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PREPARATION OF REPLICAS
FOR ELECTRON MICROSCOPY OF
IRRADIATED CERAMIC FUELS

by

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ABSTRACT

A technique for preparing replicas of irradiated uranium-plutonium dioxide nuclear fuel is described. Metallographically polished and etched specimens can be replicated by using a combination of in-cell and out-of-cell procedures. In addition, a technique is described whereby preselected, small, accurately locatable areas can be fractured and replicated. This latter technique is useful in determining fission-gas-bubble distributions as a function of radial position in the irradiated fuel. This technique has been successfully applied to metallographic specimens from experimental mixed-oxide fuel elements irradiated in EBR-II.

I. INTRODUCTION

Increased interest in experimental information relating to microscopic mechanisms operating in nuclear fuels, which is necessary for understanding their behavior, requires the use of more sophisticated experimental methods. Electron microscopy employing observations of both surface replicas and thin sections is one such technique being used to great advantage in the study of nuclear materials. This report describes a technique now being used in the Fuels Performance Group of the Materials Science Division. This technique involves the preparation of replicas of polished and etched surfaces and fracture surfaces on metallographic specimens of irradiated ceramic fuels. The technique is at present being employed in the study of irradiated (U,Pu)O₂, but can be used with any fuel of interest.

II. EXPERIMENTAL PROCEDURE

The procedure to be described is a two-stage replica technique that follows partially from one previously employed at ANL for the examination of carbide fuels.¹ Several steps are involved in the preparation of the

replicas, general procedures for which can be found in the literature.^{2,3} The formation of the initial impressions on replicating tapes and a preliminary cleaning step are carried out remotely in the Materials Science Division Alpha-Gamma Hot Cell, and most of the remaining steps, such as additional cleaning and dissolution of the tapes, are performed in a fume hood located in a controlled laboratory.

The process begins in the alpha-gamma hot cell with either a metallographically mounted, polished, and etched specimen or a mounted, polished, and etched specimen containing fracture craters that have been produced in preselected areas of the fuel. (The production of the fracture craters is discussed in detail later in this report.) A pool of acetone is deposited on the specimen surface and is held there by the action of surface tension. A strip of acetyl cellulose tape* (0.08 mm thick) large enough to overlap the specimen mount on all sides is then applied to the acetone-covered surface. As the acetyl cellulose tape is softened by the acetone, it gradually displaces the acetone, which evaporates, and conforms to the surface features of the specimen forming the replica. The plastic tape is allowed to harden fully (~15 min) and is then stripped from the specimen surface. This process is repeated twice more to clean the specimen surface. These first three tapes are discarded, and several more tape impressions are made. Following stripping, the plastic tapes are ultrasonically cleaned in a solution of 7 vol % HNO_3 (concentrated) and 5 vol % HF (concentrated) in distilled water to remove as many adhering particles of fuel as possible. At this point, the partially decontaminated plastic tapes are removed from the alpha-gamma hot cell and transferred to a fume hood.

In the fume hood the plastic tapes are trimmed to remove the excess plastic from the specimen impressions. Additional cleaning steps are carried out until the α and β - γ activities are reduced to a fixed level. The cleaning steps are limited to 20 min each to prevent ultrasonic heating of the cleaning solution and any possible attendant changes in the replicas. Total cleaning times range up to about 2 hr for a set of tapes, and the levels of α and β - γ activity range from 1200 to 7000 d/min and 10 to 100 mR/hr, respectively. After cleaning, the tapes are flattened by heating between glass slides at a temperature not exceeding 80°C for ~30 min.

The cleaned and flattened replica tapes are mounted, impression side up, on glass slides and shadowed with a Pt-20% Pd alloy. The shadowing is carried out at 10^{-5} Torr, and a source-to-specimen distance of 4 in. is used. Replicas of polished and etched surfaces are shadowed at 30°, whereas replicas of specimens containing fracture craters are shadowed normal to the polished surface. A vertical deposition of carbon is applied

*The trade name of the acetyl cellulose, manufactured by Oken Shoji Co., Ltd., Tokyo, Japan, is Bioten R.F.A.

after shadowing. The carbon deposition is performed under the same conditions of vacuum and source-to-specimen distance as is the shadowing operation.

A layer of paraffin is deposited on the shadowed and carbon-coated replica surface by lowering the replica surface briefly into a pool of molten paraffin. The pool of molten paraffin is formed on the top of a flat-ended aluminum cylinder placed on a hot plate; the diameter of the cylinder is the same as the diameter of the specimen impression. The paraffin coating provides support for the fragile platinum-palladium-carbon replica during subsequent dissolution of the plastic tape. The tape expands during dissolution, and without the support of the paraffin layer the replica would be destroyed.

At this stage in the process, a stereomicroscope is used to examine the paraffin-coated replicas through the glass slides on which they are mounted. This allows the different structural regions of the mixed-oxide fuel specimens or the fracture craters to be located accurately on the replicas. Small pieces ($\sim 1/16$ in. square) containing an area of a particular structural region, or a single fracture crater, are cut from preselected positions on the paraffin-coated replica. The small pieces are then mounted, plastic side down, on 0.125-in.-diam copper grids using acetone to produce a slight dissolution of the plastic to fix the pieces to the grids.

The next two steps in the procedure involve slow dissolution of the plastic tape, followed by slow dissolution of the paraffin support layer, leaving the platinum-palladium-carbon replicas settled on and fixed to the copper grids. In our opinion, both the tape and the paraffin are best dissolved by using a modification of a technique described by Beals and Bigelow.⁴

Fig. 1. Stainless Steel Mesh Basket and Basket Holder with Paraffin-coated Replicas. Neg. No. MSD-160055.

Two to four of the cut and grid-mounted replica tapes with paraffin support layers are placed in a wire-mesh basket of variable design,^{5,6} as shown in Fig. 1. The basket is mounted on a horizontal cold finger (water cooled) in a reflux condenser column, as shown in Fig. 2. The solvent used to dissolve the tape is placed in a flask at the bottom of the column and brought to a boil with an electric heater. The solvent vapor rises in the condenser column and condenses at the cold finger, bringing the solvent into contact with the plastic tape through the action of surface tension. In this manner, the plastic tape is dissolved first.

Obviously, the solvent used for dissolving the tape must not dissolve the paraffin. After the plastic tape is dissolved completely (up to about 1 hr), a different solvent is placed in the boiling flask, and the process is repeated to dissolve the paraffin (up to 1 hr). Acetone is the solvent normally recommended for dissolving the acetyl cellulose tape; however, exposure to irradiation and prolonged cleaning in the acid solution tends to make the tape insoluble in acetone. If the acetyl cellulose tape is found to be insoluble in acetone, dimethyl formamide can be used with excellent results. The higher boiling point of dimethyl formamide usually requires some form of additional cooling of the condenser column to prevent melting of the paraffin. The paraffin is dissolved in xylene.

(a) Side view of cold finger.
Neg. No. MSD-160056.

(b) Enlarged view of cold finger with basket holder and basket in place for dissolution of tape. Basket holder is inverted for dissolution of paraffin. Neg. No. MSD-53816.

Fig. 2. Reflux Condenser with Stainless Steel Mesh Basket Mounted on Cold Finger, Which Is Not Inserted in Column. Flask and heater are in place.

Dissolution of the paraffin completes the preparation of the replicas, and they can be removed from the condenser column and introduced into the electron microscope for examination.

An important variation of the technique of producing replicas of metallographically polished and etched specimens has been developed that allows the replication of accurately locatable fresh fracture surfaces in small areas of irradiated mixed-oxide fuels. Replicas of metallographically polished and etched specimens are adequate for detailed observation of general structural features, such as grain boundaries and subgrain boundaries, but are not suitable for the determination of fission-gas-bubble distributions. Polishing and

etching the specimens produce disturbed surface material and enlargement of existing gas bubbles, as well as inclusion pullout and etch pitting. Bubble-size distributions determined under these conditions are open to serious question. A clean fracture surface provides conditions more suitable to the determination of fission-gas-bubble-size distributions. Small (~ 0.03 -in.-diam) fracture craters are produced in selected areas of previously prepared metallographic specimens by a vibratory impact technique. The fracture craters are produced by bringing a vibratool with a fine point into contact with the specimen at any desired point. Figure 3 shows the apparatus employed. The vibratool is mounted on a three-dimensional translational micromanipulator, which is, in turn, secured to the horizontal portion of the stand. The specimen is magnetically secured to the vertical portion of the stand. The procedure is carried out remotely in the alpha-gamma hot cell while the specimen is viewed through a magnifying telescope. After the fracture craters have been produced, a partial-composite low-

Fig. 3. Apparatus for Production of Vibratory-impact Fracture Craters in Irradiated Ceramic Fuels. Neg. No. MSD-160057.

magnification photomicrograph is made of the portion of the fuel specimen containing the fractures, including the fuel-to-cladding interface. This allows the radial positions of the craters to be determined accurately. Following the production of the fracture craters, replicas are made as described previously.

III. RESULTS AND DISCUSSION

The technique described in this report has been successfully applied to several metallographic sections from irradiated mixed-oxide fuel elements. Both polished and etched surfaces and surfaces containing fracture craters have been replicated and examined. Figure 4 shows a partial composite of a transverse metallographic specimen from a fuel element that was irradiated in EBR-II. To be noted here are the fracture craters (irregularly shaped black areas). To establish the location of high-magnification electron micrographs taken of replicas of the fracture craters, a composite was made from a series of low-magnification electron micrographs (100 to 200X) of the fracture crater under study. Corresponding points on this and the optical composite can then be identified and their radial positions established accurately. The radial locations of the high-magnification electron micrographs are then established by locating these high-magnification areas on the low-magnification composite. Figure 5 shows electron fractographs

Fig. 4. Partial Composite of a Transverse Metallographic Specimen from a Fuel Element That Was Irradiated in EBR-II. This composite shows the location of four fracture craters in the fuel, as indicated by arrows. Mag. 20X. Neg. No. MSD-160058.

(a) 0.045 in. from fuel surface. Mag. 1300X.
Neg. No. MSD-170001.

(b) 0.056 in. from fuel surface. Mag. 1300X.
Neg. No. MSD-170002.

Fig. 5. Electron Fractographs of Two Areas in the Columnar Grain Region of Mixed-oxide Fuel Element Shown in Fig. 4. The direction of the central void is indicated by the arrows. Both areas were taken from the replica of the fracture crater just to the right of center in Fig. 4.

of two areas in the columnar grain region of the fuel element. Both intergranular- and transgranular-type fractures are observed. Fission-gas-bubble morphologies, size distributions, and number densities are derived as a function of radial position in the fuel from such micrographs.

In general, the technique can be applied to any irradiated fuel material of interest; however, the selected area replica fractography is naturally limited to brittle fuels. The replica recovery rate using this technique is greater than 90%.

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