method, a chemical method, and a protective-oil method.

METALLOGRAPHIC PROCEDURES

The arc-melted cerium carbide specimens were mounted in epoxy resin, ground successively on 320, 400, and 600 grit silicon carbides papers using ethyl alcohol as the lubricant, and then polished 5 min on a Metcloth-covered wheel using Linde A abrasive and ethyl alcohol. Following this polishing, one of three methods, to be described, was employed so the specimens could be prepared, observed, and photographed properly under the microscope. The chemical and electrolytic methods were effective only with single phase CeC_2 , while the protective-oil method could be used with all compositions. In the chemical and electrolytic methods a stainless steel screw was driven into the epoxy mount to make electrical contact with the CeC_2 specimen.

Chemical Method

The adjective "chemical" as used to describe this method is employed only in the sense that an externally applied emf is not used. As explained later, the method actually involves an electrolytic process.

After a mechanical polish, the CeC_2 specimen was chemically polished by partially immersing, as indicated in Fig. 1, 15 sec in equal parts acetic, lactic, and nitric acids.* The dark brown film formed on the polished

*Strengths of concentrated reagents employed were 100% glacial acetic acid, 85% lactic acid, and 70% nitric acid.

surface during the chemical polish was then removed by washing with ethyl alcohol. After washing in ethyl alcohol the specimen was totally immersed, as indicated in Fig. 1, 30 sec in equal parts acetic, lactic, and nitric acids. Totally immersing the specimen mount so that the stainless steel screw contacts the acetic-lactic-nitric acid solution resulted in passivation of the specimen surface rather than chemical polishing. During passivation a golden brown transparent film formed on the polished surface. This film rendered the surface sufficiently passive so the specimen could be observed in open air for the period required for microscopic observation and photomicrography.

Totally immersing the specimen mount so the stainless steel screw contacts the electrolyte in effect creates an electrolytic cell. As CeC_2 dissolves in the electrolyte cations go into solution and electrons are left behind on the CeC_2 . Since stainless steel dissolves in the electrolyte to a much lesser extent than does the CeC_2 , it becomes the positive pole while the CeC_2 becomes the negative pole of an external circuit. Since in the electrolyte cations are attracted to the stainless steel and anions are attracted to the CeC_2 , the stainless steel becomes the cathode and the CeC_2 the anode of the internal circuit.

We performed a simple experiment to establish the polarity of the cell just described. We immersed the mounted CeC_2 specimen in the acetic-lactic-nitric acid electrolyte so the stainless steel screw contact remained out of the electrolyte. We then measured the emf existing between the CeC_2 and a second stainless steel screw placed in the electrolyte and found the emf to be about 1.5 v, the stainless steel being the positive pole, and the CeC_2 the negative pole. The resistance of the voltmeter kept the current so low that the CeC_2 was chemically polished rather than anodized. We then connected an ammeter between the CeC_2 and the stainless steel. Initially, the current measured 1.6 ma but fell to a value of 0.02 ma after about 1 min. While the ammeter was connected a golden brown film formed on the CeC_2 and the CeC_2 became passivated. At this time the ammeter was replaced with a voltmeter and the emf then existing between the CeC_2 and the stainless steel was found to be 0.10 v. The voltage and current behavior point to the formation of an anodic film on the CeC_2 and an indication of the passivating efficiency of the film. Koch and Picklesimer⁴ have reported forming similar protective films on lanthanum and cerium metallographic specimens by using an impressed emf.

Thus, the passivation of CeC_2 by acetic-lactic-nitric acids is an anodic process. Evidently the emf developed between CeC_2 and stainless steel when both are immersed in the acid electrolyte provides the electrical potential required for passivation of the CeC_2 .

Electrolytic Method

After a mechanical polish, the CeC_2 specimen was chemically polished in equal parts acetic, lactic, and nitric acids just as in the chemical method.

After the chemical polishing, the specimen was washed with ethyl alcohol and then anodized 10 sec at 5 v in a solution of equal parts acetic, lactic, and sulfuric acids,* which is the same solution Chamberlain and Paige employed in the metallographic preparation of uranium and plutonium carbides.⁵ This electrolytic anodization gives the surface a golden tint and leaves the surface passive so the specimen can be observed in room air.

Protective-Oil Method

In the protective-oil method, single-phase CeC_2 and two-phase specimens of CeC_2 and Ce_2C_3 were treated somewhat differently since single-phase CeC_2 could be chemically polished, while two-phase cerium carbide specimens could not. The acetic-lactic-nitric chemical polish etched and pitted the two-phase specimens.

Cerium dicarbide was first chemically polished by immersion in equal parts acetic, lactic, and nitric acids. This was best done by immersion since swabbing tended to remove material unevenly, leaving swab traces on the surface. A cover glass was placed on the specimen after first washing with ethyl alcohol; silicone oil was then added to the polished surface to displace the alcohol. This must be done without allowing the polished surface to come directly in contact with the room air. Any excess oil emerging from the edge of the cover glass was removed by blotter paper. Fortunately, the refractive index (1.517) of silicone oil is near that of the cover glass so there was essentially only one additional reflective surface to reduce the brilliance of the microscope image. Care should be taken that the cover glass is free of dust and lint.

Since the two-phase cerium carbide specimens could not be prepared by the electrolytic or chemical methods, the protective-oil method was employed. After mechanically polishing with Linde A abrasive, the two-phase specimens were mechanically polished an additional 30 sec with Magomet MgO abrasive on a Microcloth-covered wheel using ethyl alcohol as the lubricant. After washing with ethyl alcohol, silicone oil plus a cover glass were placed on the polished surface, as was done with the dicarbide specimen.

RESULTS

The first attempt at preparing CeC_2 consisted simply of polishing the specimen with Linde A abrasive on a Metcloth-covered wheel using ethyl alcohol as the lubricant. After polishing was completed, silicone oil was added to the surface and a cover glass placed on the specimen. Although the CeC_2 structure was revealed with polarized light, the results from this procedure, as given in Fig. 2, left much to be desired.

*Strengths of concentrated reagents employed were 100% glacial acetic acid, 85% lactic acid, and 95-98% sulfuric acid.

The next development was to chemically polish the CeC_2 specimen with acetic-lactic-nitric acids and then anodize the specimen in acetic-lactic-sulfuric acids. The resulting bright field and polarized light microstructures are given in Fig. 3. The twins presumably are due to a cubic-tetragonal transition which occurs on cooling. Krikorian et al.,⁵ have reported that a tetragonal-to-cubic transition occurs in CeC_2 on heating at 1090°C.

We next tried to find a chemical method for passivating the polished surface of CeC_2 . At first we erroneously attributed the good results shown in Fig. 4 to the use of a procedure in which the CeC_2 was first swabbed with the acetic-lactic-nitric acid chemical polish and then swabbed with the acetic-lactic-sulfuric acid solution. The passive film, which formed on the polished surface, was actually due to a stainless steel screw which was in contact with the CeC_2 when the specimen was swabbed in the acetic-lactic-nitric acid solution. Since a passive film was already on the polished surface, swabbing in the acetic-nitric-sulfuric acid solution really had no effect. Figure 5 shows the results obtained using the chemical method in which CeC_2 is first chemically polished by partial immersion in acetic-lactic-nitric acid and then passivated by total immersion in the same solution.

The third method developed for preparing CeC_2 metallographically was the protective-oil method. In this method, the CeC_2 was first chemically polished by immersion in the acetic-lactic-nitric acid solution, silicone oil added to the surface, and a cover glass placed on the specimen. Figure 6 shows the resulting microstructure as viewed in bright field, polarized light, and sensitive tint plate (full wave retardation) rotated to give maximum contrast.

Since the two-phase cerium carbide specimens were not amenable to the electrolytic and chemical procedures used for CeC_2 , the protective-oil method was used. Figures 7 and 8 show the microstructures for carbide specimens of $\text{CeC}_{1.87}$ and $\text{CeC}_{1.48}$ combined carbon compositions. The Ce_2C_3 appears gray and the CeC_2 appears white under bright field illumination. Polarized light is necessary to show the twinned structure of the CeC_2 phase.

Reasonably satisfactory methods have been developed for metallographically preparing the CeC_2 specimens, but two-phase specimens containing CeC_2 and Ce_2C_3 could only be prepared for microscope observation through the use of a protective oil (silicone oil) and a cover glass to prevent reaction with moisture. The sesquicarbide phase always exhibited fractures, the origin of which may be due to an improper polishing procedure. As yet, we have found no method which prevents these fractures.

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Fig. 1. Total and Partial Immersion Methods for Treating Cerium Dicarbide in Equal Parts Acetic, Lactic and Nitric Acids.

Fig. 2. Cerium Dicarbide Mechanically Polished on Metcloth Using Linde A Abrasive and Ethyl Alcohol. Silicone oil and a cover glass were placed on specimen to prevent reaction with moisture. (a) Bright field. (b) Polarized light.

250 X

(Reduced 10%)

Fig. 3. Cerium Dicarbide Anodized Electrolytically at 5 v for 10 sec in Equal Parts Acetic, Lactic, and Sulfuric Acids. Specimen was chemically polished, before anodizing, by partial immersion for 15 sec in equal parts acetic, lactic, and nitric acids. (a) Bright field. (b) Polarized light. 250 X
(Reduced 10%)

Fig. 4. Cerium Dicarbide After Swabbing with Equal Parts Acetic, Lactic, and Nitric Acids and Then Swabbing with Equal Parts Acetic, Lactic, and Sulfuric Acids. (a) Bright field. (b) Polarized light. 750 X
(Reduced 10%)

Fig. 5. Cerium Dicarbide Chemically Passivated by Total Immersion for 30 sec in Equal Parts Acetic, Lactic, and Nitric Acids. Before passivating, specimen was chemically polished by partial immersion for 15 sec in same equal parts solution. (a) Bright field. (b) Polarized light.

250 X
(Reduced 10%)

Fig. 6. Cerium Dicarbide Polished Chemically by Immersion in Equal Parts Acetic-Lactic-Nitric Acids. Silicone oil and a cover glass were placed on surface to prevent reaction with moisture. (a) Bright field. (b) Polarized light. (c) Sensitive tint with half-wave plate rotated to give maximum contrast. 250 X

Fig. 7. Two-Phase Cerium Carbide Specimen of $\text{CeC}_{1.87}$ Combined Carbon Composition Mechanically Polished on Metcloth Using Linde A Abrasive and Ethyl Alcohol. Silicone oil and cover glass were placed on surface to prevent reaction with moisture. (a) Bright field. Gray phase is Ce_2C_3 , white matrix phase is CeC_2 . (b) Polarized light. 250 X
(Reduced 10%)

Fig. 8. Two-Phase Cerium Carbide Specimen of $\text{CeC}_{1.46}$ Combined Carbon Composition Mechanically Polished on Metcloth Using Linde A Abrasive and Ethyl Alcohol. Silicone oil and a cover glass were placed on specimen to prevent reaction with moisture. (a) Bright field. Gray matrix is Ce_2C_3 , white phase is CeC_2 . (b) Polarized light. 250 X

(Reduced 10%)

Paper 5

21-43625

✓ POTENTIOSTATIC METALLOGRAPHIC ETCHING EXPERIMENTS*

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ABSTRACT

The potentiostat, which is an instrument for maintaining any desired electrical potential relative to a standard electrode, provides a means for maintaining a particular optimum potential at which a specific phase in the microstructure can be selectively etched electrolytically and differentiated from the remaining phases. The particular potential for optimum selectivity must be found experimentally, and the potentiostat aids in this by allowing the potential to be varied as desired.

The purpose of the experiments described in this report was to obtain experience in the application of a potentiostat to the etching of metallographic specimens and to acquaint ourselves with the possible use of potentiostatic etching for phase identification.

The experiments performed concerned (1) the etching of two-phase alloys of tin and zinc in which little or no solid solubility is exhibited, (2) the etching of austenitic stainless steels which contained ferrite, and which were free of ferrite, and (3) the etching of heat treated type 310 stainless steel containing sigma phase. In the tin-zinc alloys, we observed the zinc phase to be selectively etched in 1N NaOH at - 1.2 v vs saturated calomel electrode (SCE) and the tin phase to be selectively etched at - 0.9 v (vs SCE). We observed the ferrite phase of cast 19-9 stainless steel to etch preferentially in 1N H₂SO₄ at 1.35 v (vs SCE). When the cast 19-9 specimen was etched in 1N HCl we observed the ferrite to etch preferentially at - 0.42 v (vs SCE) and the austenite to etch preferentially at - 0.16 v (vs SCE). We were unable to preferentially etch the sigma phase of the type 310 stainless steel in either 1N HNO₃ or 1N HCl at any potential. We did observe

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that recrystallized austenite (formed in 25% cold worked type 310 stainless steel at 650°C) surrounding the sigma phase particles could be preferentially etched at 0.00 v (vs SCE) in 1 N HCl electrolyte which had been in use and contained dissolved metallic ions.

INTRODUCTION

Since the potential existing at an electrode largely determines the particular chemical reaction(s) which takes place at the electrode, important information is obtained from controlled potential electrolysis experiments. In a controlled potential electrolysis, a circuit for which is shown in Fig. 1, the potential of the working electrode relative to a reference electrode is maintained constant by varying the total applied voltage between the working electrode and an auxiliary counter electrode to compensate for changes in electrode potentials, overvoltages, and iR drop during the course of the electrolysis. Since manual adjustment of the applied voltage is tedious, control of the potential is usually by means of a potentiostat, which is an instrument for automatically maintaining any desired potential between the working electrode and the reference electrode. The potentiostat maintains the desired potential despite electrical or chemical changes which may be occurring in the system.

Controlled potential electrolysis technique with potentiostatic control has been applied in analytical chemistry²⁻⁴ and in corrosion studies. In metallography, potentiostatic etching has been employed in the etching of metal specimens.⁵⁻⁷ In potentiostatic etching a particular optimum potential is maintained by means of a potentiostat so that a specific phase in a specimen can be selectively etched and thus identified.

The experiments described in this report concern (1) the etching of two-phase alloys of tin and zinc in which little or no solid solubility is exhibited, (2) the etching of two different austenitic stainless steels, one with ferrite and the other without ferrite, and (3) the etching of type 310 stainless steel containing sigma phase. In these experiments an anodic polarization curve (potential-current diagram) was first determined, after which the specimen was repolished and etched potentiostatically at the potentials corresponding to the current maxima indicated by the polarization curve.

APPARATUS

The experimental setup depicted in Figs. 2 and 3 included a Duffers Model 600 potentiostat, two electrolytic cells (one containing a Beckman fiber junction saturated calomel reference electrode and one containing an auxiliary platinized platinum electrode plus the specimen working electrode), a 12 v automotive storage battery, and a salt bridge (glass tubing with capillary ends) connecting the two cells. Electrolytes used in the cells

included 1N NaOH, 1N H₂SO₄, 1N HNO₃, and 1N HCl. In any given experiment, the same electrolyte was employed in both cells and in the salt bridge.

The metallographic specimens, which were mounted in either epoxy resin or Bakelite, were prepared by grinding on silicon carbide papers, and mechanically polishing, first on silk using Linde A abrasive and then on microcloth using Linde B abrasive. A stainless steel sheet metal screw driven into the mount to contact the specimen served as the electrical contact.

ETCHING OF TWO-PHASE TIN-ZINC ALLOYS

Tin-zinc alloys were selected for the initial experiment since these alloys could be made fairly easily, and Green et al.,⁷ had previously shown that both tin and zinc phases in a binary alloy could be selectively etched through the application of a suitable electrical potential in a NaOH electrolyte.

Alloy specimens of 0, 15, 50, 70 and 100 wt% zinc were prepared. The pure tin specimen was prepared simply by melting in a graphite crucible held over a Bunsen burner. The pure zinc specimen was prepared by melting at 500°C for 1 hr in a graphite crucible suspended in a vertical furnace, stirring occasionally with a quartz rod. The tin-zinc alloys were prepared in a graphite crucible by melting the tin first and immersing the zinc in the molten tin; the tin-zinc alloys were then melted by heating 1 hr at 500°C.

Anodic Polarization Curves

The potential-current diagrams for pure zinc, pure tin, 15 wt% Zn-85 wt% Sn alloy, 50 wt% Zn-50 wt% Sn alloy, and 75 wt% Zn-25 wt% Sn alloy are presented in Figs. 4 and 5. The current peaks corresponding to the dissolution of zinc occurred between - 1.15 and - 1.3 v, and most commonly at - 1.2 v. The current peaks corresponding to the etching of tin occurred at about - 0.9 v.

The polarization curves we obtained for the tin-zinc alloys were reasonably reproducible. As Fig. 6 illustrates, our polarization curves were not in agreement with those of Steigerwald and Greene,⁸ particularly with regard to the location of the current maxima. The current maxima of Steigerwald and Greene's curves were located at slightly more negative potentials than we observed. The shape and form of our polarization curves were in general in agreement with theirs, however.

Etched Microstructure

We were able to selectively etch each of the alloy specimens so that at one potential the tin phase was etched and at a different potential the

zinc phase was etched. As an example, Fig. 7 shows the 75 wt% Zn-25 wt% Sn specimen after etching 1 min in 1N NaOH at - 1.2 v, and Fig. 8 shows the same specimen after etching 1 min in 1N NaOH at - 0.9 v. At - 1.2 v the zinc phase is etched, while at - 0.9 v the tin phase is etched.

ETCHING STAINLESS STEELS

Anodic polarization curves, shown in Fig. 9, were first determined for a cast 19-9 stainless steel containing ferrite and a type 347 stainless steel containing no ferrite.* A 1N H_2SO_4 solution was employed as the electrolyte and the range - 0.5 to + 1.7 v was covered. Two current peaks at - 0.25 and + 1.35 v were obtained for the cast 19-9 specimen, but only one small peak at - 0.25 v was obtained for the type 347 stainless steel specimen.

Both the cast 19-9 specimen and the 347 specimen were then etched at the 1.35 v peak observed for the cast specimen. Figure 10 shows the etched microstructures which resulted after etching the cast 19-9 specimen 2 min and after etching the 347 specimen 12 min. Although the grain boundaries were etched slightly, the ferrite phase in the cast specimen was etched predominantly. Apparently the peak observed at 1.35 v for the cast 19-9 specimen is associated with the etching of the ferrite phase.

The anodic polarization curve shown in Fig. 11 was determined for a type 304 stainless steel specimen* using 1N HCl electrolyte over a range of - 0.5 to + 1.7 v. After the curve was completed the 304 specimen exhibited deep pits and an etched grain structure, as shown in Fig. 12. The 304 specimen was polished and etched at - 0.10 v and then polished again and etched at 0.20 v. Figure 13a shows the etched grain structure obtained at - 0.10 v with 1N HCl, while Fig. 13b shows the pitting obtained at + 0.20 v with 1N HCl.

The region of negative potential of the anodic polarization curve shown in Fig. 11 was examined more closely for the 304 specimen which contained no ferrite and for the cast 19-9 specimen which contained ferrite. The two anodic polarization curves which resulted are shown in Fig. 14. The greater height of the peak obtained with the 304 specimen as compared with that of the 19-9 cast specimen is partly due to the greater area of the 304 specimen. Even though the area of the 304 specimen was larger, a greater current was obtained from the cast 19-9 specimen at potentials less than - 0.26 v than was obtained from the 304 specimen. Since the 19-9 specimen contained ferrite and the 304 specimen did not, we speculated that at some potential more negative than - 0.26 v the ferrite phase of the 19-9 specimen would be etched preferentially. Indeed, we found that the ferrite phase was etched when the cast 19-9 specimen was etched 5 min at - 0.42 v in HCl and the austenite was etched preferentially when the cast 19-9 specimen was etched 5 min at -0.16 v

*The chemical composition of the cast 19-9 specimen and the nominal compositions of the types 347 and 304 stainless steel specimens are given in the Appendix.

in 1N HCl. Figure 15a shows the etched microstructure with the ferrite etched preferentially at - 0.42 v, while Fig. 15b shows the etched microstructure with the austenite etched preferentially at - 0.16 v.

ETCHING TYPE 310 STAINLESS STEEL CONTAINING SIGMA PHASE

The three type 310 stainless steel* specimens which were to be etched potentiostatically were each heat treated 1980 hr at 650°C. Prior to this heat treatment, one was in the annealed condition,** one was cold worked 10%, and one was cold worked 25%. The amount of sigma formed during the 650°C heat treatment depended upon the amount of cold work in the specimen; the 25% cold worked specimen having the greatest amount of sigma. The metallographic identification of the sigma and carbide phases was established essentially by the methods developed by Gilman.⁹ Figure 16 compares the microstructure of the 25% cold worked specimen after etching with Vilella's etchant (95 ml ethyl alcohol, 5 ml conc HCl, 1 g picric acid), after etching electrolytically in conc NH₄OH, and after etching electrolytically in 10 N KOH. Both sigma and carbide phases are revealed, Fig. 16a, after swabbing 60 sec with Vilella's etchant. Only carbides are revealed, Fig. 16b, after etching electrolytically at 1.5 v for 20 sec in conc NH₄OH. Only sigma phase is revealed, Fig. 16c, after etching electrolytically at 1.5 v for 2 sec in 10 N KOH. The distribution of the sigma in the 25% cold worked specimen is similar to that which Lena and Curry¹⁰ observed for type 310 stainless steel which was 40% cold rolled and heat treated 300 hr at 1250°F (675°C). According to their data the isolated areas of sigma represent regions in which strained austenite of one composition has recrystallized to form sigma and unstrained austenite of another composition. Lena and Curry also noted the absence of carbide in the recrystallized austenite surrounding the sigma. This absence they attributed to an increase in the solubility of carbon in the austenite associated with the formation of sigma.

Anodic polarization curves obtained when each of the 650°C heat treated type 310 stainless steel specimens was placed in 1N HNO₃ electrolyte are given in Fig. 17. All three of the specimens exhibited similar curves even though they had different amounts of cold work prior to the 650°C heat treatment. No current peaks were observed in the curves and so it was not possible to associate a particular potential with the preferential etching of a given phase. After the polarization curves were determined, the 10% cold worked and 25% cold worked specimens were repolished and etched potentiostatically at 1.05 v, then repolished and etched potentiostatically at 1.35 v, and finally repolished and etched potentiostatically at 2.00 v. Figures 18, 19 and 20 show the etched microstructures obtained at 1.05, 1.35, and 2.00 v in 1N HNO₃. There was no appreciable difference in etching behavior at the three potentials although, of course, the attack is more severe at the higher positive potentials, which can be compensated for by decreasing the etching time.

*Nominal composition of type 310 stainless steel is given in Appendix.

**Quenched from 1900-1950 F.

The potentiostatic etching behavior of type 310 stainless steel in 1N HCl was quite different from that in 1N HNO₃. Figure 21 shows the anodic polarization curves obtained for each of the type 310 stainless steel specimens in 1N HCl. Only one peak was observed, which was at 0.00 v, for the 310 specimen which had been cold worked 25% prior to the 650°C heat treatment. After the polarization curves were completed the three type 310 stainless steel specimens were repolished and etched potentiostatically at - 0.28 v, and then repolished and etched potentiostatically at 0.00 v in the 1N HCl electrolyte. Figures 22 and 23 show the etched microstructures obtained at - 0.28 and 0.00 v in 1N HCl. At neither potential was sigma phase attacked appreciably. At - 0.28 v the regions in which carbides were concentrated were attacked mainly, while at 0.00 v recrystallized austenite surrounding the sigma particles was attacked mainly.

Using a fresh 1N solution of HCl we tried to duplicate the results, shown in Fig. 23c, obtained at 0.00 v in which the recrystallized austenite surrounding the sigma particles was attacked. But when freshly prepared 1N HCl was used the recrystallized austenite was attacked very little, as shown in Fig. 24a. We again employed the same used 1N HCl solution and obtained the results shown in Fig. 24b, which duplicates the earlier results. The attack of the recrystallized austenite would appear to be associated with a buildup of metallic ions in the electrolyte. We then employed as the electrolyte a synthetic 1N solution of HCl containing 0.74 g/l NiCl₂·6 H₂O and 0.85 g/l FeCl₃·6 H₂O. With this synthetic solution we were then again able to etch the recrystallized austenite, as may be seen in Fig. 24c.

CONCLUSIONS AND RECOMMENDATIONS

These potentiostatic etching experiments yielded quite encouraging results as to the application of the potentiostat as a metallographic tool for the identification of microstructural phases. The successful application of the potentiostat depended upon finding both a suitable electrolyte and the optimum electrical potential for selectively etching the particular phase to be identified. We successfully selectively etched the tin-rich and zinc-rich phases in the tin-zinc alloys and the ferrite phase in austenitic stainless steel; but we were not entirely successful in selectively etching the sigma-containing type 310 stainless steel.

Potentiostatic etching provides an alternate method to the usual chemical etching methods employed in metallography. The principal value of potentiostatic etching, however, is the selective etching and possible identification of particular phases in the microstructure. To establish criteria for proper identification of microstructural phases by this method, potentiostatic etching should be used in conjunction with other methods of analysis, particularly analyses as performed with the electron microprobe and the microchisel. With this in mind, further investigation might include

the combination of potentiostatic etching studies with

1. Electron microprobe analysis,
2. Use of the microchisel,¹¹ which is a mechanical device for extracting microstructural phases for either x-ray diffraction or microchemical analysis.

More specifically, the potentiostat may have an application in the selective etching and identification of phases in uranium systems of carbon and nitrogen.

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APPENDIX

Chemical Compositions of Stainless Steel Specimens

	Cast 19-9 (wt %)	Type 304 SS (wt %)	Type 310 SS (wt %)	Type 347 SS (wt %)
Carbon	0.05	0.08 max	0.25 max	0.08 max
Manganese	0.86	2.00 max	2.00 max	2.00 max
Silicon	0.98	1.00 max	1.00 max	1.00 max
Chromium	19.08	18 to 20	24 to 26	17 to 19
Nickel	8.72	8 to 12	19 to 22	9 to 13
Cb-Ta				10 X C
Phosphorus	0.008			
Sulfur	0.012			
Aluminum	0.017			

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A = Ammeter for measuring current in working electrode-auxiliary electrode circuit

V = Voltmeter for measuring applied voltage

A.E. = Auxiliary electrode

W.E. = Working electrode

S.C.E. = Saturated calomel electrode

H.R.V. = High resistance voltmeter for measuring potential of working electrode vs saturated calomel electrode

Fig. 1. Manual Controlled Potential Electrolysis

Fig. 2. Schematic Diagram of Potentiostatic Etching Apparatus

Fig. 3. Potentiostatic Etching Apparatus

Fig. 4. Anodic Polarization Curves for Pure Zinc and Pure Tin.
1 N NaOH electrolyte.

Fig. 5. Anodic Polarization Curves for Tin-Zinc Alloys. 1 N NaOH electrolyte.

Fig. 6. Comparison of 15 wt% Zn-85 wt% Sn Polarization Curve with Steigerwald and Greene's Curve for 15.9 wt% Zn Specimen. 1 N NaOH electrolyte.

Fig. 7. Microstructure of 75 wt% Zn-25 wt% Sn Alloy After Etching 1 min at - 1.2 v (vs SCE) in 1 N NaOH. Zinc phase has been etched.

Fig. 8. Microstructure of 75 wt% Zn-25 wt% Sn Alloy After Etching 1 min at - 0.9 v (vs SCE) in 1 N NaOH. Tin phase has been etched.

Fig. 9. Anodic Polarization Curves for Cast 19-9 and Type 347 Stainless Steel. 1 N H_2SO_4 electrolyte.

Fig. 10. Stainless Steel Etched Potentiostatically at 1.35 v (vs SCE) in 1 N H_2SO_4 . (a) Cast 19-9 stainless steel etched for 2 min. (b) Type 347 stainless steel etched for 12 min.

(Reduced 10%)

Fig. 11. Anodic Polarization Curve for Type 304 Stainless Steel.
1 N HCl electrolyte.

Fig. 12. Surface of 304 Stainless Steel Specimen After Completion of
Polarization Curve for 1 N HCl Electrolyte.

(Reduced 10%)

Fig. 13. Type 304 Stainless Steel Etched Potentiostatically in 1 N HCl.
(a) Etched 2 min at - 0.10 v (vs SCE). (b) Etched 2 min at
0.20 v (vs SCE).

(Reduced 10%)

Fig. 14. Anodic Polarization Curves for Type 304 and Cast 19-9 Stainless Steels. 1 N HCl electrolyte.

Fig. 15. Cast 19-9 Stainless Steel Etched Potentiostatically in 1 N HCl.
 (a) Etched for 5 min at - 0.42 v (vs SCE). Ferrite etched preferentially.
 (b) Etched for 5 min at - 0.16 v (vs SCE). Austenite etched preferentially.

(Reduced 10%)

Fig. 16. Microstructure of Type 310 Stainless Steel Cold Worked 25% and Heat Treated Subsequently at 650° C for 1980 Hr. (a) After swabbing 60 sec with Vilella's etchant (95 ml ethyl alcohol, 5 ml conc HCl, 1 g picric acid). (b) After etching electrolytically at 1.5 v for 30 sec on conc NH_4OH . (c) After etching electrolytically at 1.5 v for 2 sec in 10 N KOH.

(Reduced 10%)

Fig. 17. Anodic Polarization Curves for Type 310 Stainless Steel Specimens After 1980 Hr at 650°C. 1 N HNO₃ electrolyte.

Fig. 18. Type 310 Stainless Steel Cold Worked and Heat Treated 1980 Hr at 650° C. Polished and then etched potentiostatically at 1.05 v (vs SCE) for 10 min in 1 N HNO₃ electrolyte. (a) 10% prior cold work. (b) 25% prior cold work.

(Reduced 10%)

Fig. 19. Type 310 Stainless Steel Cold Worked and Heat Treated 1980 Hr at 650 C. Polished and then etched potentiostatically at 1.35 v (vs SCE) for 10 sec in 1 N HNO₃ electrolyte. (a) 10% prior cold work. (b) 25% prior cold work.

(Reduced 10%)

Fig. 20. Type 310 Stainless Steel Cold Worked and Heat Treated 1980 Hr at 650 C. Polished and then etched potentiostatically at 2.00 v (vs SCE) for 2 sec in 1 N HNO₃ electrolyte. (a) 10% prior cold work. (b) 25% prior cold work.

(Reduced 10%)

Fig. 21. Anodic Polarization Curves for Type 310 Stainless Steel Specimens After 1980 Hr at 650°C. 1 N HCl electrolyte.

Fig. 22. Type 310 Stainless Steel After Heating 1980 Hr at 650°C. Polished and then etched potentiostatically at - 0.28 v (vs SCE) for 10 min in 1 N HCl. (a) Prior condition - annealed. (b) Prior condition - cold worked 10%. (c) Prior condition - cold worked 25%.

(Reduced 10%)

Fig. 23. Type 310 Stainless Steel After Heating 1980 Hr at 650°C. Polished and then etched potentiostatically at 0.00 v (vs SCE) for 1 min in 1 N HCl. (a) Prior condition - annealed. (b) Prior condition - cold worked 10%. (c) Prior condition - cold worked 25%.

(Reduced 10%)

Fig. 24. Type 310 Stainless Steel Cold Worked 25%, Heat Treated 1980 Hr at 650° C. Polished and then etched potentiostatically at 0.00 v (vs SCE) in 1 N HCl. (a) Etched 1 min in fresh 1 N HCl. (b) Etched 1 min in "used" 1 N HCl. (c) Etched 2 min in 1 N HCl containing 0.74 g/l $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ and 0.85 g/l $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$.

(Reduced 10%)

✓ 19
A Fractographic Study of Helium-Injected 304 Stainless Steel

by

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ABSTRACT

Tensile specimens of 304 stainless steel were irradiated with alpha particles to simulate helium generation which occurs in stainless steel during neutron irradiation. Samples containing 1×10^{-5} and 3×10^{-3} atom percent helium, as well as control samples containing no helium, were tensile tested at 1000°, 1200°, and 1400°F subsequent to irradiation.

Replicas of the fractured surfaces examined in the electron microscope revealed a shear-rupture type failure in the samples tested at 1000°F. The failure at 1200°F was a mixture of shear-rupture type, quasi-cleavage type, and intergranular separation, the latter two modes increasing with increasing helium content. Extensive thermal etching occurred on the fracture surfaces of samples tested at 1400°F. However, the general appearances of the fractures indicate that the helium-containing samples failed by intragranular separation, whereas the control sample failed by a mixture of inter- and intra-granular fracture.

Also included in the study were replicas of polished surfaces parallel to the tensile axis and transmission electron microscopy of thin foils.

INTRODUCTION

The effectiveness of stainless steel as a cladding material in nuclear reactors is diminished because of its loss of high temperature ductility after neutron irradiation.¹ This high temperature ($> 1000^\circ\text{F}$) embrittlement has been attributed to the presence of helium bubbles in the stainless steel.² The helium is present as a result of the (n, α) type reactions which occur during irradiation.³ The precise mechanism by which helium may reduce the ductility in these materials has not yet been determined. One method available for the study of these fracture mechanisms is electron fractography of hot tensile samples.

Fractography is the study of the features of the fracture surface and is a technique that should be used in conjunction with other techniques, such as light microscopy, replication and transmission electron microscopy of the sample normal to the fracture. The features of the fracture surface can reveal the type of fracture, the path of the fracture, and other details such as the effect of second phase or inclusion particles on the fracture.

In this study, electron fractography, as well as other metallographic examinations, were performed on 304 stainless steel which had been tensile tested at 1000°, 1200°, and 1400°F after cyclotron irradiation with alpha particles - a technique which provides high helium concentrations in several hours.

EXPERIMENTAL

The sub-sized tensile specimens (.009" x .040" x 1.0") of 304 stainless steel were annealed for 5 hours at 1850°F to produce fully annealed austenite and then cyclotron irradiated in two groups. The groups received 1×10^{-5} and 3×10^{-3} atom percent helium. In order to minimize the complicating effects of carbide precipitation during tensile testing, the irradiated as well as control samples were annealed 10 hours at 1400°F prior to tensile testing in order to precipitate the carbon (as $M_{23}C_6$) which had been dissolved during the 1850°F anneal. The tensile tests were carried out at 1000°, 1200°, and 1400°F in vacuum.

Cellulose acetate replicas were made of the fracture surfaces and chromium-shadowed carbon replicas made of the plastic replicas. Both 5 mil and 2 mil cellulose acetate were used and found to be satisfactory. A drop of replicating solution (cellulose acetate dissolved in acetone) was placed on the plastic tape and the sample gently pressed into the plastic. The plastic was allowed to dry for several minutes before stripping. The procedure was repeated at least twice with the first impression, used to eliminate debris from the fracture, thrown away. Since the cross-sectional area of the fracture is quite small for these samples (.009" x .040"), it becomes important to recognize that a portion of the sample surface not in the fracture plane may be replicated. Erroneous conclusions about the fracture may be drawn if external surfaces are interpreted as being a part of the fracture surface.

In addition to fractography we also examined polished sections and thin foils parallel to the tensile axis. The samples used for the polished sections were nickel plated prior to polishing in order to help preserve the fracture edge. They were mechanically and electrolytically polished for replication, which consisted of two-stage cellulose acetate - Cr shadowed carbon replicas. We were able to examine the samples several mils from the fracture along the gauge length.

Samples for thin foils were first mechanically thinned to 4 or 5 mils and then electrolytically thinned to electron transparency in 6 parts H_3PO_4 - 4 parts H_2SO_4 at 9 volts at room temperature.

RESULTS AND DISCUSSION

The results of the tensile tests are plotted as percent elongation vs. test temperature in Fig. 1. The ductility, which is independent of helium concentration at the 1000°F test, is a function of helium content at the higher test temperatures. The ductility loss in the control sample above 1300°F is not uncommon.⁴

Electron fractographs of the control and 3×10^{-3} a/o He samples tested at 1000°F are seen in Fig. 2. These fracture surfaces are typical of shear rupture failure due to micro-void coalescence, represented by the dimples which are apparent in the fractographs. Carbide (M_{23}C_6) particles can also be seen in the fracture surfaces.

Fracture surfaces of the samples tested at 1200°F are shown in Fig. 3. These samples show a mixture of shear rupture (dimples) and quasi-cleavage type fracture. Quasi-cleavage describes a planar transgranular fracture which is not related to the crystallographic cleavage plane (or planes) of the material. The fractures of the control and the 10^{-5} a/o He samples are very similar with the major mode of failure being shear rupture and a minor amount of quasi-cleavage occurring. The 3×10^{-3} a/o He sample has fractured mainly by the quasi-cleavage mode and intergranular separations with minor amount of shear rupture failure. The fact that the fractures of the control and 10^{-5} a/o He samples are similar to each other and different from the 3×10^{-3} a/o He sample is reflected in the ductility curves of Fig. 1.

Detail of the fracture surfaces of samples tested at 1400°F was lost because of thermal etching (Fig. 4). However, the general appearances of the fractures give some information. The control appears to be a ductile fracture with dimple surfaces etched. The 10^{-5} a/o He sample fracture surface gives an indication of intergranular failure and the 3×10^{-3} a/o He sample shows a strong indication of intergranular failure. The general conclusions which can be drawn from the fractographs concerning the failure modes are:

- 1) samples tested at 1000°F exhibit shear rupture type;
- 2) at 1200°F there is a mixture of shear rupture and quasi-cleavage in the control and low helium samples and a mixture of quasi-cleavage and intergranular separation in the high helium sample;
- 3) at 1400°F the control sample failure appears generally to be of the shear rupture type, whereas the helium containing samples appear to have intergranular failures.

Examination of the tensile samples in a plane parallel to the tensile axis can add information and insight into the interpretation of the fractographs. Replicas and thin foils of samples tested at 1000°C are shown in Figs. 5 and 6. The grains are elongated and occasional voids can be seen associated with the grain boundary carbides ($M_{23}C_6$). The dislocations are tangled with some cell formation apparent. There are no helium bubbles in the helium - containing sample and the two samples are quite similar in microstructure.

Replicas of the samples tested at 1200°F reveal elongated grains with numerous voids at grain boundary carbides in the control and low helium samples, whereas the high helium sample shows virtually no elongation of grains and large intergranular separations, generally perpendicular to the tensile axis. The thin foils indicate dislocation arrangements similar to those in samples tested at 1000°C. Helium bubbles, 50-100 Å in diameter, were detected in the sample containing 3×10^{-5} a/o He (Fig. 7). The bubbles, most of which are associated with dislocations, are uniformly dispersed throughout. No bubbles were detected in the lower-helium containing sample.

Examination of replicas of the 1400°F test samples indicates some grain elongation near the fracture in the control sample, very little grain elongation in the 10^{-5} a/o He sample, and no grain elongation in the 3×10^{-3} a/o He sample (Fig. 8). In each sample the amount of grain boundary voids has increased over the samples tested at 1200°F. Thin foils reveal helium bubbles, ranging from 70 to 300 Å in diameter, on grain boundaries and dislocations in the sample containing 3×10^{-3} a/o He (Fig. 9). No bubbles were detected in the lower helium sample.

These results support the earlier conclusions made on the basis of fractography alone. Again it is important to point out that although fractography in itself yields definite information concerning the mode of failure, it is a technique limited in resolution not only by the replicating process but also by the coarse features of the fracture surface. The maximum bubble size found in this study was 300 Å which is at the threshold of resolution and therefore no bubbles were seen in the fractographs.

CONCLUSIONS

The combination of fractography and conventional electron metallography of these tensile samples allow us to draw the following conclusions:

- 1) At 1000°F the failure mode is of the shear rupture type and is independent of helium content in the range examined (up to 3×10^{-3} a/o He);
- 2) With increasing test temperature (from 1000°F) the mode of fracture changes from shear rupture to intergranular separation;

- 3) The rate at which the fracture mode changes increases with increasing helium concentration.

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Fig. 1. Total elongation vs. test temperature for type 304 stainless steel with and without helium. Samples were annealed 10 hours at 1400°F prior to testing.

Fig. 2. Electron fractographs of 304 stainless steel tensile tested at 1000°F.
 Pre-test treatment: (a) 5 hours at 1850°F → 10 hours at 1400°F;
 (b) 5 hours at 1850°F → 3×10^{-3} a/o He → 10 hours at 1400°F.

Fig. 3. Electron fractographs of 304 stainless steel tensile tested at 1200°F.
 Pre-test treatment: (a) 5 hours at 1850°F → 10 hours at 1400°F;
 (b) 5 hours at 1850°F → 1×10^{-5} a/o He → 10 hours at 1400°F;
 (c) 5 hours at 1850°F → 3×10^{-3} a/o He → 10 hours at 1400°F.

(Reduced 10%)

Fig.3 Continued

Fig. 4. Electron fractographs of 304 stainless steel tensile tested at 1400°F.
 Pre-test treatment: (a) 5 hours at 1850°F → 10 hours at 1400°F;
 (b) 5 hours at 1850°F → 1×10^{-5} a/o He → 10 hours at 1400°F;
 (c) 5 hours at 1850°F → 3×10^{-3} a/o He → 10 hours at 1400°F.

(Reduced 10%)

Fig. 5. Replicas of polished surfaces of 304 stainless steel tensile tested at 1000°F. Pre-test treatment: (a) 5 hours at 1850°F → 10 hours at 1400°F; (b) 5 hours at 1850°F → 3×10^{-3} a/o He → 10 hours at 1400°F.

(Reduced 10%)

Fig. 6. Thin foils of 304 stainless steel tensile tested at 1000°F. Pre-test treatment: (a) 5 hours at 1850°F $\longrightarrow$ 10 hours at 1400°F; (b) 5 hours at 1850°F $\longrightarrow$ 3×10^{-3} a/o He $\longrightarrow$ 10 hours at 1400°F.

(Reduced 10%)

Fig. 7. Thin foils of 304 stainless steel tensile tested at 1200°F. Pre-test treatment: (a) 5 hours at 1850°F $\longrightarrow$ 1×10^{-5} a/o He $\longrightarrow$ 10 hours at 1400°F; (b) 5 hours at 1850°F $\longrightarrow$ 3×10^{-3} a/o He $\longrightarrow$ 10 hours at 1400°F.

(Reduced 10%)

Fig. 8. Replicas of polished surfaces of 304 stainless steel tensile tested at 1400°F. Pre-test treatment: (a) 5 hours at 1850°F → 10 hours at 1400°F; (b) 5 hours at 1850°F → 1×10^{-5} a/o He → 10 hours at 1400°F; (c) 5 hours at 1850°F → 3×10^{-3} a/o He → 10 hours at 1400°F.

(Reduced 10%)

Fig. 8 Continued

Fig. 9. Thin foils of 304 stainless steel tensile tested at 1400°F. Pre-test treatment: (a) 5 hours at 1850°F → 10 hours at 1400°F; (b) 5 hours at 1850°F → 1×10^{-5} a/o He → 10 hours at 1400°F; (c) 5 hours at 1850°F → 3×10^{-3} a/o He → 10 hours at 1400°F.

(Reduced 10%)

X SOME PHASE EQUILIBRIA IN THE Th - ^N THORIUM - NITROGEN
SYSTEM (A CONDENSATION)

R. Benz, C. G. Hoffman and G. N. Rupert

The thorium nitride phases have been identified by various investigators. The Th_3N_4 was first reported by C. Matignon and M. Delepine and later found to have a rhombohedral Al_4C_3 - type crystal structure. The crystal structure of ThN was reported by Rundle and Chiotti to be face - centered cubic.

The melting point of ThN depends upon composition and therefore upon N_2 pressure. Chiotti reported 2630°C in He and Olson and Mulford found 2790°C in N_2 . Gerds and Mallett reported the solubility of N in Th.

The present work investigated the Th-N phases equilibrated under various conditions, the results are reported and summarized in a Phase diagram.

1. The first series of tests was to determine the peritectic and peritectoid temperatures. This was done by observing heating and cooling arrests using the thermal analysis apparatus designed by Rupert. 1 and 2

Crystal bar Th melted at $1754 \pm 15^\circ\text{C}$. The thermal arrest of the fcc-bcc transition was at 1370°C on heating and 1365°C on cooling. The transition covered 25°C temperature range on both cooling and heating at a rate of $2^\circ/\text{sec}$. At a somewhat higher rate of temperature change ($12^\circ/\text{sec}$) the range was of course somewhat greater.

1. G. N. Rupert; "Versatile High Temperature Thermal Analysis Apparatus" presented at First International Conference on Thermal Analysis, Aberdeen - Scotland, September 6-9, 1965.
2. G. N. Rupert; Rev. Sci. Instr. 36 1629, 1965.

Figure 1. The Th-Th₃N₄ phase diagram.

Th + ThN with various N:Th ratios up to 0.96 were subjected to thermal analysis. There was a thermal arrest at $1605^{\circ}\text{C} \pm 20^{\circ}$ with all N:Th ratios from 0.08 - 0.88 as shown in fig 1. This was not detected for the extreme ratios of 0.01 and 0.96. A second effect in this region was a change in cooling rate. This began at about 1570°C and broadened continuously toward 1400°C as the N:Th ratio was decreased from 0.1 to 0.01. This was related to the dissolution of N into Th during heating and reprecipitation on cooling.

The third thermal effect, a cooling rate change, was most pronounced at 1645°C and extended over a temperature range of 40°C and is associated with the precipitation of ThN from bcc Th during cooling and dissolution during heating.

The peritectic arrest occurred at $1800^{\circ}\text{C} \pm 25^{\circ}\text{C}$, and with it was a cooling rate change near the melting point of Th.

The N:Th ratio in the N rich boundary of Th was determined by area analysis of polished sections. This was found to be 0.08 for the fcc Th at 1550°C and the same for bcc Th at 1750°C . The lattice parameter of fcc Th in quenched condition was $5.090 \pm 0.009\text{\AA}$. Fig 2 shows the ThN precipitate in the Th phase.

Fig 2.

250BF

All metallographic samples were mounted in lucite, ground wet through 600 grit wet-or-dry paper, and polished with 6 micron diamond paste on metcloth in kerosene and finished on 1 micron diamond paste in kerosene on selvyt. This may seem unnecessary to most metallographers and indeed it is, but so many very hard materials are polished in this laboratory that it is quicker, easier and less expensive to polish everything with diamond paste, even graphite and aluminum. In other words this is standard procedure for everything.

Some samples were air etched and the rest were etched with 50% HNO_3 in H_2O , which coincidentally retards excessive air oxidation of the samples.

2. ThN liquidus

Liquid Th was saturated at 2000, 2139 and 2400°C by heating Th + ThN cylinders in Vacuo, and at 2644°C by heating a Th + ThN cylinder in 15 Torr of N_2 , which is very slightly below the decomposition pressure of ThN. The N:Th ratios were found metallographically (area analysis) to be 0.12 at 2000°C, 0.14 at 2139°C, 0.21 at 2400°C and 0.53 at 2344°C. Fig 3 shows the liquid composition at 2000°C.

Fig 3.

250BF

3. An upper limit to the Th rich ThN phase boundary was determined by the final N:Th ratio when samples were heated different periods of time at selected temperatures from 1537°C to 1930°C. This was done with samples which were initially rich in nitrogen, and also with samples which were initially richer in Th. Those which were Nitrogen rich evolved N₂ comparatively rapidly and reached equilibrium or near equilibrium much more rapidly than those richer in Th, where the Th distilled very slowly. The results are plotted with V-shaped symbols in Fig 1. The phase boundary was determined metallographically by area analysis of a series of Th + ThN cylinders. The N:Th ratios computed from the relative proportion of the Th precipitate found within the ThN grains are 0.97 at 1576; 0.96 at 1665°C; 0.91 at 1775°C; 0.89 at 1870°C; 0.87 at 2000°C; 0.92 at 2400°C and 0.96 at 2645°C. These results are plotted in Fig 1 and are used to draw the solvus and solidus at the Th rich ThN phase boundary. Fig 4 shows the Th precipitate in the ThN grains.

Fig 4

250BF

At 1615°C, 1835° and 2065°C the N rich phase boundary was determined by equilibrating for 7 days in 14 Torr N₂, 4 days in 119 Torr and 3 days in 600 Torr of N₂ respectively. These pressures are just below the decomposition pressures of Th₃ N₄. The proportions of Th₃ N₄ was determined metallographically also, and good agreement was found with the results by ignition. Fig 5 shows the Th₃ N₄ in ThN.

Fig 5

250BF

4. Congruent Melting Point of ThN.

Cylinders of ThN were melted in N_2 gas at various pressures, 3 atm, 2 atm, 1 atm and some at fractional atmospheres, and the temperature of incipient fusion noted. The fusion temperature gradually increased with the N_2 pressure up to 2 atmospheres and then dropped off a bit. The maximum was $2820^\circ\text{C} \pm 30^\circ\text{C}$ in 2 atm of N_2 , which is in agreement with the value by Olson and Mulford. The N:Th ratio was found to be 0.99 ± 0.02 by ignition. Fig 6 shows the microstructure of this material, tiny particles of Th metal in ThN matrix.

Fig 6

1000BF

Figs 7, 8 and 9 show the microstructures of three of the incongruently melting mixtures.

Fig 7
Melted at 2760°C
N:Th ratio 1.03
Dark grains - ThN
Light areas - Th_3N_4 + $\text{Th}_2\text{N}_2\text{O}$

250BF

Fig 8
Melted at 2640°C
N:Th ratio 0.87
Light - ThN (bits of Th in them)
Dark - Th

1000BF

Fig 9
Melted at 2800°C
N:Th ratio - 0.95
Light - ThN
Dark - Th

1000BF

Paper 3

21: 36877

✓ PREPARATION OF IRRADIATED HIGH TEMPERATURE SERVICE
NICKEL-BASE ALLOYS FOR METALLOGRAPHY*

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ABSTRACT

Irradiated tensile samples fabricated from several nickel base alloys were examined metallographically after testing to study microstructural relationships to physical properties, testing criteria, irradiation induced phenomena, and heat treatment histories. Specimens were examined optically and replicas were made for electron microscopy. Preparation, etching, and replicating techniques are described; differences between irradiated and non-irradiated materials are discussed; and illustrations of results are presented.

INTRODUCTION

In the Radiometallurgy Laboratory at Battelle-Northwest over the past three years irradiated reactor structural materials have been tested and examined as part of a program to expand technology relating to irradiation behavior of several classes of materials. One phase of the work has been tensile and physical properties testing of high temperature service nickel base alloys. To date, alloys irradiated up to 10^{21} nvt have been tested at temperatures ranging from ambient to 700 degrees C. Paralleling the testing, metallographic and electron microscope studies were conducted to relate microstructural changes to specimen histories and observed physical properties. This paper describes the procedures for preparing and etching specimens for metallography and techniques for obtaining replicas for electron microscopy.

*Work was performed under contract AT(45-1)-1830 between the United States Atomic Energy Commission and Battelle Memorial Institute.

In general procedures for preparing nickel base alloy specimens irradiated up to 10^{19} nvt are the same as those for unirradiated specimens, except for shielding requirements. Procedures for highly irradiated specimens usually are not the same as for their unirradiated counterparts. It is these highly irradiated specimens that are discussed along with problems associated with their processing.

CONCLUSIONS

Although considerable more irradiated specimens will have to be processed before refined procedures can be defined, some conclusions can be made at this time.

1. Clear epoxies and other plastic mounting materials can not be used for potting specimens, because they are deteriorated by high radiation. Samples should be processed in mechanical mounts or with epoxies containing filler materials. (Bakelite mounts were not tested to determine their stability.)
2. Etching specimens is somewhat a cut and try method. One basic etchant, 92% HCl and 8% HNO₃ in concentrated or inhibited form, has worked very well with most alloys. Alloys which were most difficult to etch were those containing significant amounts of refractory metals.
3. To date at our facilities, the only possible method for electron microscope studies has been to examine carbon replicas made from cellulose acetate stripping film replicas. Limited transmission work has been done on moderately irradiated specimens, but has not been possible with highly irradiated samples because of the inherent radiation problems.

PREPARATION OF SPECIMENS

Mounting

Because of high radioactivity specimens are placed in mechanical mounts or potted in epoxy containing filler material. Radiation damage to clear epoxy mounts is so great that the epoxy adjacent to the specimen deteriorates in a few days and will not hold the specimen. Metal or oxide filled epoxy survives longer, but is stable for only a few months. The bulk of our specimens were processed in metal mounts with the specimen held in place with set screws or by other mechanical means.

Grinding

Specimens were faced off or ground to a desired cross section on a wet belt sander using 120 or 180 grit belts. Subsequently grinding was done on orbital grinder-polishers through 240, 400, and 600 grit papers. Water was the lubricant in all stages of grinding and specimens were cleaned between steps in an ultrasonic cleaner.

Sample surfaces were etched 20 to 30 seconds between grinding steps to clean and remove any smeared metal that may have been deposited. The etchant was made up of 75% HCl and 25% HNO₃.

Polishing

Samples were polished on orbital grinder-polishers through 0.3 μ and 0.05 μ Al₂O₃ powder in distilled water. Fine weave nylon(1) or cotton(2) napless cloth was used with the 0.3 μ Al₂O₃ slurry. Final polish with the 0.05 μ Al₂O₃ slurry was carried out in two steps. The first step was with napless cotton cloth, and the second was a short final polish on a napped cloth(3). Care was taken not to overpolish in the final step as these alloys tended to exhibit relief when polished with napped cloth. Specimens were etched after each polishing step except the final one with the same etchant used between grinding stages. However, etching time was reduced to ten seconds.

Etching

Etching highly irradiated specimens usually posed the problem of determining an etchant which would produce desired results. Etched specimens were not only examined optically but had to be suitable for replication for electron microscopy. In nearly every case an etchant that was used for unirradiated controls would not produce a satisfactory etch on irradiated specimens.

When work with highly irradiated alloys first began, attempts were made to establish an etching procedure for each alloy based on the procedure used for the unirradiated controls. This approach was not very successful because irradiated specimens reacted to etchants differently than unirradiated specimens. The problem was finally overcome by treating irradiated specimens as unfamiliar materials and establishing new etching procedures. Information compiled by Lund and Wagner(4) was an invaluable reference while experiments with new etchants were in progress. When a successful etchant was devised for one alloy during the experimental period it was cross checked by testing it on other alloys. As testing progressed, one etchant was found that produced a good etch on nearly all the alloys that have been processed in the laboratory. This etchant also worked very well with the few irradiated cobalt base alloys we have seen.

The basic etchant used with most of our highly irradiated alloys was a solution of 92% HCl and 8% HNO₃. Inhibited variations of the etchant were made by adding either distilled water and glycerin. Best results were obtained

with specimens whose surfaces were clean and free of smeared metal. Also, the nitric acid used in the etchant was free of nitrous oxide to avoid staining. Specimens were etched by immersion for 10 to 30 seconds. Final determination of etching time and whether or not the etchant required inhibiting was done on a cut and try basis. Fortunately, it was found that groups of specimens of a single alloy type with the same irradiation history could be etched with the same etchant with minor variations in etching time, irregardless of differences in heat treatment, fabrication, and amount of cold work.

REPLICATION FOR ELECTRON MICROSCOPY

Replicas were made with .005 inch thick cellulose acetate stripping film⁽⁵⁾. The film was softened in acetone and applied to etched specimens. After the acetone evaporated, the replicas were stripped from the specimens. Usually three replicas were made of each specimen. The acetate replicas were transferred to another facility where the remainder of preparation for examination was done. From the acetate replicas, positive carbon replicas were made and shadowed in the conventional manner. The carbon replicas were then examined on the electron microscope.

Results

An example of work that has been done is shown in the illustrations. To date metallography and replication of highly irradiated specimens of the following alloys have been completed with good results. The specimens from each alloy represented a wide range of irradiation, fabrication, and heat treatment histories. The alloys were Hastelloy F, Hastelloy X, Hastelloy R-235, Hastelloy X-280, Inconel 600, Inconel 702, Inconel 718, Inconel 750, PDRL-102, and PDRL-120.

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OPTICAL PHOTOMICROGRAPHS

250X

FIGURE 1
Hastelloy X-280 Irradiated to
 1.2×10^{20} nvt

750X

FIGURE 2
Inconel 718 Irradiated to
 9.0×10^{19} nvt. The Specimen was
Overaged and Strained.

750X

FIGURE 3
Inconel 750 Irradiated to
 1×10^{20} nvt

750X

FIGURE 4
PDRL-120 Irradiated to 4.2×10^{20}
nvt. The Photomicrograph Shows
a Strained Area.

ELECTRON MICROGRAPHS

3000X

FIGURE 5
Inconel 718. Replica was made
from the Surface Shown in Fig. 2

10,000X

FIGURE 6
Fig. 5 is Shown at Higher
Magnification

3000X

FIGURE 7
Hastelloy X-280 Irradiated to
 1×10^{20} nvt

10,000X

FIGURE 8
PDRL-120 Irradiated to 1.4×10^{21}
nvt. Area Shown is near the
Fracture in a Tested Tensile Specimen.

SIMPLIFIED METALLOGRAPHIC TECHNIQUES
FOR
URANIUM ALLOYS AND OTHER METALS

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SIMPLIFIED METALLOGRAPHIC TECHNIQUES FOR URANIUM ALLOYS AND OTHER METALS

Ross J. Jackson, W. L. Johns, and Arthur E. Calabra

Abstract: A simplified metallographic preparation method has been developed and proves suitable for many uranium alloys, as well as for beryllium and stainless steel. Samples used in the study are taken from a cut-off wheel or 600-grit paper and placed in an electrolytic cell. Through the procedures developed, mounting and polishing steps have been eliminated and economies in operations achieved.

INTRODUCTION

Investigations were begun to develop simplified metallographic procedures suitable for uranium alloys, as well as for beryllium and stainless steel. Two procedures gave satisfactory results. In the first procedure, a standard (normal) electropolishing cell was used. In the second, use was made of an electrolyte-abrasive slurry on a rotating cathode.

Elimination of mounting and polishing steps was possible through the described procedures, and in addition economies in operations were realized.

DISCUSSION

Experimental: Two experimental procedures were developed. Procedure A involves a normal electropolishing cell and is used for uranium alloys, stainless steels, and beryllium. Procedure B employs an electrolyte-abrasive slurry on a rotating cathode and is used for beryllium.

PROCEDURE A — A standard electropolishing cell is used. The electrolyte is a proprietary phosphoric acid-base solution marketed as "Power-Kleen" which is used commercially to "brighten" metals. The supplier of this electrolyte is Molectrics, Inc., 459 N. Eucalyptus Avenue, Inglewood 3, California. The solution behaves similar to an orthophosphoric acid, sulfuric acid, and a water mixture with added metal cations. Data obtained from a spectrographic and chemical analysis of a similar solution are given in Table I. The polishing and etching conditions found to be optimum are listed in Table II.

PROCEDURE B — This method combines electrolytic and mechanical polishing techniques simultaneously and leads to rapid metal removal rates. A commercially available Struers DP-IV Electrolytic Lap-Polishing Unit is used. The electrolyte and other variables involved in this procedure are listed in Table III.

TABLE I. Spectrographic and Chemical Analysis of Electrolyte Used in Procedure A.

Spectrographic Analysis: Results are in percents.

Al — 0.005	Cu — 0.02
P — Major	Fe — 0.2
Be — <0.00025	Mn — 0.007
Ca — 0.001	Ni — 0.015
Cr — 0.015	Si — 0.003
	Mg — 0.001

Chemical Analysis:

pH	— <0.05
H ₃ PO ₄	— 10.30 Molar
Specific Gravity, 60/60°F	— 1.68
Cl ⁻	— Negative
NO ₃	— Negative
SO ₄ ⁼	— Positive (Probably about 3.6 M in H ₂ SO ₄)

RESULTS

Procedure A: Sequence photomicrographs illustrating the simplified metallographic procedure for a uranium alloy and a stainless steel are shown in Figures 1 and 2, respectively. The first three photographs in each sequence show the attainment of an etched surface starting from 600-grit scratches. The last two photographs illustrate the reversibility of the method.

Figure 3 is a current versus time plot for various voltages. The graph shows that about 90 seconds are required for stabilization of the current. Figure 4 is a current density versus voltage plot using a series circuit. The data for this curve were obtained after a stabilization period of 90 seconds. The curve shows a polishing plateau at 0.4 amperes per centimeter² (amps/cm²). The best etching characteristics were obtained below 0.1 amps/cm².

FIGURE 1. Sequence photomicrographs illustrating the simplified metallographic procedure for a gamma-quench uranium 15 at.% niobium alloy. (a) 600-grit scratches, (b) Electropolished 0.3 amps/cm² for 6 minutes, (c) Electroetched 0.1 amps/cm² for 4 minutes, (d) Repolished at 0.3 amps/cm² for 3 minutes, (e) Re-etched at 0.1 amps/cm² for 4 minutes. Bright-field illumination. Magnification 200X.

TABLE II. Optimum Polishing and Etching Conditions Using Procedure A. Solution Temperature Held Constant at 23°C.

Material	Polishing Current Density (amps/cm ²)	Polishing Time* (min)	Etching Current Density (amps/cm ²)	Etching Time (min)
Uranium Alloys: Gamma-quench U-Nb, U-Mo, U-RE, and U-Nb-Zr	0.4	6	0.10	4
Uranium	0.4	6	View polished surface with polarized light.	
Stainless Steel, 304	0.4	4	0.06	15
Beryllium	0.1 (≈ 15 volts)	5**	Etching accompanys polishing. Surface also responds to polarized light.	

* Polishing time starting from 600-grit scratches.

** Apply potential prior to immersing sample. The solution chemically attacks beryllium.

TABLE III. Parameters for Electrolytic-Lap Preparation of Beryllium (Procedure B).

Variable	Value
Electrolyte-Abrasive Slurry	2 volumes Nitric Acid 1 volume Hydrochloric Acid 147 volumes Ethylene Glycol 20 volumes 0.05-micron gamma-alumina
Cathode	Stainless steel covered with nylon cloth
Voltage	25 volts for 1 cm ² sample
Current	0.6 amps/cm ²
Time from 600-Grit Scratches	2 min

Figures 5 through 12 are photomicrographs of materials prepared with the proposed procedure. Figure 12 is an electron micrograph of a replicated surface prepared using the prescribed technique. Figure 13 is a transmission-electron micrograph of a uranium alloy thinned in the electrolyte.

The technique is also suitable for obtaining zero root-mean-square (rms) finishes on machined surfaces. Metal removal rates as high as 0.003 cm/min have been obtained at high current densities. At these high current densities however, it is difficult to cool the electrolyte. For beryllium, the solution acts as a chemical polish. Scratches are readily removed in this manner, but the resulting microsurface is heavily pitted. For this reason, it is necessary to apply the potential prior to immersing the beryllium sample in the electrolyte.

For gamma-quenched uranium alloys that have been subsequently aged at 400-600°C, the method is not applicable. In these instances, the sample is given a mechanical polish followed by an electrolytic etch in 10-percent oxalic acid in water at 10°C for 4 minutes at 2 volts.

Procedure B: Photomicrographs illustrating the use of Procedure B on commercially pure beryllium are shown in Figure 14. Figure 14(a) is the initial surface showing 600-grit scratches. Figure 14(b) is after 30 seconds of electrolytic-lap polishing and shows partial removal of scratches. Figure 14(c) is after 120 seconds and shows the same area in the scratch-free condition.

For both procedures using beryllium, the method is lacking in that inclusions are consumed. This is a deficiency that is common to most electrolytic procedures involving beryllium.

Both methods however yield induced-deformation-free surfaces in which many microstructural features are resolved. When inclusion retention and an induced-deformation-free surface are required, it is best to use the following method. Grinding on 240, 320, 400 and 600-grit papers followed by polishing on 6 microns, 3 microns, and 1 micron diamond paste.

Intermediate to each of the above steps is a 15-second dip in a 10 percent H₂SO₄ in water solution to remove deformed metal. The sample is then placed for 24 hours on a vibratory polisher using 0.05-micron gamma-alumina suspended in water to which has been added 20 ml of 10 percent CrO₃ in water. This is followed by a 5-second swab with a 2 percent HF solution in ethyl alcohol. The sample is then viewed under polarized illumination.

CONCLUSIONS

Both of the proposed simplified metallographic procedures, A and B, have proven to be useful and versatile in that various metals and alloys have been successfully prepared.

The processes yield reproducible results. There are also economies in elimination of the mounting and mechanical polishing steps.

FIGURE 2. Sequence photomicrographs illustrating the simplified metallographic procedure for Type-304 stainless steel. (a) 600-grit scratches, (b) Electropolished at 0.4 amps/cm² for 4 minutes, (c) Electroetched at 0.06 amps/cm² for 15 minutes, (d) Repolished at 0.4 amps/cm² for 2 minutes, (e) Re-etched at 0.06 amps/cm² for 10 minutes. Bright-field illumination. Magnification 200X.

FIGURE 3. Current versus time plots for various voltages for the orthophosphoric base solution. Type-304 stainless steel sample. Sample size 1.0 cm². Stainless steel cathode. Anode to cathode distance 1.0 inch.

FIGURE 4. Current density versus voltage plot for the orthophosphoric base solution in a series circuit cell. Type-304 stainless steel sample. Sample size 1.0 cm². Stainless steel cathode. Anode to cathode distance 1.0 inch. Solution temperature 21°C. Reading taken after a 90-second hold. Region B-C represents the polishing plateau.

FIGURE 5. Beryllium, as-cast. Prepared under Procedure A. Bright-field illumination. Magnification 150X.

FIGURE 6. Beryllium, as-cast. Prepared under Procedure A. Polarized illumination. Magnification 200X.

FIGURE 7. Uranium 15 at/% niobium alloy. Sample held 2 days at 1100°C and water quenched. Banded α'' structure. Magnification 50X.

FIGURE 8. Uranium 15 at/% niobium alloy. Sample held 5 days at 1100°C and water quenched. Banded α'' structure. Magnification 500X.

FIGURE 9. Uranium 19 at.% niobium alloy. Sample held 20 hours at 900°C and cooled at 1000°C/second. Banded, single-phase structure. Magnification 100X.

FIGURE 10. Same sample and surface conditions as in preceding photograph under polarized illumination. Magnification 100X.

FIGURE 11. Uranium 15 at.% niobium alloy. Sample held 24 hours at 850°C and cooled at 10°C/second. Subgrain boundaries and etch pits in banded, single-phase structure. Magnification 200X.

FIGURE 12. Replica electron micrograph of preceding sample. Etch pits and subgrain boundary in banded structure. Chromium-shadowed carbon replica, Magnification 4000X.

FIGURE 13. Transmission electron micrograph of a uranium 15 at.% niobium alloy thinned in the electrolyte used in Procedure A. Sample held 24 hours at 850°C and cooled at 1060°C/second. Banded, single-phase α'' structure. Magnification 28,000X.

FIGURE 14. Sequence photomicrographs showing the preparation of beryllium using Procedure B. (a) Starting surface showing 600-grit scratches, (b) Shows partial removal of scratches at 30 seconds of electrolytic-lap polishing, (c) Shows scratch-free surface after 120 seconds of electrolytic-lap polishing. Polarized illumination. Magnification 100X.

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X METALLOGRAPHY OF HYPO-, HYPER-, AND STOICHIOMETRIC
SINTERED $(U,Pu)C_x$ *

By

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ABSTRACT

Procedures for the metallographic preparation of hypo-, hyper-, and stoichiometric sintered $(U_{0.8}Pu_{0.2})C_x$ samples are described. These include cutting, mounting, grinding, and polishing techniques as well as chemical and electrolytic etching for optical and electron microscopy.

INTRODUCTION

$(U_{0.8}Pu_{0.2})C_x$ fuel pellets prepared by sintering often vary in composition from the intended stoichiometry as determined by metallographic examination. Identification of the metallic, dicarbide, and sesquicarbide phases by a standard etching technique suitable for optical and electron microscopy was the purpose of this study. These $(U,Pu)C_x$ pellets are proposed for use as fuel in the LMFBR program (Liquid Metal Fast Breeder Reactor) in conjunction with compatibility studies of sodium-bonding the fuel to the container.

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

EXPERIMENTAL PROCEDURE

Specimen Preparation

The (U,Pu)C_x fuel pellets (nominally 0.265 in. diam x 0.300 in. high) are sectioned with a diamond cut-off wheel using silicone oil (Dow Corning #200) as the lubricant. The sectioned samples are then vacuum-impregnation mounted in Shell Epon 815 resin. A layer of MgO pellets is added to the mount face to compensate for the hardness variation between the sample and the relatively soft epoxy resin.

The mounted samples are metallographically prepared in gloveboxes under a reduced pressure of washed atmosphere (40% humidity). This moisture will rapidly oxidize unprotected (U,Pu)C_x specimens. To prevent this reaction, all samples in process are transported and stored for short periods under silicone oil. For long duration storage, the samples are placed in a desiccator back-filled with helium several times and evacuated to 15 in. Hg.

Grinding of the mounted specimens through 180, 240, 320, and 600 grit SiC papers with lapping oil as the lubricant and 10 lb pressure on an Automet attachment prepares the samples for transfer to the polishing box (Fig. 1). The ground mounts are rough polished with 15-μ diamond paste on Texmet for 10 min followed by 45 min with 6-μ diamond paste and 20 min with 1-μ diamond paste on Texmet. The 6-μ and 1-μ polishing steps use an automatic polishing attachment (Whirlimet). The lubricant for all polishing steps was silicone oil and the samples are cleaned ultrasonically between steps with Vythene. Samples are final polished for 30 min with 0.05-μ Al₂O₃ in silicone oil on Microcloth using a Vibromet polisher (Fig. 2).

Immediately after etching, the (U,Pu)C_x samples are examined and photographed with a Reichart-MeF metallograph equipped with a glass contamination barrier and 0.005 in. air gap to the specimen above the standard microscope stage shown in Fig. 3.

Etching Techniques

The (U,Pu)C_x samples were etched chemically by immersion in and swabbing with a 1:1:1 solution of nitric and acetic acids and water, and electrolytically by a Disa Electropol Mark 5 etcher with a 1:1:1 lactic-nitric-acetic acid electrolyte and a chromic-acetic acid electrolyte.

Electron Microscopy Preparation

"Cold" replicas of the (U,Pu)C_x specimens were prepared by first replicating with Faxfilm to remove loose contaminated particles. The Faxfilm

replica was discarded (alpha count 25,000/min) and the sample immediately coated with Parlodion. The microscope screen grids were embedded in the replicating solution and, after curing, the replica was stripped in the usual manner. The Parlodion replica alpha count averaged 10,000/min, but after washing in an aqueous solution of 25% HCl, 10% H₂SO₄, and 5% HF for 1-1/2 h the alpha count was down to 1,000/min. Pt-C shadowing and C replication resulted in the final C replica having an alpha count of 200/min.

RESULTS

Chemical etching times varied with the sample composition. Prolonged chemical etching of stoichiometric specimens never defined grain boundaries suitably for photomicrography. The chromic-acetic acid electrolytic etch attacked all compositions, but the micrographs exhibited lack of contrast between precipitates and matrix. The lactic-nitric-acetic acid electrolyte, at a potential of 2.5 V dc for 10 sec (touch-probe), etched all the (U,Pu)C_x compositions evenly and gave good contrast in optical micrographs.

Electron microscopy by replication of stain-etched specimens is not feasible because of the retained oxide film on the sample surface. However, it was found that, if the sample is swabbed while it is immersed in the lactic-nitric-acetic acid electrolyte at a zero potential, most of the oxide film is removed and thus replication of the true sample surface is possible.

In Fig. 4, stoichiometric (U,Pu)C, lactic-nitric-acetic acid electrolytic etch, is a highly porous sintered body with no precipitates evident and a 1:1 ratio of rounded to angular shaped grains.

In Fig. 5, hyperstoichiometric (U,Pu)C, chemically etched, exhibits heavy sesquicarbide precipitation and slight indications of the dicarbide needle phase. Grain shape is predominantly angular.

In Fig. 6 a lactic-nitric-acetic acid electrolytic etch of the sample in Fig. 5 reveals more of the dicarbide phase than previously shown.

In Fig. 7, hypostoichiometric (U,Pu)C, lactic-nitric-acetic acid electrolytically etched, shows the free metal phase in grain boundaries, within grains, and in the pores of the sintered body. Grain shape is predominantly rounded rather than angular. Figure 8 exhibits the microstructure of the sample shown in Fig. 7 after swabbing with the electrolyte.

Figures 9 through 12 are electronmicrographs of replicas from the oxide-free sample surface. In Fig. 9 a hypostoichiometric sample shows the free metal phase in a grain boundary junction. Figure 10, also hypostoichiometric, is typical of the metallic precipitate along a grain boundary.

Figure 11, a hyperstoichiometric sample, exhibits the angular M_2C_3 precipitate, and Fig. 12 shows M_2C_3 precipitating from an MC_2 needle.

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Note: Automet, Whirlimet, Texmet, Microcloth, and Vibromet are products of A. I. Buehler, Ltd.

Fig. 1. Polishing Box with Two Whirlimets and Two Manual Rotary Polishers.

Fig. 2. Vibratory Polishing Box.

Fig. 3. Metallograph Attached to Glovebox Train.

Fig. 4. Stoichiometric $(U,Pu)C$. Matrix = MC.
Electro-etched, 300X.

Fig. 5. Hyperstoichiometric (U,Pu)C. Matrix = MC,
 White Phase = M_2C_3 , Needle Phase = MC_2 .
 Chemical Etch, 300X.

Fig. 6. Hyperstoichiometric (U,Pu)C. Matrix = MC,
 White Phase = M_2C_3 , Needle Phase = MC_2 .

Fig. 7. Hypostoichiometric (U,Pu)C. Matrix = MC,
White Phase = M. Electro-etched, 300X.

Fig. 8. Hypostoichiometric (U,Pu)C. Matrix = MC,
White Phase = M. Electro-etched and Swabbed,
300 X.

Fig. 9. Hypostoichiometric (U,Pu)C. Electronmicrograph, 7500X.

Fig. 10. Hypostoichiometric (U,Pu)C. Electronmicrograph, 10,000X.

Fig. 11. Hyperstoichiometric (U,Pu)C. Electron-micrograph, 7500X.

Fig. 12. Hyperstoichiometric (U,Pu)C. Electron-micrograph, 10,000X.

(P-111)

X METALLOGRAPHIC PREPARATION OF PLUTONIUM-URANIUM NITRIDES
AND CARBONITRIDES AND OF COATED PLUTONIUM OXIDE PARTICLES

(7-11-57) by _____

R. H. Snider and R. R. Stelz

This paper describes the metallographic preparation of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ and $(\text{Pu},\text{U})\text{CN}$ and also a metallographic technique for mounting pyrolytic carbon coated PuO_2 fuel particles. The metallographic preparation discussed includes mounting, grinding, polishing, and etching. Photomicrographs are presented showing the results of the metallographic preparation.

INTRODUCTION

During the past several years Battelle-Columbus has been participating in fast breeder and coated particle fuels research programs for the Atomic Energy Commission. Recently, considerable effort has been directed toward the development of refractory fuels for high temperature reactor applications. Thus, efforts are being devoted to the development of fuels with high thermal conductivity, high resistance to deformation at elevated temperatures and good irradiation stability. The two fuels that most nearly meet these requirements are the oxides and the nitrides. Two studies of particular interest are those designated to evaluate the potential of mixed uranium-plutonium nitride fuels for application as fast breeder material and to achieve the development of mixed nitrides, mixed carbonitrides $(\text{U},\text{Pu})\text{CN}$ and ceramic-coated plutonium oxide (PuO_2) .

It is the purpose of this paper to describe the metallographic practices and/or techniques that have evolved from examining the above fuels and, secondly, for insuring retention of pyrolytic coatings and fuels in their proper perspective during preparation and examination. Except for the fact that each fuel may ultimately be employed for high temperature applications, they possess few, if any, properties in common. This is especially true in the case of the metallographic techniques required to evaluate these systems and therefore each will be discussed separately in the text that follows.

Because of the extremely toxic nature of plutonium, all metallographic operations were conducted in a glove box with a nitrogen atmosphere and under slight negative pressure. The utilization of a nitrogen atmosphere permitted extensive examination of the fuel specimens without incurring oxidation of their surfaces.

Materials

Since techniques employed in the preparation and fabrication of materials will have a significant effect upon their metallographic structures, it seems appropriate to outline the techniques employed to obtain the specimens for examination. The process utilized to obtain $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ specimens as well as the disposition of the metallographic samples from the process is shown in Figure 1, while Figure 2 shows the origin of PuO_2 core materials used in the coating process and the disposition of metallographic specimens examined of these materials. In addition, Figure 2 shows Battelle's process for fabricating PuO_2 particle material. The development of $(\text{Pu},\text{U})\text{CN}$ fuel specimens and their disposition are shown in Figure 3.

Metallographic Preparation of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$

The metallographic preparation of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ specimens for purposes of determining their essential microstructural features was comprised of mounting, grinding, polishing, and chemically etching. Most of the materials prepared and examined, including all the pellet-type specimens and all the property measurement-type specimens, were composed of single phase $(\text{Pu},\text{U})\text{N}$ with trace amounts of U_2N_3 and oxide phases. With the exception of the mounting procedure, the preparation of these materials for metallographic examination was principally the same. Compatibility specimens whose components include such cladding materials as niobium, stainless steel, and Inconel as well as $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ were metallographically prepared using the methods needed of these materials. The fuel material associated with the clad was prepared, metallographically in similar manner to that of the pellet-type specimens. None of the $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ specimens needed sectioning for purposes of mounting. However, prior to metallography, property-measurement type specimens were sectioned and shaped to form pellet-type specimens by a machine lathe. Carbon tetrachloride was used as a coolant in this operation. Good results were obtained with this procedure, though some breaking and chipping occurred due to the brittleness of these materials.

A detailed discussion of the metallographic preparation of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ specimens is described below.

Mounting and Grinding

All $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ specimens required mounting and grinding to prepare flat surfaces for polishing and metallographic examination. Pellets of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ were mounted in molds consisting of 1/4-in. O.D. lucite rings backed by adhesive metal tape. "Epon Resin 815" applied under vacuum was used as the mounting media. Curing of mounts was done overnight in a box atmosphere to allow the resin to harden. After curing the mount, surfaces were flattened by filing. Specimen mounts were ground by passing them over 240, 400 and 600 grit silicon carbide papers in successive steps. Carbon tetrachloride was used as a lubricant during all grinding steps.

FABRICATION OF $(\text{Pu}_{0.2}\text{U}_{0.8})$ MATERIALS AND THEIR INVESTIGATION

FIGURE 1. THE PROCESS UTILIZED TO OBTAIN $(\text{Pu}_{0.2}\text{-U}_{0.8})\text{N}$ SPECIMENS

DEVELOPMENT OF COATED PuO_2 PARTICLE FUEL

FIGURE 2. PuO_2 PARTICLE MATERIALS PREPARED AND EXAMINED METALLOGRAPHICALLY.

PREPARATION OF (U,Pu)CN AND STUDIES

FIGURE 3. THE PROCESS UTILIZED TO OBTAIN (Pu,U)CN MATERIALS

Large specimens of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ were mounted in 2-inch diameter lucite molds employing "Quick Mount" as the mounting media. These mounts were then cured under a nitrogen pressure of 6 to 12 psig to suppress the formation of bubbles during the curing process. (Epon Resin which had been previously employed was not used for these specimens because of its inherent tendency to impregnate the specimens and make them undesirable for further studies). The Quick Mount resin mounts were then ground through 600 grit silicon carbide paper with particular care being taken to remove only sufficient material to yield a surface suitable for polishing. The need to remove a minimum of material was dictated by the fact that the size of the samples required for later studies very nearly approximated the size of the as-received material.

Polishing

Since it was desired to ascertain the surface density and density distribution in the specimens and also to identify the phases present, it was required that a polishing technique be employed that would result in the minimum amount of pull-out and yield a surface suitable for etching. The general polishing procedure employed to obtain the desired results consisted of three steps as follows:

- (1) Initial Polish: Specimens were rough polished to remove grinding scratches on a fast wheel covered with nylon cloth and a slurry of 2 percent chromium trioxide in water with "Linde A".

- (2) Intermediate Polish: Specimens were polished on fast wheel covered with nylon cloth and a slurry of 2 percent chromium trioxide and water with "Linde B".
- (3) Final Polish: Specimens were polished to remove finer scratches on a slow wheel covered with Gamal cloth and a slurry of 2 percent chromium trioxide and water with ferric oxide.

Figures 4, shows in part, typical results obtained in polishing of specimens.

When handling compatibility specimens, two separate preparations were required in the polishing of these materials. In this instance, the cladding materials were prepared by conventional methods and the fuel materials were prepared by the method described above.

Etching

Polished specimens of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ were chemically etched to reveal their grain structure and impurity content by several swabbing techniques utilizing a solution of 50 parts lactic acid, 40 parts nitric acid and 4 parts hydrofluoric acid. These etching techniques imparted a stain to the $(\text{Pu},\text{U})\text{N}$ phase by preferentially oxidizing its grains. The two techniques which were most successful for grain definition and minor phase definition are described as follows:

One technique consisted of applying a hard swab etch to the polished surface of the material until a thin oxide layer appeared. At this point swabbing was abruptly stopped and the specimen's surface was rinsed with water and dried. In a period of 3 to 5 minutes after etching fair grain definition and good U_2N_3 and oxide phase definition appeared on the etched surface. In a period of 10 minutes after etching, there appeared to be better grain definition and little or no loss in definition of U_2N_3 and oxide phases.

A second technique consisted of applying a moderate pressure swab etch to the materials surface until a thick oxide coating became apparent. The material was then swabbed hard to remove this oxide cover and to form a new thin oxide coating. At this point swabbing was abruptly stopped and the specimen's etched surface was immediately washed and dried. This method gave similar results to the first method, however, grain definition appeared to be somewhat better at initial inspection than was obtained with the first method.

Careful etching was definitely required of these materials because over etching tended to mask the U_2N_3 and oxide phases.

Examples showing etched surfaces of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ is given in Figures 4 and 5. Figure 5, in particular, shows the delineation of the minor phase components with the increase in magnification as well as the delineation of grain structure of the $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ phase.

125X PL2589
As Polished

250X PL2597
As Polished

125X PL2588
Etched

125X PL2995
Etched

FIGURE 4. PHOTOMICROGRAPHS OF $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ PREPARED BY TECHNIQUES DESCRIBED IN THIS PAPER

Note porosity and impurities in as-polished materials and the grain structure in the etched materials.

125X

PL3000

250X

PL3001

500X

PL3002

FIGURE 5. PHOTOMICROGRAPHS OF $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ SHOWING THE DELINEATION OF GRAIN BOUNDARIES AND MINOR PHASE COMPONENTS WITH INCREASE IN MAGNIFICATION.

As in polishing, compatibility specimens required separate preparation of the component parts in their etching preparation. Cladding materials were etched by conventional methods. The fuel component was etched by either one of the techniques described above. Figure 6 shows results of etching of a nitride specimen associated with a clad material of Inconel.

500X

PL3166

Etched for Nitride

FIGURE 6. PHOTOMICROGRAPH OF A NITRIDE-INCONEL COMPATIBILITY SPECIMEN AS PREPARED BY TECHNIQUES DESCRIBED IN TEXT.

METALLOGRAPHIC PREPARATION OF (Pu,U)CN

Metallographic examinations of (Pu,U)CN were made to determine the microstructural features as related to the stoichiometry and carbon-nitrogen content of this material. The metallographic preparation required in these studies included mounting, grinding, polishing, and etching of different specimens arc melted under various nitrogen pressures and with different carbon contents. Details of the metallographic procedures which were used in handling these materials are discussed below.

Mounting and Grinding

The mounting technique employed for (Pu,U)CN specimens was essentially the same as that used for (Pu,U)N as discussed previously in this report. Grinding of specimens was done on silicon carbide paper through 600 grit. Carbon tetrachloride was employed as a lubricant.

Polishing

Polishing of (Pu,U)CN was accomplished by the following steps:

- (1) Initial polish to remove grinding scratches was made on a slow wheel covered with silk with a 6-micron diamond grit. Carbon tetrachloride was used as a lubricant.
- (2) Intermediate polish was performed on a slow wheel covered with lintless cloth. A 1-micron diamond paste was employed as an abrasive and carbon tetrachloride was applied as a lubricant.
- (3) Final polish was accomplished on a slow wheel covered with lintless cloth. A 1/2-micron diamond paste was used for an abrasive and kerosene was applied as a lubricant.

Excellent polished surfaces were obtained using the above technique.

Etching

To reveal the structure and phase composition of (Pu,U)CN specimens an electro-chemical etch was used consisting of 80 ml of ethyl alcohol (200 proof), 20 ml of nitric acid and 3 drops of hydrofluoric acid. A potential of 20-30 V.D.C. was applied to give an etch to these materials. After etching it was necessary to swab the surface with an ethyl alcohol rinse to remove the oxide coating. Figure 7 shows representative surfaces of (Pu,U)CN obtained using this etching technique.

FIGURE 7. PHOTOMICROGRAPH OF ETCHED (Pu,U)CN AS PREPARED BY METHODS DESCRIBED IN TEXT.

The metallographic preparation of coated PuO₂ particle fuels consisted of mounting, grinding, and polishing to determine the quality and thickness of pyrolytic coatings as well as to denote the relative density and character of PuO₂ core material. In order to determine with some degree of accuracy the wall-thickness of coated PuO₂ particles, a method was devised for mounting these materials so as to give preferred orientation of the particles in the mount. When followed by controlled grinding and polishing, this mounting practice allowed all or nearly all of the particles to show at the surface of the mount touching one another at or near their maximum diameters as required for measuring. This practice, of course, was only used in closely sized particle material. Details of the metallographic technique utilized in mounting coated PuO₂ particle materials as well as the methods employed in grinding and polishing are described in sequence below:

Mounting

The principle method utilized in mounting coated PuO₂ particles was comprised of a technique to give preferred orientation of the particle in the mount. In this method molds were made so as to confine the particle materials to a restricted surface area in the mounts. These molds consisted of a 1-1/4-inch diameter Lucite ring backed by a plastic flashlight lens and sealed with Duco Du Pont cement. A 1/4-inch I.D. steel washer was attached to the floor of each mold with Duco cement to contain the particle material. Particles were then funneled into the washer opening to form a single compact layer. Light tapping on the sides of the mold kept the particles from piling on top of each other. Each mold was filled with "Epon Resin 815" being careful to cover the particle material sufficiently without disturbing the particle bed. The molds were placed under vacuum for five minutes and then allowed to cure overnight in a box atmosphere. After hardening of the resin the lens was removed from the mount leaving an extremely flat surface of the specimen mount which required only the minimum amount of coarse grinding.

Grinding

The grinding procedure employed for coated PuO₂ material consisted of hand grinding on Handimet Grinder using 240, 400, and 600 grit silicon carbide papers. Grinding was discontinued when the particles approached their maximum diameters at the surface of the mounts. Carbon tetrachloride was used as a lubricant in these steps.

Polishing

Two methods were utilized with about equal success in the polishing of PuO_2 coated particle fuels for purposes of determining their coating thicknesses and evaluating the quality of the PuO_2 core materials. The initial method employed consisted of using diamond abrasive throughout all stages of polishing. A method employed later consisted of applying a coarse diamond abrasive in the first stage of polishing and using alumina abrasives during the later stages. Details of these two procedures are given below:

<u>Diamond Abrasive Polish Method</u>	<u>Alumina Abrasive Polish Method</u>
Stage 1. Specimens were polished to remove grinding scratches on a slow wheel covered with double silk cloth and six-micron diamond paste. Carbon tetrachloride was used as a lubricant.	Specimens were coarsely polished using the same method applied in Stage 1 of "The Diamond Abrasive Polish".
Stage 2. Specimens were polished on slow wheel covered with lintless cloth with 1-micron diamond paste used as an abrasive and carbon tetrachloride as a lubricant.	Specimens were polished in fast wheel covered with nylon and a slurry of 2 percent chromium trioxide in water with "Linde A".
Stage 3. Specimens were final polished on a slow wheel covered with lintless cloth with 1/2-micron diamond paste employed as an abrasive and kerosene as a lubricant.	Specimens were final polished in a fast wheel covered with nylon and a slurry of 2 percent chromium trioxide in water with "Linde B".

Photomicrographs in Figure 8 show polished areas of materials prepared by each of these methods as well as illustrate the results obtained by use of the mounting technique employed in the metallographic preparation.

Inasmuch as the PuO_2 core material was not responsive to chemical attack, structure details of these materials were not obtained. However, it is believed that these materials may be single phase and either single grains or extremely fine grained.

SUMMARY

Specimens of $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ were successfully prepared for purposes of determining their phase contents and densities. The procedure used in preparing these specimens consisted of mounting, grinding, polishing, and etching. Two

125X

PL2073

Diamond Abrasive
Polish Method

125X

PL3168

Aluminum Abrasive
Polish Method

125X

PL3090

Aluminum Abrasive
Polish Method

FIGURE 8. PHOTOMICROGRAPHS OF COATED PuO_2 PARTICLE MATERIALS PREPARED UNDER THE TECHNIQUES DESCRIBED IN TEXT.

swab etching techniques, which were utilized in this procedure, are described in this paper. Specimens of (Pu,U)CN were prepared by mounting, grinding, polishing, and etching to determine their microstructural features as related to the stoichiometry and carbon-nitrogen content. A method for electro-chemical etching of (Pu,U)CN is described. Coated PuO₂ particle materials were successfully prepared by mounting, grinding, and polishing to ascertain the thickness and quality of their coatings as well as to denote the relative density and character of the PuO₂ core material. A special technique employed to give preferred orientation of the particles in mount for purposes of determining the coating thicknesses of PuO₂ materials is described in the paper.

P-2

21:30980

X ^C METALLOGRAPHY OF PYROLYTIC CARBON- ^W AND/OR TUNGSTEN-COATED
^{UO} URANIUM OXIDE AND URANIUM CARBIDE ^{UC} FUEL SPHERES*
By

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ABSTRACT

Procedures for the metallographic preparation of pyrolytic carbon-and/or tungsten-coated uranium oxide and carbide fuel spheres are described. These include mounting, grinding, polishing, and etching techniques for optical and electron microscopy.

INTRODUCTION

The fuel microspheres described in this report are under investigation as experimental fuels in the HTGCR program (High Temperature Gas Cooled Reactor). The coating thickness and coherence, evidence of penetration of the coating by the fuel, and the formation of secondary reaction layers are determined by metallography.

Metallographic examination of individual coated fuel microspheres in some cases required mounting jigs because the pyrolytic-coated spheres floated in all the liquid resins tested. Spheres coated with tungsten did not present this problem and could be mounted in the same manner as normal metallographic specimens.

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

EXPERIMENTAL PROCEDURE

Specimen Preparation of PyC-Coated Spheres

The PyC-coated fuel spheres are first graded to size with the aid of a bench microscope. A brass mount (1 in. diam x 3/4 in. tall) is machined with a spiral groove in the center area, the groove being slightly wider and deeper than the fuel sphere diameter. The spheres are placed in the groove and covered with a low-viscosity resin (Shell Epon 815 with diethylamine catalyst). The complete mount is then vacuum treated and cured at 75°C for 16 h. This process is shown in Fig. 1.

The cured mounts are carefully wet-ground (1:1 alcohol-water) on 600-grit SiC paper to the center of the fuel spheres (average diameter known, and with frequent microscopic observation until the sphere center is reached). Sample rough polishing is accomplished with 6- μ diamond paste on Texmet for 30-45 min and 1- μ diamond paste on Texmet for 15 min. The 6- μ and 1- μ polishing steps use Metadi fluid with a Whirlimet attachment. Final polishing is done with 0.1- μ Al_2O_3 on nylon with 1:1 alcohol-water lubricant for 30 min on a Syntron vibratory polisher.

Specimen Preparation of W-Coated Fuel Spheres

The spheres are optically graded to size and vacuum-impregnation mounted in Shell Epon 815, T1 catalyst resin. After curing, the W-coated samples are ground and polished in exactly the same manner as the PyC-coated samples described previously.

Preparation for Electron Microscopy

The fuel sphere samples are lightly repolished to remove the stain etch. A cleaning replica of Faxfilm is then applied, stripped when dry, and discarded. A replica of Parlodion is then cast with the screen grids embedded, shadowed with Pt-C and final replicated with C.

RESULTS

Figures 2 through 5 are photomicrographs (500X magnification) of W-coated UO_2 microspheres, immersion etched with aqueous 15% H_2SO_4 , 20% H_2O_2 (30% strength) in 10 sec increments. Figure 2 shows a well-bonded 2- μ coating on a 156- μ diam UO_2 sphere. Figure 3 shows a 4- μ W coat on a 300- μ diam UO_2 sphere. In Fig. 4, an elliptical sphere is shown with a break in the W coating and penetration of the coating with UO_2 . Figure 5 shows the variation in UO_2 grain size.

Figures 6 through 9 are photomicrographs of PyC- and W-coated UC_2 spheres, immersion etched in 10 sec increments with 1:1:1 HNO_3 , HAc, and H_2O . Each specimen was photographed at 100X and 300X magnification. Figure 6 (100X) shows a sphere with a total diam of 800- μ , a 30- μ PyC coating and a cracked W coating of varying thickness (5 to 15 μ). Figure 7 (300X of the same sphere) shows indications of a secondary reaction layer between the PyC and W coats. Figure 8 is a partial view at 100X of a "twin" sphere. The PyC coating varies in thickness from 20 to 100 μ , and the cracked W coating (10 to 50 μ thick) intermittently shows evidence of a secondary reaction layer. Figure 9 (300X) shows the secondary reaction layer (a tungsten carbide) in the "necked-down" area of the "twin" spheres. Figure 10 is an electronmicrograph of the W and PyC coating exhibiting the secondary reaction layer.

ACKNOWLEDGEMENTS

The author wishes to thank R. H. Perkins for his interest and encouragement in this work and L. R. Bergamo for his assistance in the metallographic preparation.

Note: Texmet, Metadi, and Whirlimet are products of A. I. Buehler, Ltd.

Fig. 1. Specimen Preparation for PyC-Coated Spheres.

Fig. 2. W-coated UO_2 . Etched, 500X.

Fig. 3. W-coated UO_2 . Etched, 500X.

Fig. 4. W-coated UO_2 . Etched, 500X.

Fig. 5. W-coated UO_2 . Etched, 500X.

Fig. 6. PyC- and W-coated UC_2 . Etched, 100X.

Fig. 7. PyC- and W-coated UC_2 . Etched, 300X.

Fig. 8. PyC- and W-coated UC_2 . Etched, 100X.
Intermittent reaction layer.

Fig. 9. PyC- and W-coated UC_2 . Etched, 300X.
Reaction Layer.

Fig. 10. PyC- and W-coated UC_2 . Electronmicrograph, 7500X.

21: 39287

P-4

X OPERATION OF A LEITZ MM5 METALLOGRAPH

by

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April 24, 1967

The work reported herein was performed for the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1156.

ABSTRACT

A Leitz MM5 metallograph is in use for uranium metallography at the National Lead Company of Ohio. This paper describes the instrument and discusses its advantages and disadvantages.

INTRODUCTION

At the previous meeting of this organization, interest was expressed in our use of a Leitz MM5 metallographic microscope. This paper has therefore been prepared to describe the instrument and discuss its advantages and disadvantages in our work.

The Leitz MM5 (Figure 1) is being used both to monitor uranium production and to extend our metallographic development efforts. Three features of the MM5 make it an ideal production tool.

These are:

1. A wide-field optical system (plano objectives coupled with wide-field eyepieces).
2. A large viewing screen.
3. A xenon light source.

The wide-field optics, when compared with conventionally designed objectives and eyepieces, expand the field of view by a factor of 4. The large ground glass projection screen (13-1/2 inches in diameter) permits the metallographer to observe specimens without eye fatigue. It also permits several persons to view a specimen simultaneously. The optics involved with the projection screen

double the area of view obtainable with any other metallograph. The xenon light source² produces stable high-intensity illumination. The color balance of the xenon lamp very closely approaches that of a mixture of sunlight and skylight.

As a research and development tool, the metallograph with its individual illuminators for bright and dark field, polarization, and phase contrast optimizes the resolution and clarity obtainable at all magnifications. See Figure 2.

The Leitz MM5 metallograph thus serves well both as a production tool and as a research and development instrument.

Mechanics of the Leitz MM5

The Leitz MM5 incorporates a series of optical and technical features not usually found on other metallographs. (Some of these advances, however, have now been incorporated on the Bausch and Lomb Research II metallograph.) Figure 3 is a schematic of the light beam path found in the Leitz².

A unique feature of the Leitz is the use of plano objectives coupled with wide-field eyepieces. This combination results in an extra large field of view which is nearly distortion free from edge to edge. The usable focused image area, therefore, is much larger than on conventional microscopes.

Two light sources are standard equipment on the instrument: (1) a 12-volt, 60-watt source which is sufficiently bright for all

ordinary bright-field visual and general photographic work and (2) a xenon high-pressure lamp which is used as the high-intensity light source. The xenon lamp has the following advantages over the carbon lamp: (1) once it is adjusted it needs no further attention and (2) the source produces a continuous spectrum throughout the visible light range (color temperature, 6260° Kelvin)². The intrinsic intensity is greater than that of the carbon arc and is also independent of electric supply voltage fluctuations².

A convenient push-button system permits filtering the high-intensity light source. This system greatly simplifies brightness control when changing from visual observation to projection on the ground glass screen or to the camera.

Four different vertical illuminators are used on the Leitz MM5 (Figure 4). They are used for:

1. Low power magnifications.
2. Bright and dark field observation.
3. General survey in polarized light and oblique illumination (can also be used for bright field).
4. Phase contrast and limited bright field.

The low power illuminator has a built-in 1X objective. When an 8X eyepiece is used, the total magnification is 8X times the bellows extension or tube factor. The low power illuminator has no apertures to control the field area or light intensity. Light intensity

control must be accomplished by using the neutral density filters in the lamp housing. Figure 5 is a photomicrograph taken by use of the low power system.

The bright field - dark field illuminator is equipped with a circular light stop and field-of-view diaphragm. The former is swung into the light path when changing from bright to dark field. Figure 6 is a typical photomicrograph taken with bright field optics. Figure 7 is a typical dark-field micrograph using the same illuminator.

The vertical illuminator for polarized light and oblique illumination is equipped with a field-of-view diaphragm and an eccentric aperture for oblique illumination. The polarization equipment consists of a prism serving as the polarizer while foils are used for the analyzer. In our experience, polarization obtained with the Leitz (when working with uranium, a low birefringent material) is not as good as that obtained with the Bausch and Lomb Research metallograph, which uses a calcite crystal as a polarizer. As shown in Figure 8, the grain structure micrograph taken on the Bausch and Lomb Research shows more contrast and brilliance than the one taken with the Leitz. This is attributed to the greater efficiency of the calcite prism system³.

Figure 9 illustrates the use of phase contrast to accentuate the differences in height of particles after electropolishing. The vertical illuminator designed for phase contrast can also be used

for general bright-field work by introducing a diffusion screen into the system.

The amount of color metallography being done at this site has increased several fold because of the ease of operation with the xenon light source. The problem of stabilizing a carbon arc or of obtaining high-intensity illumination from filament lamps has been eliminated. The xenon lamp operates at a color temperature of 6260° Kelvin with a nearly continuous spectrum throughout the visible light range. The color temperature can be converted to ~3200° Kelvin so that artificial-light color film can be used. The ultraviolet content of the xenon light source is high and must be removed by filtering. Figure 10 is a black-and-white reproduction of a color micrograph taken with the Leitz MM5.

Discussion

The Leitz MM5 Microscope has proven to be a very good general tool for both development and production work at the National Lead Company of Ohio with only one serious shortcoming. In the metallography of uranium and its grain structure, the use of polarized light is very important, and, as was mentioned earlier, the Leitz MM5 is somewhat disappointing in this respect. A less serious criticism is that the monorail camera support is not as rigid as it might be, and the operator has to be careful not to touch the support rail after focusing. As for bright field, dark field, and phase contrast work, the Leitz appears to be second to

none. Resolution obtained with bright and dark fields is excellent. The phase contrast feature is useful for determining height differences. When the specimens are flat, the 5 x 7 negative is in focus from edge to edge at 1500X magnification.

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FIGURE 1 The Leitz MM5 Metallographic Microscope, as Installed at the National Lead Company of Ohio

Bright Field & Polarized Light	Low Power	PI 3.2x/0.06	PI 8x/0.18	PI 16x/0.25	PI 32x/0.50	PI 80x/0.95	PI 160x/0.95	PI 160x/1.40
Phase Contrast	—	—	Phaco PI 8x/0.18	—	Phaco PI 32x/0.50	Phaco PI 80x/0.95	Phaco PI 160x/0.95	Phaco PI 160x/1.40
Dark Field	—	—	—	D PI 16x/0.25	D PI 32x/0.50	D PI 80x/0.75	—	—
Stand. Magnification with GW8x	8x	20x	50x	100x	200x	500x	1000x	
Range with GW 6.3x to GF 25x Eyepieces	6.3x to 25x	16x to 63x	40x to 160x	80x to 320x	160x to 630x	400x to 1600x	800x to 3200x	
Field Diameter with GW 6.3x to GF 25x Eyepieces	28.0 mm to 10.0 mm	11.2 mm to 4.0 mm	4.4 mm to 1.6 mm	2.2 mm to 0.8 mm	1.1 mm to 0.4 mm	0.44 mm to 0.16 mm	0.22 mm to 0.08 mm	
Projection Equipment	12.5:1	32:1	80:1	160:1	320:1	800:1	1600:1	

FIGURE 2 Magnification Chart for the Various Objectives and Eyepieces Used on the Leitz MM5 (Table by courtesy of Ernst Leitz, Inc.)

FIGURE 3 Light Beam Path and Optics Used in the Leitz MM5 (Drawing by courtesy of Ernst Leitz, Inc.)

1. GROUND GLASS PROJECTION SCREEN
340 mm (APPROX. 13½ IN.) DIA.	6. CONDENSER	11. CENTRAL SHUTTER
2. VERTICAL ILLUMINATOR	7. 12 VOLTS 60 WATTS
FILAMENT LAMP	12. PHOTOGRAPHIC EYEPIECE
3. OBJECTIVE	8. HEAT FILTER	13. DEFLECTING PRISM FOR
PROJECTION ON GROUND
GLASS SCREEN
4. DEFLECTING MIRROR FOR PROJECTION	9. CONDENSER	14. EYEPIECES IN BINOCULAR
TUBE
5. DEFLECTING MIRROR FOR FILAMENT
LAMP ILLUMINATION	10. GROUND GLASS SCREEN
IN REVOLVING DARK
SLIDE CARRIER	15. FILTERS FOR XENON LAMP
		16. XENON LAMP XBO 450 w

FIGURE 4 The Four Different Vertical Illuminators and Their Objective Lenses: (A) Phase Contrast, (B) Low Power, (C) Bright Field and Dark Field, (D) Polarized Light and Oblique Illumination.

FIGURE 5 Photomicrograph Illustrating the Use of the Lower Power Illuminator (6X)

FIGURE 6 Bright-Field Micrograph Illustrates the Use of the Bright-Field Illuminator with Bright Field Objectives (1500X)

FIGURE 7 Dark Field Photomicrograph Using the Bright Field-Dark Field Illuminator with Dark Field Objectives (1000X)

TAKEN WITH LEITZ MM5

TAKEN WITH B & L RESEARCH

FIGURE 8 Comparison of Polarized Light Micrographs of Uranium Using the Leitz MM5 and the B and L Research Metallographs (100X)

FIGURE 9 Micrograph Using the Phase Contrast Illuminator and Objective (1000X)

FIGURE 10 Photomicrograph of Sintered Carbide Cutting Tool (Original in Color) (1500X)

✓ REPLICAS FOR POROSITY DETERMINATION IN AS-SINTERED

URANIUM DIOXIDE

By

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ABSTRACT

A replicating procedure was developed to determine the microporosity, i.e., visible pore fraction at 6000X, of as-sintered UO_2 pellets. Replicas from fractured and polished UO_2 pellets were made, and subsequently examined in the electron microscope. This paper describes in detail the steps necessary for the preparation of sound replicas and some results on as-sintered pellets.

Introduction

Various procedures are available for metallographic examination of sintered uranium dioxide. However, these methods are not satisfactory for the study of pore growth and migration during sintering. High density UO_2 pellets are prepared from initially green UO_2 powder, pre-compacted to approximately 50% theoretical density. The dry slug is then granulated and subsequently lubricated. The granulars are cold pressed and sintered at temperatures near 1650°C in molybdenum boats. Sintering processes decrease the porosity volume fraction, and the theoretical density, 10.96 g/cc, is approached. The replica technique described here is being used to study pores as sintering progresses.

Experimental Work

To obtain a representative area for determining the porosity, various types of surfaces of UO_2 pellets were investigated and the feasibility of each considered. As-sintered UO_2 pellets were received and broken into irregular pieces for investigation. Some pieces were stripped clean with adhesive tape for fractography analysis while others were mounted and polished on 320 and 600 grit silicon carbide wet paper. After ultrasonic cleaning in alcohol, and a hot water rinse, the final polish was performed with Linde B suspended in a two per cent chromic acid solution. The specimens were subsequently etched with a solution of three parts H_2O_2 to one part H_2SO_4 .

Two stage carbon replicas were made by pressing a strip of replicating tape, softened with acetone, on a clean UO_2 surface. Upon complete drying the tape was stripped from the surface, producing a negative replica. The negative replica was then placed in a vacuum bell jar system, and a platinum-carbon pellet was vaporized at a shadow angle of approximately 45° . A carbon rod was subsequently vaporized directly above the replica and the vacuum broken. The negative replica was then placed on a Cu grid and allowed to dissolve in an acetone bath. To avoid cracking, the replica and grid are placed on stationary screens for support and for faster dissolution. The replica was then ready for examination.

Direct carbon negative replicas, pre-shadowed with Pt-C, produced sound replicas on very porous UO_2 pellets, as shown in figure 1. Here, the direct carbon layer was etch-removed with concentrated nitric acid. Once the carbon layer started to lift from the surface, the sample and replica were placed in a beaker of distilled water. The distilled water lifted the replica from the specimen and the replica floated to the surface. Sectioning may be done before etching with a scalpel or the replica, floating on the surface, may be picked up with a glass slide and sectioned. Care was taken to keep the replica thoroughly wet until it was placed on a Cu grid and dried with alcohol. In a two-stage carbon replica the softened tape penetrated the larger irregular pores producing long shadows obscuring the surface, figure 2. The direct carbon replicas were made after the two-stage carbon replica, since etch removal altered the surface and further investigation was impossible.

Due to the non-homogeneous structure of low density pellets, closed pore migration and growth was not distinguishable, as is shown in figure 3, where a small grained area neighbors a large grained area. Since commercial fuels approach 100% theoretical density, pellets of densities above 94% were investigated.

Even though direct carbon replicas of extremely porous pellets produced better results than two-stage carbon replicas, pellets of densities greater than 94% replicated adequately with both techniques. A two-stage carbon replica is more reliable for irradiated UO_2 since it can withstand a rigorous decontamination cycle and duplicate replicas can be obtained. Still, with careful handling and modifications within the "hot cell", direct carbon replicas could be made.

Figure 4 shows light micrographs of polished pellets of 92, 94 and 96% wet theoretical densities. These micrographs show an unevenly distributed porous matrix. Two-stage carbon replicas were made of several areas with no significant results. Two-stage carbon replicas of smooth flat surfaces cracked readily on dissolution of the replicating tape leaving minute areas suitable for examination. However, since the shape of the pores was distorted by polishing, measurements were not made.

The polished surfaces were also etched and replicated. Figure 5 shows a typical area where preferential etching has outlined grain boundaries and dislocations. This surface was unrepresentative of closed micro- porosity, and further investigation of polished surfaces was halted.

Fractured surfaces of pellet densities above 94% were replicated with direct carbon and two-stage carbon techniques. Pore growth, pore migration and cleavage appeared in these replicas. Replicas of fractured surfaced can be made with minor surface preparation and are relatively crack-free.

Figure 6 shows large faceted closed pores with variations of pore shape and pore size. Concentric growth steps appear only on pores larger than 10,000 Å. On these pores, the size of the growth steps depends upon the shape of the pore. In figure 7, some of the smaller pores are spherodized while others are bounded by planes.

Figure 8 shows combination of two faceted pores. Still all pores do not combine in such a regular manner, as is shown in figure 9. Here several pores have agglomerated to form one large pore with varying growth steps.

Of interest in the fractured pellets is the evidence of pore growth and pore migration occurring during sintering, as is shown in figure 10. Here the fracture surface shows transgranular cleavage with disrupted crack propagation at locations within the grain where strings of pores have occurred. During sintering, small pores are swept up by the moving grain boundary, and through diffusion along the boundary, grow to a critical size. When the pore strength becomes an obstacle to grain boundary migration, the boundary breaks away leaving the string of pores shown in figure 11. The average pore radius here was 4000 Å for pores separated at 10,000 Å along the grain boundary. Breakaway occurred after the grain boundary had moved 16,000 Å from its initial position.

Conclusions

From the surfaces investigated, pore growth and pore migration was best represented on fractured UO_2 . Even though two-stage carbon replicas give reliable results, direct carbon replicas are faster and reproduce irregular porous areas. Thus, investigation is recommended with direct carbon replicas of fractured UO_2 .

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Fig. 1: Direct Carbon Replica of Fractured UO_2
92% Theoretical Density. 4800X.

Fig. 2: Two Stage Carbon Replica of Fractured UO_2
94% Theoretical Density. 2970X.

Fig. 3: Direct Carbon Replica of Fractured UO_2
92% Theoretical Density. 8700X.

Fig. 4: Polished UO_2 92-94-96% Theoretical Density.
200X.

Fig. 5: Two Stage Carbon Replica of Polished and Etched UO_2 92% Theoretical Density. 5760X.

Fig. 6: Direct Carbon Replica of Fractured UO_2 94% Theoretical Density. 14,500X.

Fig. 7: Direct Carbon Replica of Fractured UO_2
96% Theoretical Density. 8,300X.

Fig. 8: Direct Carbon Replica of Fractured UO_2
96% Theoretical Density. 12,000X.

Fig. 9: Direct Carbon Replica of Fractured UO_2
94% Theoretical Density. 15,400X.

Fig. 10: Two Stage Carbon Replica of Fractured
Surface 96% Theoretical Density.
8,050X.

Fig. 11: Two Stage Carbon Replica of Fractured
Surface 96% Theoretical Density.
12,000X.

X PREPARATION OF THIN FILM SPECIMENS OF IRRADIATED STAINLESS
STEEL TUBING FOR TRANSMISSION ELECTRON MICROSCOPY*

By

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ABSTRACT

The initial designs of pressurized water reactors employed stainless steel as the fuel cladding material. In the evaluation of the cladding performance from one of these reactors (Yankee), it was necessary to develop the techniques for preparing thin film specimens of irradiated tubing for transmission electron microscopy. The principal difficulty that presented itself was the high gamma activity from the residual Co^{60} products of iron transmutations. This note describes the steps required in foil preparation and some results on Type 348 stainless steel cladding.

Procedure

The foil preparation method required "hot cell" operations for the initial sampling, followed by electropolishing out-of-cell in the electron microscopy laboratory.

*This work was jointly sponsored by Westinghouse and the USAEC under contract No. AT(30-1)-3017.

In the hot cell, a $3/8$ " long section was cut from the fuel rod (fuel plus cladding sheath), and the fuel removed. The steel ring thus obtained had an outside diameter of 0.340" and a 0.021" wall thickness, and is represented by step (a) in Figure 1. The ring was sectioned longitudinally, step (b) and mounted in an epoxy with a predrilled Bakelite mounting mould, step (c). The section was rough ground on silicon carbide abrasive papers using an automatic Whirlmet apparatus. Grinding continued until a large flat surface was obtained, as depicted by step (d) of Figure 1. Fine grinding with a minimum of pressure improved the surface finish of the inside diameter face.

In order to obtain a flat surface from the outside diameter, the pre-drilled mount was sectioned, inverted and taped to a dummy mount with double-sided pressure sensitive tape, step (e). Grinding proceeded as in step (f) to a stage where the clad was approximately 0.005" thick. After these operations, the specimen retrieved from the mount, by chemical dissolution of tape and epoxy, was approximately $3/16$ " square.

The radiation level of this thin wafer was below the hazard level, e.g. 100mR @ one foot, and was suitable for limited handling in the microscopy laboratory, out-of-cell.

The final stages of film preparation were the standard techniques for electropolishing stainless steel. Best results were obtained with the Glenn-Raley⁽¹⁾ low voltage method.

Results

Specimen damage due to the grinding operation did not appear to be a problem. Figure 2 shows the irradiated microstructure of a Type 348 stainless steel. This structure represents an exposure of 26,000 hours at 345°C and a neutron dose of 8×10^{21} n/cm² (>1 Mev). There is no evidence of extraneous dislocations introduced by grinding or handling these samples. This procedure is now being used on zirconium-base alloys with equal success.

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1. R. C. Glenn and J. C. Raley, An Improved Procedure for Thinning Metallic Specimens for Transmission Electron Microscopy ASTM STP No. 339 (1962).

Fig. 1: Schematic Diagram of Cladding Preparation.

Fig. 2: Microstructure of Irradiated Fuel Cladding. (a), (c) Zero degree tilt and, (b), (d) Small angle tilt with respect to electron beam. a, b (10,000X); c, d (25,000X)

✓ TECHNIQUE FOR THINNING PLUTONIUM FOR TRANSMISSION
ELECTRON MICROSCOPY

A. W. BREWER AND F. J. FRAIKOR

ABSTRACT

The technique for preparation, handling, and examining thin foils of Pu-1 w/o Ga for transmission electron microscopy are described.

INTRODUCTION

In order to better correlate microstructures with bulk properties of plutonium and its alloys, it became apparent that direct examination in an electron microscope would be necessary, particularly to see dislocation configurations and their interaction.

Electropolishing

The technique of electropolishing has been the most frequently used method for the preparation of thin foil specimens for transmission electron microscopy. Douglass, at Los Alamos, has shown that the electropolishing method was feasible for plutonium foils using a modified "window" technique with a chromic-acetic acid electrolyte.¹

Since the jet electropolishing method has proved very successful in producing even, uniform thin foils in a variety of materials,² it was decided to adapt a Glenn Dual Jet Thinning* unit to

*Commercially available from G.E.M.S., Inc., Jeannette, Pa.

plutonium and plutonium alloys. This apparatus consists of a dc power supply (Figure 1) which provides a maximum of 3,000 ma and 100 volts, a box made of Plexiglas (Figure 2), with a pump to circulate a liquid cooling agent if necessary. A glass jar (Figure 3) holds the electrolyte in which the jets and specimen are immersed to perform the thinning. A second pump is provided to circulate the electrolyte through hollow cathodes and causes the electrolyte to impinge on both sides of the specimen (anode) thereby assisting in the removal of the viscous layer.

Electrolytes Used

Table I lists a number of various electrolytes which were tried on Pu-1 w/o Ga specimens. The electrolyte that shows the most promise is the nonaqueous solution developed initially for cleaning uranium by E. L. Childs and F. E. Evans.³ this solution consists of ethylene glycol saturated with 600 grams per liter of sodium hypophosphite.

Handling Techniques

All of the thinning operations are accomplished in an "A" Type satellite glovebox (Figure 4). Since a satellite glovebox depends on a primary glovebox for its negative pressure, the satellite box does not have the usual air inlet, thereby minimizing air currents during the thinning operation. After carefully cutting 10 x 18 mm size specimens from 0.8 mm thick Pu-1 w/o Ga foil, the specimen is clipped to the thinning holder and placed in the thinning unit. Stop-off lacquer around the specimen edges is not necessary because edge attack was found to be generally minimal.

After thinning, the specimen is quickly and thoroughly rinsed with methanol. The desired area is cut on a plastic plate under methanol and transferred in a small specimen container within a sealed container to a box made of Plexiglas (Figure 5), similar to that devised by Douglass.¹ This transparent enclosure is provided with open gloveports to facilitate the ease of handling and mounting of the thin specimens. Care is exercised in handling the specimen to prevent foil deformation. Respirators are worn during the loading operation as a precautionary measure until the specimen is in the microscope specimen chamber under vacuum or discarded in a sealed container. The specimen is mounted between 75-mesh copper grids and examined at 100 kev in a Phillips EM-200 electron microscope equipped with a rotating, tilting stage.

RESULTS

A photomicrograph of typical dislocation images in a Pu-1 w/o Ga foil is shown in Figure 6. Subsequent thickness measurements by a dislocation intercept method reported by Ishida,⁴ shows that these thin areas are approximately 400 Å thick. These very thin areas are prone to drastic electron beam-heating due to plutonium's poor thermal conductivity and the high electron beam intensities required to penetrate the dense lattice. Furthermore, the metal is always covered by a thick PuO₂ layer even under the vacuum of the electron microscope. The cumulative effect of all these difficulties thus far has prevented a definitive correlation of observed dislocation structure with bulk metal properties. It is hoped that a video image intensifier system which will be installed on the EM-200 will provide a suitable means for minimizing beam heating and enable photomicrography of more representative areas in the foils.

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TABLE I

<u>Electrolyte</u>	<u>Voltage- Current</u>	<u>Results</u>
20% sodium chromate in acetic acid	26V-100 ma	Rapid edge attack. Tendency to form an acetate film on specimen surface.
10% HNO ₃ in ethy- lene glycol	8v-300 ma	Very rapid attack, badly stained.
"Power Kleen"*	10-30v-500- 900 ma	Rapid edge attack, pitted.
20% Ortho phos- phoric acid in methanol	25V-600 ma	Thick brown film.
40% Ortho phos- phoric acid in methanol	15V-500 ma	Good polish but left brown film.
80% ortho phos- phoric acid in methanol	10V-900 ma	Very good polish.
100% ortho phos- phoric acid	6V-1200 ma	Poor polish, pitting.
Sodium hypophos- phite in 1,2- ethanediol	20V-800 ma	Excellent thinning, slight tendency for bluish white film on surface.

*Commercially available from Microlytics, Los Angeles, California

Figure 1. JET THINNING UNIT DC POWER SUPPLY

Figure 2. JET THINNING UNIT BOX MADE OF PLEXIGLAS.

Figure 3. JET THINNING UNIT GLASS JAR, SPECIMEN,
AND HOLLOW CATHODES.

Figure 4. "A" TYPE SATELLITE GLOVEBOX

Figure 5. LOADING BOX MADE OF PLEXIGLAS

Figure 6. PHOTOMICROGRAPH OF TYPICAL DISLOCATIONS
MAGNIFICATION 130,000:1

TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION OF THE
STRUCTURE OF WELDED TYPE 304 ELC STAINLESS STEEL

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Due to uncertainty as to what was being observed in optical micrographs of the structure of 304 ELC stainless steel samples, the structure was investigated by transmission electron microscopy. These samples have a fusion weld and a 308 stainless steel filler weld. Because very little has been reported in the literature on the structures of welds as observed in the electron microscope, and their structures are also of interest, we undertook their investigation.

Figure 1 is a low magnification optical photograph of the whole weld area. Samples of the weld were obtained by thin-sectioning 5-10 mil slices parallel to the direction observed in Figure 1. These slices were ground on 600 grit SiC paper to a thickness of 3-4 mils to remove cutting effects. Then the samples were thinned using the Bollman technique in a solution of 30% HNO_3 in methanol at 4-5°C. This solution appears to polish the weld, the heat affected zone, and the parent metal at the same rate;

*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract AT-33-1-GEN-53.

in general, the delta ferrite, which is present in the filler weld, is retained.

The areas of interest for the weld study were the welds themselves, the fusion weld-filler weld interface, and the weld-parent metal interfaces.

Figure 2 is an optical micrograph showing the ferrite in the filler weld. Figure 3 is a surface replica showing the ferrite configuration more clearly. This same configuration is observed in the thin foil by transmission electron microscopy as is seen in Figure 4. The sub-grain boundaries and dislocation arrangements both in the 308 stainless steel and around the edge of the ferrite are shown in Figure 5. In Figure 6 the substructure of the weld and the ferrite are more clearly seen. This type substructure has been reported previously by other investigators¹ in samples which have undergone creep at high temperatures and will be referred to as a "creep" structure. This is actually substructure in the grains in the weld. The boundaries observed were sub-boundaries as shown by the dislocation slip trace traveling through three of the boundaries. This indicated that the subgrains on both sides of the boundaries have the same crystallographic orientation. Figure 7 shows the structure of the ferrite.

The filler weld-parent metal interface is shown in Figure 8.

The ferrite in this area stops at the interface, and long thin stringers project back into the weld area. There is no discernible boundary or pileup of dislocations at the interface; however, there is a small area along the interface which appears to be thinner than the rest of the foil. This thin area was attributed to a small amount of segregation, possibly of nickel.

The structure of the fusion weld is shown in Figure 9. This photomicrograph was taken near the filler weld-fusion weld-parent metal intersection. The foil was, unfortunately, from a sample which had been stressed at high temperature; consequently some of the substructure may be due to the creep which apparently occurred during heating. Nevertheless, some creep would be expected due to thermal stresses during welding, and a comparison with the filler weld structure from unstressed samples indicates the "creep" structure in Figure 9 is reasonable.

Figure 10 shows an area in the fusion weld. A dark shadow outlines what we will call a cell structure. Careful examination shows there is no boundary associated with this cell and no accumulation of dislocations. One of the boundary areas is shown in Figure 11. The question arises, then, why this outline occurs. An optical micrograph of the fusion weld in Figure 12 shows that this cell structure is all that is observed when the welds are etched. The explanation of both of these effects is shown in

Figure 13, which is a tracing of electron microprobe results obtained from an area similar to that in Figure 12. This shows a segregation effect in which the nickel concentration increases and the iron concentration decreases at the cell boundaries. The boundary crossed here extends over 8.0 microns. The boundary is sharp in the probe trace because the sample was moved mechanically from the cell area to the boundary area. The chromium concentration did not noticeably change across the weld area.

Cellular structure has been observed on a macroscopic scale previously by Rutter and Chalmer² among others. They observed the structure on the surface of tin crystals containing lead and other impurities. They postulated that the substructure arises due to the formation of a zone of constitutionally supercooled liquid adjacent to the interface. In our case, we postulate from the appearance of the iron-nickel and iron-chromium phase diagrams that, on cooling, the first solid phase to form will have a low nickel content, leaving the liquid phase next to this solid high in nickel concentration. Since a higher concentration of nickel reduces the freezing point, this is indeed a constitutionally supercooled liquid. This causes a segregation effect since the rapid freezing of the weld does not allow the nickel to diffuse rapidly enough to reach equilibrium concentrations. This postulation agrees with the previous theory.

From the appearance of the weld structure in optical micrographs such as Figure 1, one might conclude that the observed structure is a result of columnar grains which grew in from the side of weld areas and which are observed in a transverse cross section of the sample. This is not true as shown above.

The fusion weld-parent metal interface is quite wide and is shown in Figure 14. In this case a grain boundary separates the parent metal from the heat affected zone; there is considerable substructure in the interface area. This section, too, was from the strained sample and may be partially affected by creep.

Figure 15 shows the fusion weld-filler weld interface; here again there is no apparent boundary separation.

The effect of stress on the heat affected parent metal in the strained sample is shown in Figure 16. The area shown is a twinned grain, and the "creep" type substructure is apparent in the twin area. Figure 17 shows this same area at higher magnification.

In conclusion the filler weld had the same segregation effect as was shown in the fusion weld. The observed microstructures of both welds, as seen optically on etched samples, are pseudo-structures, due mostly to these segregation effects. Except for the observable delta ferrite, no other grain structure characteristics are revealed under ordinary etching procedures. Prolonged

etching with most of the recommended etches will bring out what appear to be faint grain boundaries in the weld, but they are usually obscured by the relief due to the cell structure.

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Acknowledgments:

The author would like to thank Dr. Gordon Powell of Ohio State University for his assistance and consultation on this work. He also thanks Dale Roesch for obtaining the electron probe data and Dean Jones for technical assistance.

1. Low magnification (15X) optical micrograph of the 308 filler weld, the fusion weld and the heat effect area in type 304 ELC stainless steel. The fusion weld is in the upper left area of the micrograph.

2. Optical micrograph of the δ ferrite in the 308 stainless steel filler weld (500X).

3. A carbon shadowed replica of the filler weld showing the ferrite configuration more clearly (1500X).

4. Transmission electron micrograph of ferrite in the filler weld having a configuration similar to that shown in Fig. 3 (4000X).

5. The weld structure and dislocation arrangement between the ferrite and the matrix at 5500X.

6. The "creep" like structure of the weld with sub-boundaries and dislocation pileups at 7500X. A dislocation slip trace (as shown) can be seen crossing three sub-boundaries and stopping at the ferrite inclusion.

7. The structure of a ferrite particle at the edge of a foil is shown here at 9500X.

8. The filler weld-parent metal interface at 2000X. The parent metal is in the upper left portion of the micrograph.

9. The "creep" structure of the fusion weld near the intersection of the fusion weld with the filler weld and the parent metal (1500X).

10. A "cell structure" is outlined in the fusion weld. The "cell" area is indicated at A and the "cell" boundary B. (2000X).

11. The "cell" boundary area at 9500X.

12. Optical micrograph showing the same "cell" structure as shown in Fig. 10 (200X). The "cell" area is "a" and the boundary "b".

13. Electron probe trace of the fusion weld. The relative intensities are on the vertical axis and distance is on the horizontal axis.

14. Fusion weld-parent metal interface (3000X).

15. Fusion weld-filler weld interface (5500X).

16. Heat affected parent metal showing "creep" structure (1500X).

17. Twinned area of Figure 16 at 5500X.

✓ ~~THE~~ INVESTIGATION OF THICK FILMS OF VAPOR-DEPOSITED
ALUMINUM AND GOLD BY TRANSMISSION ELECTRON MICROSCOPY

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As part of the evaluation of vapor deposition techniques, the structures of several vapor-deposited metals were investigated to correlate grain size and substructure with the physical properties of the deposited film.

In most cases the vapor deposits were too thick to study by direct transmission electron microscopy (2-4 μ); consequently, thinning techniques had to be developed for use with the metal in question. A further problem in the study of these deposits was the small size of the material to be thinned, and the physical problem of suspending the vapor-deposited metal in the thinning solution became significant. The metals were deposited on Lucite[®] polymethyl methacrylate, and glass. Cross sectioning revealed that these films were uneven, which added to the problem of obtaining good foils for electron transmission.

Test films of aluminum were deposited in a vacuum of 10^{-5} torr on glass slides to develop techniques for preparation of thin foils.

*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under contract AT-33-1-GEN-53.

Some of these foils were thin enough (~ 2000 Å) to study without thinning. These were removed from the glass with dilute HF and observed directly. Figures 1 and 2 show a typical sample. The grains were small and nonuniform, and the only evidence of strain was from curling caused by handling. The largest grains were about 1.5 microns in diameter.

Thick films of aluminum (up to ~ 4 μ) were thinned by an explosive chemical reaction. A chemical polish of concentrated H_3PO_4 - H_2SO_4 - HNO_3 at 90°C was unsatisfactory; however, when the foil was first rinsed with ethanol, and then a drop of the acid solution added, the foil was successfully thinned with little stress introduced in handling. The original thick film was immersed in ethanol and placed on a glass slide; then a drop of the acid solution was placed on top of the sample. After the initial violent reaction was over, solution was added drop-wise until reaction ceased. The sample was then rinsed with ethanol and the process repeated until the sample was thinned.

Figure 3 shows the structure of the thick aluminum films. The grain size is much larger for this material. In this micrograph what appears to be oxide particles, or the coalescence of vacancies, can be observed to remain aligned along former grain boundaries. Apparently, some grain growth occurred during the deposition process,

probably due to film heating during deposition. The foil was relatively strain-free, indicating that the handling techniques and thinning procedures did not introduce strain, and that the dislocation densities should be representative of the deposit. Figure 4 is a high magnification micrograph taken to differentiate between coalescence of vacancies, dislocations and oxide particles. Neither this nor electron diffraction were successful.

After these initial studies of test films on glass, vapor deposits were next made under more variable conditions. Aluminum was vapor deposited on Lucite polymethyl methacrylate, and the films were removed by immersing the deposit and substrate in solvent (Koldmount[®] liquid, Vernon Benshoff Co.). These films were then chemically thinned by the above described procedure.

Figure 5 shows a typical vapor deposit of aluminum on the plastic. The grains were small, and no preferred orientation was apparent. Figure 6 shows the same structure at high magnification. The grain size was more uniform, but smaller than the initial test films deposited on glass.

Thinning problems similar to those with aluminum exist for gold, with the additional problem that the foils must be about half again as thin to resolve the structure of the gold. Thin films of gold (about 800 Å thick) were deposited on quartz, then stripped with Permacel transparent cellulose acetate tape. The tape was

dissolved in butylcellosolve. The structure is shown in Figure 7.

The grains were slightly smaller than in the aluminum-on-glass deposits. The largest gold grains were about 0.6 micron in diameter. Similar deposits were annealed on the quartz at 800°C to observe the effect of such treatment. The next two figures (8 and 9) show that even after recrystallization and considerable grain growth, there was some evidence of strain, possibly due to differences in thermal contraction on cooling between the quartz substrate and the film.

Thinning techniques were tried on rolled gold foil (~75 μ thick) and on vapor-deposited gold ranging from 12 to 0.1 microns thick. A cyanide electropolish was satisfactory for the rolled gold. It was thinned in a solution of KCN-K₄Fe(CN)₆-NaK tartrate-NH₄OH-H₃PO₄ at about 7 volts using the window technique. The same solution and conditions with the vapor deposited gold gave highly etched and uneven foils.

Since the vapor deposited gold films were small and flimsy, an attempt was made to develop a chemical polishing technique similar to that used for the aluminum. Neither aqua regia nor various KCN solutions worked. A dilute solution of bromine in ethanol was partially successful, but this solution etched and preferentially attacked certain grains. (This solution, incidentally, gives a good, quick etch for regular gold samples).

Further attempts were made to electropolish the gold using special holders to keep the films from curling. By increasing the voltage to about two to three times that required for the rolled gold, some small areas were thinned sufficiently to observe the structure. A solution of 10% HBr in either ethanol or methanol using the dual-jet technique worked on rolled gold, but so far, no good polish has been found for the vapor deposited gold.

The following micrographs show the results obtained by thinning. Figure 10 shows the structure of rolled gold thinned with cyanide. Figures 11 and 12 show rolled gold foils also thinned in cyanide; at the higher magnification the broken grains and dislocation pile-ups that one would expect from such a sample are visible. Figure 13 shows a similar foil which was thinned in HBr and methanol.

Figures 14 and 15 show the structure of a vapor-deposited gold film about 0.1 mil thick, which was thinned in the cyanide solution at about 18 V. The grain size has increased over that of the gold on glass. The large grains are highly twinned, and the grain size is irregular. Under less controlled conditions vapor-deposited gold on quartz, like the aluminum on Lucite, was finer grained than the initial test films on glass. Although no good films were obtained, small areas were observed on the electron microscope.

In conclusion, the structures of both the gold and the aluminum in vapor deposited thick films were fine grained and strained. For a given deposition process the grain size increased with film thickness. Heat from the aluminum deposition process caused some grain growth, or at least, the movement of grain boundaries. The gold developed highly twinned grains, both in the thin and the thick films. The attempts at thinning produced good chemical and electrochemical etches for gold, which do not involve cyanide or uncontrollable aqua regia; but a good thinning solution for vapor deposited gold has not yet been developed.

Acknowledgments:

The authors would like to thank Dr. Gordon Powell of Ohio State University for his consultation and Dr. Thomas W. Wood for vapor depositing the test films.

Figure 1 - As deposited aluminum (~ 2000 Å thick) showing non-uniform grain size. (11,400X).

Figure 2 - The same foil as Figure 1 at 36,000X.

Figure 3 - A thick film of aluminum showing increased grain size and evidence of grain growth. (11,400X).

Figure 4 - Chemically thinned thick foil as seen at 36,000X.

Figure 5 - "Process type" aluminum from Lucite substrate showing very fine grain size and affects due to scratches on the substrate surface. (16,800X).

Figure 6 - The same film as seen in Figure 5 at 36,000X.

Figure 7 - As deposited gold (~ 800 Å thick) showing non-uniform grain size and twins in the larger grains. (36,000X).

Figure 8 - Substrate annealed gold. (16,800X).

Figure 9 - Same sample as in Figure 8 at 21,600X.

Figure 10 - Rolled gold structure in a foil thinned using a conventional CN electropolish. (6600X).

Figure 11 - Rolled gold structure at 11,400X.

Figure 12 - Rolled gold structure at 16,800X.

Figure 13 - Rolled gold foil thinned in 10% HBr in ethanol.
(16,800X).

Figure 14 - Thick film of vapor deposited gold (.1 mil), thinned
in CN^- solution, showing increased grain size and
growth twins. (5000X).

Figure 15 - Thick film of vapor deposited gold at 11,400X.

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APPLICATION OF ELECTRON METALLOGRAPHY TO
PRECIPITATION STUDIES OF HASTELLOY N*

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ABSTRACT

Various techniques available in electron metallography must be used to complement each other in order to gain a clear understanding of precipitation reactions. Besides transmission microscopy of thinned bulk samples, we have found that techniques for extraction of all precipitates in contact with a surface are important to reveal precipitates not observed in transmission or by usual replication techniques. Extraction replicas permit detection of sheets of very thin grain boundary precipitates as well as those seen by the usual techniques. Electron diffraction patterns may be easily obtained, without interference from the matrix, to get precipitate crystallography. The use of a microprobe attachment on the electron microscope permits qualitative identification of precipitates and, in many cases, a quantitative analysis.

INTRODUCTION

Hastelloy N, a nickel-base molybdenum-chromium-iron alloy which was developed at Oak Ridge National Laboratory (ORNL) specifically for its excellent creep strength and resistance to corrosion by molten fluoride fuel salts, exhibits the pronounced loss in high-temperature ductility typical of nickel-base alloys. As shown in Fig. 1, irradiation further reduces the high-temperature ductility, its effect being essentially superimposed on that of unirradiated material. Since Hastelloy N is the structural material for the Molten Salt Reactor Experiment reactor vessel which has an operating temperature of 650°C, well into the range of the ductility decrease, it is imperative that the material be more fully understood and improved for future use in molten-salt systems. Preliminary examination of several unirradiated

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

specimens by transmission electron microscopy indicated grain-boundary precipitation occurring in the same temperature range as the drop in ductility. Thus, an investigation was initiated to determine the pattern of precipitation in this system and its relation to mechanical properties, and to identify harmful as well as beneficial precipitates.

TRANSMISSION ELECTRON MICROSCOPY

Initial precipitation studies employed transmission electron microscopy. Matrix precipitation often was not detected although large blocky M_6C carbides were present both in the matrix and in grain boundaries. Figure 2, a low magnification optical micrograph, shows the distribution of the blocky carbide precipitate and the heterogeneous nature of this system. This alloy was quite unattractive for transmission work. Difficulty arose in routine preparation of transmission samples having uniform thin regions extending more than 50 μ from the edge of a hole, creating problems associated with biased sampling and erroneous interpretation of results. The extensive grain-boundary precipitate from an aging treatment or from high-temperature testing was not always homogeneous. Transmission techniques were also limited in that the true nature of grain-boundary precipitates could not be studied, since we were seeing only a thin cross section of the grain boundary. Also thin precipitate films were usually undetectable in transmission.

Several of these problems are illustrated in Fig. 3, a transmission micrograph of Hastelloy N irradiated at 650°C for 5000 hr and tested at 650°C. We see a great deal of precipitate both at grain and incoherent twin boundaries but none at coherent twin boundaries. However, most coherent twin boundaries in the particular material were found to have large amounts of precipitates. Strain fields often exist around particles to obscure observation, such as the dark area in the center caused by a large carbide in the grain boundary.

Despite the limitations of transmission electron microscopy, it does provide information that is unobtainable by other techniques, such as the presence of fine precipitates and factors concerning the dislocation structure. Thin foils were prepared from bulk materials, as previously described,¹ using an electrolyte consisting of 30% HNO_3 , 5% H_3PO_4 , and 65% methyl alcohol, with phosphoric acid added to obtain uniform rates of thinning of both carbides and matrix.

EXTRACTION REPLICAS

In order to overcome the limitations of the transmission technique and to study the precipitates more fully over large regions of the sample, electrolytic extraction techniques were utilized. Specimens were mounted and mechanically polished, the final polishing step using half-micron diamond abrasive. Provision was made for an electrical contact, usually through the back of the mount. After polishing, the samples were lightly

¹C.K.H. DuBose and J. O. Stiegler, Semiautomatic Preparation of Specimens for Transmission Electron Microscopy, ORNL-4066, February 1967.

etched, either chemically or electrolytically, to reveal all precipitates and to remove any smeared matrix material. Carbon replicas were obtained² using a solution of 10% HCl in ethyl alcohol with a current density of 0.1 amp/in.² or less. Etching times varied, depending on the amount of connected grain-boundary precipitates. In some cases the samples were etched for 24-48 hr to dissolve sufficient matrix and to release the grain-boundary precipitates.

Extraction techniques permit observation of precipitates in the same distribution as that existing in the bulk sample, with the exception that grain-boundary precipitates are no longer supported by the matrix and collapse against the substrate. However, this permits direct observation of the grain-boundary precipitates on essentially the surface of the original grain boundary. This is demonstrated in Fig. 4 by an electron micrograph of an extraction from Hastelloy N which was aged at 870°C, showing grain-boundary precipitation where the precipitate has fallen against the replica. If the polished sample surface or replica were parallel to the plane of the micrograph, the distribution of dendritic-like precipitates in the bulk sample would project towards the viewer at an angle corresponding to that of the grain boundary. If we were then to remove a thin slice, parallel to the page, from the projecting precipitate, the results would be the morphology seen optically or in transmission, as in Figs. 5 and 6, respectively. Figure 7 shows another example of cellular grain-boundary carbide formation and also the appearance of the replica when the precipitate is not fully retained.

When Hastelloy N is annealed at high temperatures, optical micrographs show a lamellar precipitate in the grain boundaries. Extractions from this material show a variety of morphologies, several of which are seen in Fig. 8. Variations in contrast are due to differences in thickness of the precipitates. Here we see thin dendritic-like sheets, probably on the order of 100Å in thickness, as well as the lamellar type which is 20 to 50 μ thick. The thin sheets are usually undetectable by transmission techniques.

Hastelloy N which has been modified by decreasing the molybdenum concentration and adding small amounts of titanium shows an improvement in properties. The microstructure appears to be quite clean, both by optical and transmission examination. Extraction replicas, however, reveal a considerable amount of grain-boundary precipitation. Figure 9a shows an interaction between a small precipitate particle and a thin film of precipitate extracted from a grain boundary. Ti(C,N), identified by electron diffraction, is the major precipitate found in this titanium-modified system and, like M_6C in the standard Hastelloy N, may assume various morphologies. Ti(C,N) is present in Fig. 9. In Figs. 9c and 9d, Ti(C,N) exists with another phase, as yet unidentified. The thin film and thread-like precipitates in Figs. 9c and 9d are Ti(C,N) with the unidentified phase taking the form of the thicker spines and polyhedral particles, Fig. 9d.

²High-Temperature Materials Program Progress Report No. 61, GE-NMPO, GEMP-61, Sept. 30, 1966, p. 128.

ELECTRON DIFFRACTION

The identification of crystal structure and the determination of lattice parameters of precipitates are greatly simplified using extraction replicas since matrix interference is eliminated. Diffraction patterns are very easily obtained from thin grain-boundary precipitates and the large blocky carbides often have thin edges due to metallographic polishing, thus allowing sufficient transmission to obtain satisfactory patterns.

We generally evaporate a thin layer of gold or copper onto the replica before insertion into the microscope. This provides a standard for determining the lattice parameters, and eliminates the camera constant error associated with slight changes in lens currents. If microprobe analysis is to be carried out simultaneously, the standard must be chosen so as to not interfere with the analyzed elements. Diffraction patterns obtained from these precipitates are often quite complex and measurement of spots quite tedious, but we have a method which permits relatively good accuracy and rapid solution for routine identifications.

A circle, corresponding to the (111) ring of the standard when a photographic plate of the diffraction pattern is projected through an enlarger to a convenient size, is inked on white cardboard. (We have found a gold (111) ring of 20- to 25-cm diam convenient.) Additional boards may be made for precipitates encountered frequently, such as M_6C or TiC , with rings for various (hkl) positions calibrated to the standard (111) ring. Thus, a rapid diffraction pattern evaluation may be made and spots not belonging to the phase in question can be readily noted. Measuring of spots on patterns from unidentified precipitates is carried out on white paper after standardizing plate magnification to the standard ring in the pattern. Since no wet processing is used, distortion associated with photographic paper shrinkage is eliminated.

ELECTRON MICROPROBE

Another promising aspect of extraction replicas appears to be with microprobe analysis of individual particles. We have added a Hitachi HXA-1 electron probe microanalyzer accessory to one of our electron microscopes, which permits at least a semiquantitative determination of composition. A beam size of $\sim 2\mu$ is employed (second condenser crossover); but, since matrix effects are eliminated by using extraction replicas, only x-rays from the precipitate particles are analyzed. Areas for analysis may be selected with great accuracy and small particles may be analyzed, electron diffraction patterns obtained and high resolution electron micrographs made without removing the area from the beam. The thin grain-boundary precipitate films may also be analyzed very easily.

Complete qualitative analysis of a particle may be made in $\sim \frac{1}{2}$ hr. The limit of detectability is on the order of 10^{-14} grams of pure material, or in the case of nickel, a sphere of ~ 600 Å radius.

Qualitative analysis of the blocky carbides in Hastelloy N with respect to the matrix shows a large increase in molybdenum and a decrease in nickel, which is in agreement with conventional microprobe studies carried out previously. Although we have not performed any quantitative analysis at this time, this technique appears to be very valuable, particularly when used in conjunction with conventional microprobe work.

SUMMARY

The various techniques available for electron microscopy have limitations and must be combined for effective investigations of the structural state. Transmission techniques permit observation of dislocation structure and fine matrix precipitate, but many types of grain-boundary and large matrix precipitates are difficult or impossible to study by this method.

Extraction techniques permit the study of thin grain-boundary precipitates undetectable in transmission. Other advantages include retention of "bulk" morphology, study of grain-boundary precipitate and precipitate on fracture surfaces, ease in obtaining electron-diffraction patterns, and applicability to microprobe work.

Recently developed microprobe attachments for the electron microscope permit chemical analysis of particles without interference from the matrix, a problem encountered with the bulk microprobe. Electron micrographs, selected area electron-diffraction patterns, and chemical analysis of either a given area in a transmission sample or a precipitate in an extraction replica are now possible without removal of the specimen from the microscope.

Fig. 1. Effect of Irradiation on the Tensile Ductility of Hastelloy N after Irradiation at 650°C for 4800 hr in the Molten Salt Reactor Experiment to a Fluence of 1.3×10^{20}

Fig. 2. Low Magnification Optical Micrograph of Hastelloy N Showing Heterogeneous Distribution of Precipitates after Annealing 1 hr at 1177°C. Etched in lactic regia.

Fig. 3. Transmission Electron Micrograph of Hastelloy N 5081 after Tensile Fracture at 650°C.

Fig. 4. Extraction Replica from Hastelloy N, Aged 4 hr at 870°C.
All precipitates are M_6C .

Fig. 5. High Magnification Optical Micrograph from Hastelloy N,
Aged at 870°C. (see Fig. 4)

Fig. 6. Transmission Micrograph of Grain Boundary Carbides after Aging at 870°C. (See Fig. 4)

Fig. 7. Cellular Grain Boundary Carbides in Hastelloy N.

Fig. 8. Extraction Replica Showing Various Morphologies of Precipitates in Hastelloy N Annealed at 1370°C.

Fig. 9. Precipitates Extracted from Grain Boundaries of Titanium-Modified Hastelloy N.

- (a) Interaction between small unidentified particle and Ti(C,N) film.
- (b) Common Ti(c,N) morphology.
- (c) Ti(C,N) in thread-like and thin film morphologies. An unidentified phase is present as small particles on the Ti(C,N) film.
- (d) Ti(C,N) film with an unidentified phase in the form of the spines and small particles.

✓ Correlation of Microstructure With Mechanical
Properties of Irradiated Tungsten*

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Abstract

Transmission electron microscopy has been used to study the microstructure of mechanically tested polycrystalline tungsten which had been irradiated to fast ($E > 1$ Mev) neutron fluences ranging from 8.5×10^{17} to 1.5×10^{21} n cm⁻². A fluence threshold exists between 5.9×10^{18} and 3.8×10^{19} n cm⁻² ($E > 1$ Mev), above which distinct defect cluster formation occurs. These clusters appear to contribute to the hardening of the material, leading to embrittlement in tensile specimens tested at 400°C. The microstructure of irradiated tungsten creep-rupture tested at 1100°C showed the presence of distinct dislocation loops, thought to result from interstitial aggregation. Although the microstructural features observed in irradiated tungsten appear to be related to fast ($E > 1$ Mev) neutron fluence rather than thermal neutron fluence, the irradiation induced strengthening observed at 1100°C shows better correlation with thermal neutron fluence. The presence of rhenium and osmium atoms produced by thermal neutron transmutation reactions is believed to account for the property changes at 1100°C.

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Correlation of Microstructure With Mechanical Properties of Irradiated Tungsten

Introduction

The need for materials capable of operating in high temperature nuclear reactor systems has focused attention on the body-centered cubic refractory metals and alloys. As part of the effort to evaluate the behavior of these materials in nuclear environments, transmission electron microscopy has recently been utilized for the direct observation of radiation-induced microstructural features. Defect clusters, in the form of black dots, have been seen in molybdenum⁽¹⁻³⁾ and tungsten⁽⁴⁾ after neutron irradiation at pile ambient temperature ($< 100^{\circ}\text{C}$), and in molybdenum bombarded with fission fragments at 80°C ⁽⁵⁾. When irradiation was carried out at elevated temperatures⁽⁶⁾, or when specimens irradiated at pile ambient temperature were subsequently annealed⁽¹⁻⁵⁾, loops were formed which were identified as interstitial in nature.

In support of a program investigating the effects of neutron irradiation on the physical and mechanical properties of b.c.c. refractory metals⁽⁷⁻¹⁰⁾, transmission electron microscope observations have now been made on irradiated and tested tungsten tensile and creep-rupture specimens. The present paper describes the results of this study, and establishes a correlation between the radiation-produced microstructure and the resultant mechanical properties.

Experimental Techniques

Specimens used in this study were fabricated from commercially pure (99.98%) tungsten powder, sintered and swaged into 0.34 cm and 0.51 cm diameter cylindrical rod stock and recrystallized for 1 hr. in hydrogen at 1900°C . The major substitutional impurities totaled approximately 60 ppm, and consisted of iron, molybdenum, aluminum, and silicon. The total interstitial content was about 65 ppm by weight, and consisted of carbon, oxygen, nitrogen, and hydrogen.

Tensile specimens were prepared from the 0.34 cm diameter stock by centerless grinding, followed by a 1 hour stress-relief anneal at 1600°C in hydrogen⁽⁸⁾. Creep-rupture specimens were prepared in a similar manner from the 0.51 cm stock, and were subsequently annealed in hydrogen at 1750°C for 1 hour^(9,10). Finished tensile specimens had 0.20 cm and 3.18 cm gage diameters and lengths, respectively; the corresponding dimensions of the creep-rupture specimens were 0.25 cm and 4.54 cm.

Irradiations were carried out at pile ambient temperatures ($\sim 70^\circ\text{C}$) to the various neutron fluences indicated in Tables 1 and 2. All irradiations were carried out in the Oak Ridge Research Reactor (ORR) except for the highest fluence creep-rupture specimen, which was irradiated in the Engineering Test Reactor (ETR) in Idaho. During irradiation, the specimens were contained in helium-filled aluminum capsules which were in contact with the reactor coolant water. Nickel and iron fast-neutron (n, p) reactions were used to determine the effective neutron flux above 1 Mev. Cobalt and iron (n, γ) reactions were used for determining the thermal neutron flux.

Included in both groups of specimens was a mated pair, one of which was irradiated without shielding for thermal neutrons and the other of which was irradiated inside a 0.51 mm thick cadmium shield. This shielding decreased the thermal neutron fluence by a factor of ten but left the fast neutron fluence practically unaffected. These paired specimens were used to compare the relative effects of thermal and fast neutron irradiation.

Following irradiation, the specimens were mechanically tested^(8,10) and, after failure, prepared for transmission electron microscopy. To study the effect of stress on the radiation-produced microstructure, thin foils were prepared from the reduced section near the fracture as well as from the unstressed button heads of each specimen. Disks 0.5 mm thick were sliced from the test rods and were then electrolytically⁽¹¹⁾ thinned to electron transparency by an immersed double jet technique. Thinning was carried out in an electrolyte of 1.5% NaOH in water at an applied potential of 15 to 20 volts.

Examinations were made in a JEM-6A electron microscope operating at 100 kV and equipped with a tilting and rotating stage. To minimize contamination rate and thereby increase the useful lifetimes of the thin foils in the intense electron beam, a liquid nitrogen cooling device was used in the specimen chamber.

Results

The specimens included in this study fall into two groups: (1) a group irradiated to various neutron fluences and tensile tested at 400°C ($0.18 T_m$)*, and (2) a group irradiated to various neutron fluences and creep-rupture tested at 1100°C ($0.37 T_m$)*. For comparison, unirradiated control specimens were also tested and examined.

* T_m is the absolute melting temperature.

1. Specimens Tested at 400°C

Specimens included in this group were irradiated to fast ($E > 1$ Mev) neutron fluences ranging from 4.0×10^{18} to 1.2×10^{20} n cm⁻² prior to tensile testing at 400°C ($0.18 T_m$). During testing the specimens were held at this temperature for about one hour. Data for this set of specimens are listed in Table 1.

This series of specimens showed dramatic evidence of the build-up of defect clusters with increasing neutron exposure. The build-up is illustrated by the micrographs of Figs. 1 and 2, which show button heads and reduced sections, respectively.

Microstructures in stressed and unstressed regions of the tested, unirradiated specimen appeared significantly different. Examination of the unstressed button head showed that the microstructure initially consisted of large tungsten grains subdivided into many small subgrains by hexagonal dislocation networks, such as seen in Fig. 1(a). These networks are assumed to be composed of dislocations having Burgers vectors of $a/2 \langle 111 \rangle$, $a \langle 100 \rangle$, or $a \langle 110 \rangle$, similar to networks which have been analyzed in other b.c.c. metals⁽¹²⁻¹⁴⁾. Strain during testing caused a general degradation of these dislocation networks into randomly tangled arrays, as shown in Fig. 2(a). Both Figs. 1(a) and 2(a) show that the dislocation substructures were superimposed on a structureless matrix.

Specimens from the two lowest fluences, 4.0 and 5.9×10^{18} n cm⁻², showed microstructures basically similar to the unirradiated specimens; however, a population of very fine black dots was present in the matrix of the button heads. Figures 1(b) and 2(b) show micrographs typical of these low fluence specimens. The tiny black dots present in the button heads were estimated to be approximately 25-50 Å in average size and were present in concentrations of about 1.4×10^{16} /cm³.

The four specimens from this group irradiated to fast fluences of 3.8×10^{19} n cm⁻² or greater showed appreciable build-up of defect clusters throughout the matrix. As shown in Figs. 1(c) and 2(c), both button heads and reduced sections contained large numbers of enlarged dot clusters about 100 Å in diameter, and occasionally also resolvable loops of 200 - 300 Å diameter. This coarsening of the clusters was more noticeable the higher the neutron fluence. Cluster densities for all four specimens were estimated to be between 2 and 3×10^{16} /cm³, but these values are probably low and represent apparent saturation values arising from counting errors introduced by image overlap⁽¹⁵⁾. Since broadening of the diffraction spots and Kikuchi lines was observed in the electron diffraction patterns as the fluence increased, indicative of increasing lattice distortion, cluster densities probably also continued to increase.

In addition to the foregoing effects, the subgrain boundary dislocation networks were much less evident in the higher fluence specimens. However, this effect is ascribed to overlap by the large number of cluster images rather than to an actual depletion of the networks, since tilting showed approximately the same subgrain distribution as in unirradiated or low fluence samples. No evidence of denudation of clusters near subgrain or grain boundaries was seen.

As indicated in Table 1, this group of samples included a pair which received nearly identical fast neutron fluences of 3.8 and 3.9×10^{19} n cm⁻². However, one member of this pair was shielded with cadmium which decreased the thermal neutron fluence by approximately an order of magnitude. Although this cadmium-shielded specimen showed a somewhat lower strength and a greater degree of embrittlement than its unshielded mate, no microstructural differences could be seen in the electron microscope. The micrographs of Fig. 3 illustrate the similarity of the two specimens.

2. Specimens Tested at 1100°C

Specimens in this group were irradiated to fast ($E > 1$ Mev) neutron fluences ranging from 8.5×10^{17} to 1.5×10^{21} n cm⁻² and then creep-rupture tested at 1100°C ($0.37 T_m$). Because of the heating during testing, this series of specimens basically illustrates the effects of high temperature annealing on the radiation-produced microstructure. However, the results are probably also related to heating time, since each specimen was held at the test temperature for a different period of time, depending upon its rupture life. Data for this group of specimens are listed in Table 2.

Typical microstructures are shown in Figs. 4 and 5, showing button heads and reduced sections, respectively. Unirradiated and low fluence (5.9×10^{18} n cm⁻² and below) specimens had similar microstructures, consisting of dislocation networks in the button heads, Fig. 4(a), and tangles in the reduced sections, Fig. 5(a). No evidence was seen of dot clusters in the matrix as occurred in the button heads of the 400°C tensile specimens.

Specimens irradiated to fast fluences of 3.8×10^{19} n cm⁻² or greater prior to testing showed clusters and resolvable dislocation loops in the matrix, but in quantities considerably below those of the 400°C tensile specimens irradiated to similar fluences. Button heads contained appreciably greater numbers of the defects than the reduced sections, as can be seen by comparing Figs. 4(b) and 4(c) with Figs. 5(b) and 5(c). Concentrations of clusters and loops in the button heads of the specimens irradiated in the 10^{19} and 10^{20} n cm⁻² fast

fluence range were estimated to be approximately $10^{14}/\text{cm}^3$. The reduced sections, and button head of the $10^{21} \text{ n cm}^{-2}$ sample, contained concentrations at least an order of magnitude lower.

The average size of the defect clusters increased with fast neutron fluence. In the specimens irradiated to 3.8 and $3.9 \times 10^{19} \text{ n cm}^{-2}$, most of the defects appeared as dot clusters approximately $100 \text{ \AA}$ in diameter, with some resolvable loops approaching $300 \text{ \AA}$ diameter. In the specimen irradiated to $1.2 \times 10^{20} \text{ n cm}^{-2}$ most of the defects appeared as loops averaging $200 \text{ \AA}$ in diameter, with large loops approaching $500 \text{ \AA}$. Finally, in the highest fluence specimen, $1.5 \times 10^{21} \text{ n cm}^{-2}$, greatly enlarged loops were present. Average and maximum sizes of these enlarged loops were approximately $1000 \text{ \AA}$ and $2000 \text{ \AA}$, respectively.

Like the previous group, this group of specimens also contained a pair of unshielded/cadmium-shielded specimens which received similar fast neutron fluences but widely differing thermal neutron fluences. Although the unshielded specimen, which received the higher thermal neutron fluence, exhibited a lower creep rate and longer rupture life than the cadmium-shielded specimen, electron microscopy again failed to show any significant changes in microstructure.

A further observation in all of the samples of this group was the rather high degree of retention of some relatively intact dislocation subgrain boundary networks in the reduced sections. One of these retained networks is shown in Fig. 6. As shown in this micrograph, the networks appeared to contain higher dislocation densities than networks in the button heads. This is indicative of a rearrangement of the subgrains into orientations of greater lattice mismatch during high temperature testing.

Discussion

Unstressed button heads of the 400°C tensile specimens serve to illustrate the appearance of the as-irradiated microstructure as a function of neutron fluence. Although these specimens had received a short post-irradiation "anneal" at 400°C ($0.18 T_m$) during testing, comparison with previous work on as-irradiated single crystal tungsten⁽⁴⁾ showed that this heat treatment did not significantly alter the defect structure. The only effects possibly attributable to the 400°C heating were the observation of tiny dot clusters at lower fluences than previously reported, and the presence of a few resolvable loops in specimens irradiated to the higher fluences. Both of these effects represent somewhat more advanced stages of clustering than found for corresponding fluences in the previous work.

The observed annealing of radiation-induced defects in the button heads of specimens from the 1100°C ($0.37 T_m$) creep-rupture tests is in good agreement with previous results on irradiated single crystal tungsten heated to 1090°C⁽⁴⁾. This annealing eliminated the tiny dot clusters from the low fluence ($< 10^{19} \text{ n cm}^{-2}$) specimens, and considerably reduced the number of clusters in the higher fluence ($> 10^{19} \text{ n cm}^{-2}$) specimens. Annealing also caused the growth of the large dislocation loops seen in these higher fluence samples. Although diffraction contrast analysis of the clusters and loops found in the present study has not yet been carried out, comparison with work on neutron irradiated molybdenum^(1-3,6) suggests that they are probably interstitial. However, the presence of vacancy clusters cannot be ruled out, since such clusters have recently been found to form under certain conditions in irradiated molybdenum⁽³⁾, and have also been observed by field ion microscopy in irradiated tungsten^(16,17). Tilting experiments in the electron microscope are planned to determine the nature and crystallography of the loops in irradiated tungsten.

Microstructures of both 400°C and 1100°C tested specimens show that a threshold in radiation damage state exists between neutron fluences of 5.9×10^{18} and $3.8 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). This fluence range corresponds to the region of abrupt increase in the size and concentration of the clusters in the 400°C specimens, and to the initial appearance of clusters and loops in the 1100°C specimens. The threshold region probably represents the region over which the concentration of isolated point defects produced directly through neutron bombardment and displacement cascades reaches a level at which lattice forces begin to cause appreciable agglomeration into larger clusters.

It is significant that the abrupt change in microstructure over this fluence threshold region was accompanied by an equally abrupt change in fracture mode in the 400°C tensile tested specimens. Considerable dislocation movement occurred in the low fluence ($< 10^{19} \text{ n cm}^{-2}$) specimens, as shown by the extensive tangling seen in the stressed areas. The small dot clusters initially present in these specimens were evidently ineffective as barriers to dislocation glide, but instead were swept out by the moving dislocations, leaving a cluster-free matrix. Table 1 shows that failure occurred in a ductile manner for these low fluence specimens.

On the other hand, specimens irradiated to the higher fluences ($> 10^{19} \text{ n cm}^{-2}$) and tested at 400°C failed in a brittle manner. An initially surprising result was the failure to observe cleared pathways or channels through the defect clusters in these specimens. Such channeling, caused by glide dislocations sweeping up obstacles in the

lattice, has been seen in irradiated and strained molybdenum^(18,19). However, this lack of channeling in the present case can be explained by assuming that pinning by the high concentration of clusters in the high fluence specimens prevented dislocation movement and led to the observed brittle fracture. This conclusion is substantiated by the two micrographs of Fig. 3, both of which show segments of dislocation networks which are unusually well preserved in comparison with the usual tangled arrays after stress.

Both test series included a pair of unshielded/cadmium-shielded specimens in which fast neutron fluences were nearly identical but thermal neutron fluences were different. In both cases the microstructures of the two specimens comprising the pair were similar, in spite of the tenfold difference in their thermal neutron fluences. Since the fast neutron fluence was the same within a pair, it can be assumed that the visible defect clusters formed on irradiation of tungsten result from fast neutrons rather than from thermal neutrons. This is a reasonable assumption, since the fast neutron induced PKA densities and resulting displacement spike concentrations would be the same in both specimens.

From the data listed in Table 2, it appears that the mechanical properties are not directly related to the microstructure observed in the 1100°C creep-rupture specimens. However, the measured properties⁽¹⁰⁾ correlate well with the thermal neutron fluence in these specimens. This correlation, together with the observed similarity of microstructures within the pairs of unshielded and cadmium-shielded specimens, implies that thermal neutrons are responsible for the production of some type of defect which cannot be seen in the electron microscope, but which significantly strengthens the material.

The invisible strengthening defects are believed to be substitutional rhenium and osmium atoms, which are the primary and secondary transmutation products of the β decay of tungsten excited by thermal neutron (n, γ) reactions. During irradiation to the higher fluences included in the present study, appreciable quantities of these impurity atoms are formed in the tungsten lattice; i.e., the specimen irradiated to a thermal neutron fluence of $2.7 \times 10^{21} \text{ n cm}^{-2}$ ($1.5 \times 10^{21} \text{ n cm}^{-2}$, $E > 1 \text{ Mev}$) would contain about 2.5 percent rhenium atoms and 0.25 percent osmium atoms. Such randomly substituted impurity atoms, which are similar to tungsten in size and electron scattering power, would not be expected to be visible in the electron microscope, either by strain contrast or by structure factor contrast, but could contribute appreciably to hardening. It is also possible that tightly bound complexes consisting of these impurity atoms and point defects could be formed which might either pin dislocations and/or inhibit their migration.

Conclusions

(1) Neutron irradiation of tungsten produces defect clusters in the microstructure which grow into resolvable dislocation loops on annealing.

(2) An irradiation threshold exists between 5.9×10^{18} and 3.8×10^{19} n cm⁻² ($E > 1$ Mev), above which distinct clusters are formed.

(3) Observable defect clusters are related to fast neutron fluence ($E > 1$ Mev) rather than thermal neutron fluence.

(4) Changes in the 400°C tensile properties appear to be primarily related to the fast neutron fluence and the resultant defect clusters, while changes in the 1100°C creep-rupture properties appear to be primarily related to the thermal neutron fluence and the resultant transmutation products.

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Table 1. Tungsten Tensile Specimens Tested at 400°C

Specimen	Fluence (n cm ⁻²) ^a		Strength (kg/mm ²)		Elongation in 3.18 cm %
	Fast (E > 1 Mev)	Thermal	Yield	Ultimate	
1332	--	--	21.9	39.8	45.6
1325	4.0 x 10 ¹⁸	3.9 x 10 ¹⁹	32.4	42.4	39.6
1329	5.9 x 10 ¹⁸	4.1 x 10 ¹⁹	35.9	39.8	37.2
1331	3.8 x 10 ¹⁹	2.3 x 10 ²⁰	58.5	58.5	4.4
1343 ^b	3.9 x 10 ¹⁹	2.5 x 10 ¹⁹	54.8	54.8	0.3
1340	7.9 x 10 ¹⁹	4.9 x 10 ²⁰	72.0	72.0	nil
1334	1.2 x 10 ²⁰	7.0 x 10 ²⁰	82.7	82.7	nil

^aIrradiated at reactor ambient temperature (~ 70°C).

^bSpecimen shielded with 0.51 mm Cd.

Table 2. Tungsten Creep-Rupture Specimens Tested at 1100°C and 18.28 Kg/mm²

Specimen	Fluence (n cm ⁻²) ^a		Creep Rate sec ⁻¹	Rupture Life, Hours	Elongation in 4.54 cm %
	Fast (E > 1 Mev)	Thermal			
1391	--	--	6.39 x 10 ⁻⁶	6.23	30.3
1384	8.5 x 10 ¹⁷	6.8 x 10 ¹⁸	6.26 x 10 ⁻⁶	6.87	33.9
1383	4.0 x 10 ¹⁸	3.9 x 10 ¹⁹	3.60 x 10 ⁻⁶	12.61	28.0
1385	5.9 x 10 ¹⁸	4.1 x 10 ¹⁹	3.00 x 10 ⁻⁶	15.92	32.2
1395	3.8 x 10 ¹⁹	2.3 x 10 ²⁰	1.08 x 10 ⁻⁶	41.92	26.3
1394 ^b	3.9 x 10 ¹⁹	2.5 x 10 ¹⁹	3.58 x 10 ⁻⁶	14.64	28.0
1388	1.2 x 10 ²⁰	7.7 x 10 ²⁰	2.93 x 10 ⁻⁷	194.90	33.5
1403	1.5 x 10 ²¹	2.7 x 10 ²¹	1.08 x 10 ⁻⁸	315.41	6.6

^aIrradiated at reactor ambient temperature (~ 70°C).

^bSpecimen shielded with 0.51 mm Cd.

Figure 1. Microstructures of button heads of tungsten specimens tensile tested at 400°C. (a) Unirradiated. (b) Irradiated to $5.9 \times 10^{18} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). (c) Irradiated to $1.2 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$).

Figure 2. Microstructures of reduced areas near fracture of tungsten specimens tensile tested at 400°C. (a) Unirradiated. (b) Irradiated to $5.9 \times 10^{18} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). (c) Irradiated to $1.2 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$).

Figure 3. Micrographs of reduced sections of unshielded and shielded irradiated tungsten specimens tensile tested at 400°C. (a) Unshielded, fast fluence $3.8 \times 10^{19} \text{ n cm}^{-2}$, thermal fluence $2.3 \times 10^{20} \text{ n cm}^{-2}$. (b) Shielded with 0.51 mm cadmium, fast fluence $3.9 \times 10^{19} \text{ n cm}^{-2}$, thermal fluence $2.5 \times 10^{19} \text{ n cm}^{-2}$.

Figure 4. Microstructures of button heads of tungsten specimens creep-rupture tested at 1100°C. (a) Irradiated to $4.0 \times 10^{18} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). (b) Irradiated to $1.2 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). (c) Irradiated to $1.5 \times 10^{21} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$).

Figure 5. Microstructures of reduced areas near fracture of tungsten specimens creep-rupture tested at 1100°C. (a) Irradiated to $4.0 \times 10^{18} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). (b) Irradiated to $1.2 \times 10^{20} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$). (c) Irradiated to $1.5 \times 10^{21} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$).

Figure 6. Micrograph showing retained dislocation networks in reduced section of tungsten specimen irradiated to $3.8 \times 10^{19} \text{ n cm}^{-2}$ ($E > 1 \text{ Mev}$) and creep-rupture tested at 1100°C.

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✓ METALLOGRAPHIC EXAMINATION OF PLUTONIUM DIOXIDE MICROSPHERES

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ABSTRACT

The structural integrity of plasma fired plutonium dioxide microspheres has been investigated by metallographic techniques. The microspheres are highly susceptible to edge rounding and brittle plucking during grinding and polishing. A technique is described which eliminates these problems. Cross-sectioned, polished and etched microspheres are illustrated.

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INTRODUCTION

Microspheres of plutonium dioxide are of potential interest as the fissionable constituent of dispersion type reactor fuel materials. The term microsphere is used to describe any perfectly spherical particle with very small dimensions. Minute spherical particles have been produced by a variety of techniques such as abrasive rolling of small particles, by agglomeration of fine material on rolling followed by sintering, by the sol-gel process, and by plasma torch spheroidization.¹ All of these processes produce particles with widely varying properties. This work concerns only the microspheres produced in the inductive coupled plasma torch and the metallographic techniques employed to investigate their structural integrity.

A microsphere is formed when a rough ground feed particle is blown through a plasma, which is a volume of highly ionized gas at extremely high temperature. The particle is instantly heated to a temperature above its melting point, and the surface tension of the material causes it to assume a perfectly spherical shape. As the molten globule is ejected from the plasma, it loses its heat by radiation and instantly solidifies retaining the shape of a perfect sphere with a very smooth, shiny surface. Figure 1 is a field of PuO_2 microspheres. The nominal size range of particles produced by this technique is 50 - 150 microns.

PROCEDURE AND DISCUSSION

The metallographic examination of microspheres is inherently difficult because of the nature of the specimen. Their minute size makes them very difficult to handle, particularly within a glovebox; grinding exactly halfway into a 100 micron diameter specimen requires great care; and small hard particles present the problem of edge rounding.

In the early development of a metallographic technique, microspheres of Al_2O_3 and ZrO_2 were examined along with PuO_2 . They were mounted in Koldmount, as well as other liquid resins, and sectioned by grinding on 600 grit silicon carbide paper, followed by 4/0 emery paper, until the particles had been ground to near the centers. Extreme edge rounding was present after polishing in all cases. It was noted that the PuO_2 presented more difficulty than the other materials. Many large voids were observed in the PuO_2 microspheres and the sectioned

surfaces appeared to be porous, much like the surface of a sponge. See Figure 2.

It became apparent that we were experiencing a very severe case of brittle plucking from the surface of the particles. Why we experienced severe plucking with PuO_2 and not with the other oxide materials is still not apparent. They are all in the category of very hard and brittle ceramic materials. In addition, the thermal history of any plasma fired microsphere might be expected to contribute to the problem of brittle plucking. As the particles have experienced excursions from room temperature to at least 2500°C and back to room temperature in a fraction of a second, it is logical to expect them to be highly stressed and consequently very subject to cracking and plucking during polishing.

When brittle plucking occurs, it creates a second disadvantage. In addition to leaving irregular voids in the surface, the chips which are plucked from the surface, as well as particles which are completely dislodged from the mount, both contaminate the wheel and produce excessive scratching.

When plasma fired PuO_2 microspheres were sent to several different facilities for testing, other investigators examined them by metallography and duplicated our experience showing particles which appeared to be very porous. The need for an improved metallographic technique to examine the microspheres was quite apparent, and in subsequent work a better procedure was developed.

The first requirement for satisfactory work is the preparation of a suitable mount. An ideal mount consists of a monolayer of the microspheres at the bottom surface of the mount. The spheres should be uniform in diameter and they should be arranged in a continuous geometric field touching one another. In the initial grinding stage this arrangement enables the metallographer to observe the increasing diameters of the spheres. As they approach contact with one another, the equators of the spheres are being approached. Care must be taken not to exceed this point as the spheres will fall out of the mount. This arrangement of the spheres has best been achieved by first forming a small pool of a volatile solvent, such as methyl alcohol, atop the male portion of a one-inch diameter die. The microspheres are poured from a very small vial into the solvent. A vibratory tool is brought into contact with the outside of the die

causing the spheres to collapse into a monolayer and to assume a geometric arrangement. When the solvent evaporates, the spheres appear to adhere together and do not disperse when the mounting resin is carefully poured into the die cavity.

The best results have been achieved using amber bakelite. This is the hardest thermosetting resin employed and is relatively successful in avoiding edge rounding of the particles during polishing. It is important to cool the die to below 60°C before removing the mount as removal at higher temperature will frequently result in subsequent cracking or even shattering of the mount.

In the development of a technique to section PuO_2 microspheres, 600 grit silicon carbide paper was employed to grind to a position just short of the equator. This was followed by rough polishing with alumina to remove the scratches and the outer damaged surface. The brittle plucking which occurred during polishing was attributed to the use of the alumina, so nine micron diamond was substituted for the alumina for the rough polishing stage. This reduced the plucking, but it did not eliminate it. Dropping to six micron diamond, followed by three micron and one-quarter micron diamond polishing steps, produced acceptable results, but still not completely free of plucking.

It became apparent that the plucking resulted from deep damage induced in the particles during the silicon carbide grinding step. A diamond grinding wheel was then substituted for the silicon carbide paper. This was a "fine" grade (25 micron) in which the diamond was epoxy-bonded to an aluminum wheel. However, this was too coarse and produced even more damage than experienced with silicon carbide. Consequently, it became necessary to completely eliminate the grinding stage and to start directly by rough polishing employing diamond abrasive no coarser than six microns. This makes the polishing operation a very lengthy procedure which lends itself best to automatic techniques. Buehler Automets are used with low speed polishers employing moderate pressure and the lower range of speed.

Napless papers are used in all polishing stages instead of polishing cloths. Best results have been achieved with Politex Pre-K. The use of this type polishing paper minimizes both the edge rounding and brittle plucking. Olive oil is used in all

polishing stages as the lubricant. Carbon tetrachloride and olive oil are the only two liquids used in the glovebox for metallographic preparation. The choice of these two lubricants was based on the requirements for plutonium metal and alloy work which precluded the use of water. A non-flammable, volatile solvent and a non-volatile lubricating fluid were required, both of which had to be non-reactive with the adhesive backing of the polishing paper. In addition, the solubility of olive oil in carbon tetrachloride was a requirement as carbon tetrachloride is used as the fluid for ultrasonic cleaning between stages as well as the rinse solution.

To determine the depth to which the specimen has been sectioned by rough polishing, it is more convenient to remove the Automet specimen head, clean it ultrasonically, place a drop of olive oil on the specimen and press it against the lucite window. It is then viewed with an externally mounted stereomicroscope. The olive oil is sufficiently close in refractive index to that of the plastic to make the scratches on the surface of the mount disappear. This allows the metallographer to look below the surface of the mount to judge the depth of grinding. After polishing the specimen to the desired depth, two additional hours of polishing employing one-quarter micron diamond produces flat polished surfaces free of plucking. See Figure 3.

Polishing a specimen directly from the start with three micron diamond was also attempted although this is a very slow procedure. Polishing for approximately 20 hours produced very excellent results in which the microstructure of some of the microspheres was revealed by a relief effect. It appeared to be a very fine grain transformation product. In some cases it was eutectoidal in appearance suggesting that the plutonium dioxide was substoichiometric. This type of microstructure had not been observed previously in a sectioned microsphere, probably because of the lack of a satisfactory etching technique.

Sectioned plasma fired PuO_2 microspheres are somewhat more difficult to etch than ordinary pressed and sintered material. However, a suitable etchant was eventually found. This consists of 50 parts hydrochloric acid, 50 parts hydrofluoric acid and 2 parts nitric acid. The sample is immersed in the etchant for four hours with ultrasonic agitation during the final 30 minutes. The ultrasonic treatment removes a film from the surface of the sample and prevents its recurrence during completion of etching. Figure 4 shows one complete sectioned PuO_2 microsphere after

etching by this technique, and Figure 5 shows a view of the microstructure at high magnification.

The metallographic examination of many PuO_2 microspheres shows the occasional occurrence of central voids of varying size in the particles. The voids appear to be largely the result of porosity which remains trapped in the feed particles during melting. A longer than normal dwell time in the plasma may allow small voids to coalesce forming a single void which enlarges by thermal expansion of the atmosphere in the void before solidification of the microsphere. Particles of the pressed, sintered and ground feed material possess a fine and uniformly dispersed porosity, although in a metallographic cross-section they appear to be dense and free of voids. However, examination of the feed particles after resintering at 1600°C reveals that the fine porosity has coalesced into small spherical voids.

Consideration was given to the possibility that central voids in sectioned microspheres may have been enlarged by fracturing of material at the edges of the void during metallographic polishing. For highly damaged specimens this remains a distinct possibility. However, in cases where the surface of the sphere has been successfully polished free of plucking, no sign of fracture can be detected. Critical examination of the internal surface of a void under a high power stereoscope reveals a continuous smooth surface similar to the exterior surface of the microsphere.

Microspheres of $\text{Pu}^{238}\text{O}_2$ have also been examined by metallographic techniques. These particles are of interest as the heat source fuel form for isotopically fueled SNAP generators. No appreciable difference from $\text{Pu}^{239}\text{O}_2$ microspheres could be detected in either the appearance or the microstructure. However, a significant difference was observed in the relative ease with which the $\text{Pu}^{238}\text{O}_2$ microspheres could be sectioned by rough polishing. This may be the effect of extensive embrittlement of the material resulting from internal irradiation damage.

SUMMARY

The most successful metallographic examination of PuO_2 microspheres has been achieved on sectioning by rough polishing. When only a quick inspection is required, grinding on 600 grit silicon carbide paper followed by 6, 3 and $\frac{1}{4}$ micron diamond manual polishing stages will produce useful results. When a flat polished, pluck-free surface is required, the best results can be achieved by polishing on the Buehler Automet to the desired depth with 6 micron diamond followed by a final polish with $\frac{1}{4}$ micron diamond. Superior results can be achieved, when time permits, employing 3 micron diamond from the start followed by a $\frac{1}{4}$ micron diamond final polish.

REFERENCE

- ¹ L. V. Jones, D. Ofte, K. D. Phipps and P. A. Tucker, Ind. Eng. Chem., Prod. Res. Dev., 3, 78 (1964).

Figure 1 Plasma Fired Plutonium Dioxide Microspheres, 100 X

Figure 2 Cross-Sectioned Plutonium Dioxide Microspheres, 500 X

Figure 3 Cross-Sectioned Plutonium Dioxide Microspheres, 500 X

Figure 4 Cross-Sectioned and Etched Plutonium Dioxide
Microspheres, 1500 X

Figure 5 Fused Plutonium Dioxide, Etched, 4000 X

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INERT GAS GLOVEBOX METALLOGRAPHIC FACILITY
FOR RADIOACTIVE MATERIALS

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ABSTRACT

A double-faced, stainless steel glovebox, 21 feet long, has been installed and successfully operated for metallographic studies of plutonium bearing materials. Continuously flowing dry nitrogen provides an inert atmosphere, and control of the pressure in the glovebox is completely automatic and self regulating. The glovebox is divided into eight double bays which contain a specimen mounting press, low speed grinders and polishers, vibratory polishers, ultrasonic cleaners, and facilities for chemical, electrolytic and cathodic etching. A B&L Dynazoom metallograph is mounted inside the glovebox with the trinocular eyepiece pod extending to the outside through a bellows seal. The design and operation of the facility are described.

*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract AT-33-1-GEN-53.

A glovebox line designed for metallographic work with plutonium has been installed and operated successfully. As there is no standard metallography glovebox design, the features of this facility may be of interest to others with similar metallography requirements. The intent of the design was to provide a glovebox facility suitable for metallographic work with plutonium or with other radioactive or reactive materials; to provide complete facilities for etching, examination, and photography without removal of the specimens from the glovebox; to provide sufficient space to allow work by several metallographers simultaneously; and, finally, to provide all of these facilities at a minimum cost.

The design of the facility incorporated many features that were found to be desirable in earlier experience. The glovebox was fabricated by a commercial vendor and installed by plant engineering service groups. Figure 1 is a picture of one side of the glovebox line. It is a double-faced line with 21 linear feet of working space on each side. It was constructed completely of stainless steel as it is considered a permanent type facility with access for maintenance and for replacement of equipment.

Continuously flowing dry nitrogen is employed for the glovebox atmosphere. Since it is completely adequate from the standpoint of the inert quality required for the atmosphere, this avoids the cost of gas recirculating and drying equipment as well as the floor space requirements for the equipment. This provides an atmosphere control not relying on any mechanical equipment and, as a result, free of maintenance and down-time. Dry nitrogen is flushed through the boxline at the rate of 12 cu. ft. per hour. This produces a total atmosphere change about $1\frac{1}{2}$ times per day.

Figure 2 is another picture of the facility looking at the back side of the boxline from the opposite end. In the foreground is a glovebox containing a metal lathe. This glovebox is connected to the metallography glovebox through a T-shaped passbox that permits passing material in from the outside or between the two glovebox systems.

The main exhaust header can be seen overhead. It travels up and down the length of the boxline three times providing more than 60 ft. of length before it disappears through the ceiling and connects into the main exhaust system well upstream. This provides a very long and difficult path for back diffusion of oxygen and moisture. A valve near the end of the exhaust header is used to throttle the exhaust gas in order to maintain the exact desired negative pressure in the boxline. This is normally maintained at about 3/4-inch of water negative to room pressure.

Control of the pressure in the boxline is completely automatic and self regulating, and the system is adequately protected by safety features to prevent accidental overpressurization or evacuation of the box. Pressure sensing switches control solenoid valves in the main supply and exhaust lines. Additional pressure sensing switches actuate solenoid valves in auxiliary supply and exhaust lines to maintain the desired pressure range. This prevents pressure change which might result from slight unbalance between supply and exhaust or from "in and out" movement of the gauntlets. A single electric circuit controls all of the pressure switches and solenoid valves. In emergency situations such as accidental overpressurization of the glovebox, power failure, or loss of nitrogen supply, all valves close isolating the system. When the trouble has been corrected, normal ventilation is resumed automatically.

Each of the double-faced bays of the boxline is separated by sliding doors which form partitions between the bays, and each bay of the boxline has its own separate supply and exhaust line for ventilation. This prevents pressure buildup in the boxline and enables normal ventilation with all the sliding doors closed. The incoming gas is supplied at 2 psi pressure and passes through small flow-meters. This permits uniform ventilation of each bay. The exhaust line from each bay contains a small filter, the same type which is used in an ordinary respirator, to prevent radioactive contamination from being carried into the exhaust lines upstream.

The bay on the end of the metallography line adjacent to the lathe glovebox is a general workshop area which contains a vise and a specimen mounting press. The normal movement of specimens starts in this bay and proceeds down the boxline where finer abrasives are used in each successive bay. The second bay is used for fine grinding; the third bay is used for rough polishing; and the fourth bay is used for fine polishing. In these three bays Buehler Automets are used along one side of the glovebox,

and the opposite side contains facilities for hand grinding and polishing. The fifth bay contains two Buehler Vibromet polishers which are used for rough and fine polishing. A bench metallograph is contained in the next bay of the system with the trinocular eyepiece pod extending to the outside through a bellows to facilitate examination and photography of specimens. The final two bays of the system are used for etching. A cathodic etcher is installed on one side of the glovebox, and on the other side a completely enclosed, double-width bay is used for chemical and electrolytic etching. The atmosphere of the chemical etching bay is maintained separate from the remainder of the system to prevent contamination of the entire atmosphere with acid vapor and moisture from the etchants.

As the metallography facility is quite long, passing samples along the line can sometimes be an annoying and time-consuming chore. A low cost sample conveyor is employed to ease this task. This is a miniature electric train which is now a standard tool for metallography.

Figure 3 is an end view of the metallography glovebox line showing the passboxes which open into the two etching bays. These passboxes are evacuated and backfilled with inert gas during each pass-through to avoid introducing air to the glovebox atmosphere. To prevent a spread of radioactive contamination into the room atmosphere each time an outer passbox door is opened, an exhaust system connected to each passbox is activated when the outer passbox door is opened. Air is swept into and through the passbox as long as the door remains open. A Health Physics continuous air monitor is suspended overhead to detect any possible escape of radioactive contamination.

Figure 4 is a view of the general workshop bay. The tools are suspended from hooks or placed on shelves which are located wherever possible throughout the glovebox to keep materials off the floor. Both the specimen mounting press and the vise are mounted on flat metal plates. They can be pulled forward for convenience, shoved completely aside to clear the floor, or positioned under floor clamps which hold them securely for normal use.

The majority of the bays of the glovebox, such as the one shown in Figure 5, are 30" wide x 48" deep. This photograph shows the equipment used on one side of a polishing bay. A low-speed polisher, flush mounted in the floor, is operated by a foot switch. Attached to the polisher is a Buehler Automet. The

specimen head fits conveniently into the cylindrical stainless steel tank of the ultrasonic cleaner. The tank can be pushed back and forth for use on either side of the bay. The power supply for the ultrasonic cleaner is situated on top of the glovebox, but the control switches are mounted inside the bay on both sides. Carbon tetrachloride is employed as the cleaning solution, and it is also used as a lubricant for grinding and as a rinse solution. Olive oil is the only other liquid used inside the glovebox, and it is used very sparingly as a polishing lubricant. The drain ports of all the polishers are plugged tightly as disposal of the waste solutions occurs by evaporation.

Figure 6 shows the manner in which the Buehler low-speed polishers are adapted to the glovebox to form a leak-tight seal. The polishers are flush mounted inside the glovebox although the free standing polisher is employed rather than the flush mounting model. The polisher rests on a rubber mat on an adjustable support plate which holds it firmly against the bottom of a shallow well that is an integral part of the glovebox floor. The flanged bowl of the polisher is positioned inside the well and bolted through the floor to the base of the polisher. Neoprene gaskets on both sides of the floor of the well effect a leak-tight seal. The vent ports of the polisher housing are plugged tightly to complete the leak-tight installation.

If one of the polishers should have to be replaced because of mechanical failure, the portion which would have to be replaced would be uncontaminated and easily accessible from the outside. The changeover could be made without exposing room atmosphere to the highly contaminated glovebox atmosphere.

The installation of two Vibromet polishers in one bay of the glovebox was made with little confidence that they would remain useful on a permanent basis, so the precaution was observed of providing wells in the floor of that bay for conventional polishers. It would not be difficult at any time to remove the Vibromet polishers and to install flush-mounted, low-speed polishers. Covers over the floor wells are sealed tightly providing a continuous flat surface in the bay. The Vibromets are free-standing over these covers. It has been found that the Vibromets can be operated without disturbing the use of the bench metallograph for photography in the adjacent bay.

Figure 7 is an outside view of the glovebox showing the chemical etching bay. Positioned on top is a combination AC-DC etcher which is a home-made unit. Commercially available etchers did

not meet the maximum voltage requirements, so this unit was built at a modest cost. A Magnahelix gauge which indicates the pressure within the bay is also shown in this picture. Next to it is the power supply for the ultrasonic cleaner, and in the right foreground is a stainless steel funnel and valve assembly which permits reagents to be poured directly into the glovebox into permanent reagent bottles. If reagents were passed in through the passboxes in reagent bottles, this would produce an accumulation of contaminated bottles which would have to be disposed of by bag-out procedures.

Figure 8 is an inside view of one side of the chemical etching bay. The desired voltage for AC or DC etching is set in advance on the power supply. The metallographer then activates the etcher from inside the bay merely by flipping a line switch. The only opening between this etching bay and the remainder of the glovebox facility is the small door on the extreme right through which the metallographic samples are passed.

The power supply and vacuum equipment of a Numec Model 4CVG cathodic etcher are located outside the glovebox below the cathodic etching bay. Figure 9 shows a small belljar which constitutes the etching chamber. This is the only portion of the cathodic etcher inside the glovebox. If this belljar were accidentally broken when the vacuum pump was running, the vacuum pump would suddenly start to evacuate the entire glovebox. To make certain that this cannot happen, the vacuum pump exhaust line is directed through a filter, to take out oil vapors, and back into the glovebox. This assures that the glovebox pressure would remain unchanged.

Figure 10 shows the method of installation of the bench metallograph. This is a B&L model which was chosen because of its convenient size and shape and its low cost. It is considered to be an expendable item. The unit sets on a rubber pad on top of a support rack which has adjustable legs so that it can be levelled and positioned accurately.

The metallograph was modified slightly to enable adapting in this manner. The lower portion of the eyepiece pod was a cylindrical sleeve which fit the metallograph housing. This sleeve was replaced with a casing of reduced diameter, and an additional sleeve was interposed containing a sealed optical glass plate to provide a gas-tight seal. The top of this sleeve was welded to a flat plate containing an outer circular flange to which the vinyl bellows could be secured completing

the radiation barrier.

Figure 11 is a view of the outside portion of the metallograph. The camera ordinarily supplied with this metallograph did not meet the requirements for polaroid photography as well as 4 x 5 sheet film. So the assembly was completed by adapting an eyepiece extension tube, a Leitz widefield eyepiece, and the prismatic bar, bellows and camera from a Leitz Aristophot microscope. The support bracket for the bellows and camera contains motion adjustments in three directions as well as a tilt adjustment to allow precision alignment of the bellows and camera with the microscope.

The vinyl bellows which serves as the radiation barrier is secured on the outside against a grooved plexiglass flange incorporated in the inclined plexiglass window of the glovebox. Large neoprene O-rings hold the plastic sheet firmly in the grooves of the flange. When the camera bellows is raised, the eyepiece pod can be lifted out of the metallograph housing without breaking the radiation seal. The metallograph can then be moved aside within the glovebox for maintenance or adjustment as desired.

If the vinyl bellows were to be torn or punctured it could be replaced easily. The tear would first be repaired hastily with plastic tape to avoid pulling excess air into the glovebox. Then, in a manner similar to a normal gauntlet change, a new vinyl bellows would be installed and the torn bellows removed. The changeover could be completed without pulling air into the glovebox and without introducing radioactive contamination to the room atmosphere.

Figure 12 is a photograph of the top of the glovebox over the metallograph bay showing the access route provided for the removal of inoperative large equipment and for replacement with new equipment. The sliding doors between bays of the glovebox were made large enough that any of the large equipment, such as the mounting press, the Vibromet polishers, or the bench metallograph, could be moved from one bay to another. Since there was no available wall space in the glovebox for an access port, one was provided on the top. This is a 22" diameter opening with a grooved flange about the top - much like an oversized gauntlet port. Using very large vinyl bags, new equipment can be lowered into the glovebox or old equipment can be bagged out while continuously maintaining a radiation barrier.

Installing the access port on top of the glovebox prohibited the use of a top window and fluorescent light for illumination as in all the other bays. To provide illumination for this bay a clear plexiglass cover was clamped over the access port, and the circular fluorescent lighting fixture shown in this picture rests on top of the plexiglass cover and illuminates the bay adequately.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Attendees

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R. D. Bucheit, Battelle Memorial Institute
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