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Nuclear Metals, Inc.
West Concord, Massachusetts

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Technical Papers of the Fourteenth
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AN IMPROVED METHOD OF ETCHING BY ION BOMBARDMENT

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Two applications of etching by ion bombardment are described: (1) etching of refractories and cermets, and (2) etching of metals. In the first case, the electrical nonconductors are made conductive by virtue of a surface coating of metal sputtered from a metal gauze covering the specimen; subsequent etching and redeposition in etching of the specimen surface. In the second case, UHF excitation is used to permit high etching rates at extremely low gas pressures. The equipment, methods, and results achieved are discussed.

Ion bombardment as a method for etching metals has been described by several authors. ^(1,2) Although the utility of ion bombardment for developing the microstructure of specific metallic systems has been conceded to be superior to conventional chemical and electrolytic etching methods in particular instances, widespread utilization of the technique has not as yet occurred. Extensive use of the technique is made at our laboratories for both radioactive and non-radioactive bodies.

Recent interest in the use of uranium and thorium oxide type fuel elements for nuclear reactors necessitated metallographic studies on such materials; ion bombardment as an etching method was employed and proved quite satisfactory. A logical extension of this study was a determination of the general applicability of the etching method to refractories and cermets. This paper describes the etching procedure and apparatus used and illustrates the utility of ion bombardment in the field of refractories and cermets.

The relative advantages of any given etching method over others depends to a large extent on the particular material to be examined as well as the microstructural information desired. If a large variety of microstructural information for many different types of specimens is required, the number of etching solutions and procedures becomes quite large. This situation is further complicated in that specimens prepared for optical microscopy are frequently unsatisfactory for electron microscopy. A simple, universal etch for all materials would be highly desirable. Ion

bombardment approximates such a universal etch. If a specimen is made the cathode in a chamber containing an inert gas such as krypton at a pressure of 40 microns of Hg, and if a DC voltage of the order of 4000 volts relative to a grounded anode is applied to the electrodes, a glow discharge will occur. Positive ions from the inert gas are accelerated to the cathode. The bombarded surface atoms of the cathode are ejected as a function of their energy states. A modification of this basic etching procedure, namely, the incorporation of VHF excitation to increase ionization and permit etching of specimens at pressures as low as $1\ \mu$ Hg, has led to an improved etching procedure for routine laboratory use. Normally, sputtering or etching is relatively slow, but it can be accelerated by increasing the voltage, increasing the gas pressure or by reducing the area of the specimen and cathode with insulating shields. As indicated by Penning and Moubis, the incorporation of a magnetic field in the chamber will increase the ionization.⁽³⁾ This principle has been applied to the etching of metallurgical specimens and permits etching at appreciable rates at much lower gas pressures.⁽⁴⁾

The etching chamber as it is used in our laboratory is shown in Fig. 1. The chamber consists of a demountable Pyrex glass chamber which makes a vacuum tight seal with a water cooled aluminum or zirconium cathode equipped with an O-ring. A threaded aluminum disk, the anode is attached to a tungsten wire sealed through the top chamber wall. The volume of the etching chamber is about 300 cc. The small size is convenient from the standpoint of cleaning, assembly and evacuation. As indicated on the Figure, A is the 0-5000-vDC power supply, B is the vacuum system and F is the rare gas inlet to the chamber E. The chamber is 2-inch Pyrex brand glass pipe with the flange ground flat to affect a vacuum seal with the cathode C by means of the O-ring. The polished sample is indicated as K with the collecting shields at H. The position of the coupling electrodes to 165-Mc VHF generator⁽⁵⁾ is indicated with G. In a typical application the polished specimen is placed on the cathode, the etching chamber is evacuated and the VHF generator with coupling electrodes on the outside of the etching chamber is turned on. The vacuum system is then valved off and krypton gas is permitted to flow into the evacuated chamber at a rate of $13\ \mu$ liters/min. As soon as the glow discharge initiates, at a pressure of $15\ \mu$ Hg, the vacuum valve is opened to exhaust the krypton and dislodged impurity gases. When the pressure has returned to a few microns the outgassing or cleaning stage is completed and the high voltage is applied across the anode and cathode. Successful etching can be carried out at 3,000 volts at a pressure of $3\ \mu$ with 2.6 ma current. The incorporation of VHF offers several advantages: (1) the high frequency field, 165 Mc, increases the number of rare gas ions for a given pressure of the gas; as a consequence, etching can be conducted at high-current densities but at much lower gas pressures; (2) etching at low gas pressures reduces redeposition on the surface of the sample; (3) for a given applied voltage, current densities for a sample can be increased by the use of insulator shields to values as high as $1\ \text{ma/cm}^2$; (4) contaminants adsorbed on the system

and specimen are rapidly removed by the combined action of the VHF excitation and the vacuum pumps before the high voltage is applied for etching. With some experience the depth of the etch can be determined by the amount of material which deposits on the quartz shields. When sufficient material has been removed from the specimen surface, the rare gas flow is stopped, voltage turned off and the specimen under vacuum is cooled for a period of ten minutes. This procedure applies to materials which have some electrical conductivity such as metallic specimens or cermets. For non-conductors such as porcelain, some modification in apparatus and procedure is necessary. In the latter case the non-conducting sample is placed on the cathode and a small 200 mesh stainless steel gauze is placed on the specimen surface and makes contact with the cathode. The function of the gauze is to attract the cascading ions which in turn pass through the screen openings and bombard the specimen. During etching, a very thin gray metallic film forms on the surface of the porcelain not covered by the gauze. The film arises from the sputtering and redeposition of material of the screen. As a result of electrical contact between the gauze and the sputtered film, the specimen surface becomes cathodic and does etch. The etching procedure is modified slightly in that VHF can be used to outgas the non-conducting sample but the excitation must be turned off during etching and as a result the actual etching is carried out at higher pressure, that is 50 μ . The high gas pressure is required to reduce the free mean path of the sputtered atoms of the screen which form the conducting layer. Should the excitation be turned on with such high gas pressures the sample would be heated excessively.

Optical examination of the etched specimen can be conducted with bright field or polarized light. The relief or topographical differences which develop on the cathode surface demark differences in phases, orientation, deformation bands, and the like. In contrast with most chemical and electrolytic etchants, ion bombardment produces a clean surface, free of stains or corrosion products. The inherent advantages of ion bombardment over normal etchants assume greater importance in the microscopic study of radioactive specimens. Spread of radioactive contamination is confined to the etching chamber components; the usual chemical corrosion of equipment located in the necessary enclosures is also avoided. Since the surfaces of ion etched specimens are clean, and show microstructural relief, replicas of an etched specimen made by conventional methods are suitable for both optical and electron microscopy. The optical micrographs in Fig. 2 and 3 were obtained with bright field illumination. The electron micrographs were obtained from positive carbon replicas and pertain to the very same specimen surface portrayed by the optical micrographs. The interpretation of the microstructures is not a prime objective of this paper. However, the similarity in the microstructure developed by ion etching and by proper chemical or electro-chemical etchants is obvious.

In summary, then, the advantages of ion etching over conventional etchants

for optical and electron microscopy have been described. The main attribute of ion etching is that one type of apparatus and procedure provides a simple means for etching a variety of materials, electrical conductors and non-conductors, for subsequent optical and electron microscopy. The incorporation of VHF excitation to the etching procedure offers additional advantages to the technique.

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Fig. 1 - Chamber for etching by ion bombardment. (A) 0-to-5000-v DC power supply; (B) vacuum system; (C) water cooled cathode; (D) anode; (E) chamber, 2-inch Pyrex brand glass pipe; (F) rare gas supply; (G) coupling electrodes to 165-Mc VHF generator; (H) Pyrex shield and collector; (J) Neoprene O-ring; (K) specimen.

Fig. 2 - The microstructure of refractories revealed by ion etching.

- Left - Uranium Dioxide. A: As polished-250X; B: As etched-250X; C: Electron micrograph-2000X. Note the development of grain boundaries and the shallow spherical depressions.
- Center - Aluminum Oxide. A: As polished-750X; B: As etched-750X; C: Electron micrograph-8000X. The smooth aluminum oxide particles are imbedded in a matrix of refractory oxides.
- Right - Porcelain. A: As polished-750X; B: As etched-750X; C: Electron micrograph-8000X. The presence of aluminum oxide and mullite particles in a glassy, vitreous matrix is revealed.

Fig. 3 - The microstructure of cermets revealed by ion etching.

- Left - Aluminum-Aluminum Oxide (SAP). A: As polished-750X; B: As etched-750X; C: Electron micrographs of longitudinal and transverse sections-8000X. The concentration of aluminum oxide particles at the aluminum grain boundaries is disclosed.
- Center - Kentanium-K-152-B. A: As polished-750X; B: As etched-750X; C: Electron micrograph-10,000X. The large carbide particles form the continuous phase. Note the structure within each carbide particle and the dispersion of particles in the nickel phase.
- Right - Cermet III-B. A: As polished-750X; B: As etched-750X; C: Electron micrograph-8000X. Note the structure within the titanium carbide and titanium diboride particles.

METALLOGRAPHIC OBSERVATIONS AT ELEVATED TEMPERATURE

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Room-temperature metallography is limited to viewing structures which are either stable at room temperature or which can be retained in a metastable state by quenching from a higher temperature. Elevated-temperature metallography permits observations of structural phenomena as they occur.

Three factors appear to govern the ability to observe structural changes at elevated temperatures: the effect of thermal etching, the relative emissivity or reflectivity of the phases, and surface contour changes which take place during heating or cooling as a result of volume changes during precipitation or transformation. In this work attempts were made to view the allotropic transformation in pure iron, recrystallization and grain growth in pure copper, and isothermal transformation processes in several alloys.

INTRODUCTION

Observations of structural phenomena as they occur can be made by elevated-temperature metallography. Only structures which are stable at room temperature or which can be retained in a metastable state by quenching from a higher temperature can be observed by room temperature metallographic techniques. Although there appears to be a great deal of interest in elevated temperature metallography, little information has been presented in this area. Most of the published data have been concerned with ferrous alloys; (1-7) very little can be found concerning examination of nonferrous materials. (8)

A program was initiated to acquaint personnel with the performance capabilities and limitations of the Foundation's hot-stage equipment.

EQUIPMENT

The hot stage*, mounted atop the metallograph, and the cabinet containing all necessary controls for vacuum, cooling, and power are shown in Fig. 1.

* Purchased from Unitron Instrument Division of United Scientific Co.

Constructional details may be seen in a closer view of the stage with all vacuum, power, and thermocouple connections in place (Fig. 2) and in a cross section (Fig. 3). This model stage, heated by means of a tungsten wire resistance furnace, is capable of reaching temperatures up to 1100°C.

The specimen is cylindrical in shape with a diameter of $\sim 5/16$ in. and a length of $\sim 7/8$ in. One end of the cylinder is prepared for examination. The manufacturer suggested placing a slot in the sample viewing face to accept the temperature-measuring thermocouple. However, the specimen did not rest firmly on the specimen table but tended to 'ride' on small kinks in the thermocouple wire. To alleviate this difficulty, the slot was machined parallel to and near the polished face.

Although capable of being operated under inert atmosphere, the hot stage is normally run under vacuum. All work described herein was done with a pressure of less than 0.1 microns (1×10^{-4} mm Hg).

RESULTS AND DISCUSSION

The initial observation attempted was of the $\alpha \rightarrow \gamma$ (bcc $\rightarrow$ fcc) transformation in iron. During heating, no change was observed until at approximately 400°C grain boundaries faintly appeared. The boundaries became more pronounced with increasing temperature. At 600°C a fine precipitate formed and grew with continued heating, as shown in Fig. 4, suggesting that contamination had occurred. When the sample was removed and repolished (Fig. 5), the precipitate was no longer evident. Upon re-examination of the pressures recorded during the run, it was found that a pressure surge had occurred at a temperature just below that at which the precipitate was first observed. Absorbed gases had evidently been evolved from the ceramic members of the furnace and caused contamination of the specimen face. The system is now kept under vacuum at all times to minimize this effect.

Another sample of the same iron was run; the transformation was successfully observed and photographed. Fig. 6 is the structure which was evident below the transformation temperature; Fig. 7 is the structure present at the transformation temperature, 904°C measured, 910°C accepted. Note the movement of the grain boundary at the left as the small grain was consumed; also note the first trace of transformation. The old grain boundaries began to fade as new serrated boundaries became more distinct (Fig. 8). No further change took place with increased time and temperature or upon cooling.

The next observation involved a study of recrystallization and grain growth in pure copper. The sample exhibited a typically cold-worked

structure at room temperature and up to approximately 665°C , as shown in Fig. 9. At 665°C a fine-grained structure appeared (Fig. 10). Continued heating brought no further change, except to make the grain boundaries more pronounced (Fig. 11). The sample was removed from the furnace and photographed, the structure observed is shown in Fig. 12. The sample was then repolished, etched, and rephotographed, and this structure is presented in Fig. 13. Note the marked difference in grain size before and after polishing.

The iron, as well as the copper, samples had been thermally etched at temperature. A thermally etched grain boundary becomes a physical groove in the sample surface. Once this groove is formed, it persists and may not move or mend with time. Actual movement of a boundary cannot be observed; only when it is stationary is there sufficient time for thermal etching to take place. This phenomenon accounts for the observed differences in grain size seen in the copper sample removed from the furnace and repolished. The grains grew for a time, then remained stationary long enough to become thermally etched, and continued growing again. Furthermore, phenomena do not necessarily occur at the same rate on the surface of a sample as in the sample interior. The grooves left on the surface from thermal etching of the prior structure can impede the actual movement of a grain boundary which intersects the sample surface.

Two other factors control elevated-temperature observations. One is the relative reflectivity of phases present. If there is only a slight difference in amount of reflection, the structure will be extremely difficult to resolve. As changes in structure occur, changes in volume also occur. If the volume change is large enough to produce some contour variation in the sample surface, the structure will be revealed; if not, the presence of another phase may not be observed. In order to study the effects of these two factors, further experiments were conducted.

An attempt was made to study the isothermal transformation process in selected titanium alloys. A titanium-16% vanadium alloy was placed in the hot stage, rapidly heated to 750°C , and held for 30 minutes. Upon examination, the sample exhibited a mottled appearance, as shown in Fig. 14. Power to the furnace was turned off, and the sample was allowed to cool as rapidly as possible to 600°C , a temperature at which the transformation product is known to form in reasonable times (approximately 1 hour). After 3 hours at 600°C no structural change was evident. The sample was removed and repolished; the structure of the repolished specimen is presented as Fig. 15. Transformation had clearly occurred, but was not observed in the hot stage. The mottled appearance initially observed was apparently the result of precipitation of transformation product during the heating cycle. This early precipitation masked the fine transformation product which formed at 600° . Another titanium alloy (Ti-4%Cr-3%Mo),

which is known to have a much coarser transformation product, was examined next. It was hoped that if any precipitation took place during heating, the coarser isothermal transformation product might still be revealed. This sample was run with results identical to those observed for the Ti-V alloy. Some precipitation occurred on heating, causing a mottling of the structure and masking any transformation which took place isothermally.

The maximum heating rate of the hot-stage furnace is too slow to permit observations of transformation in samples such as the titanium alloys discussed above. It is possible to redesign the hot-stage furnace to permit more rapid sample heating. A system which involves heating by passing an electrical current through the specimen itself has been designed and used with great success.⁽⁹⁾

In conclusion, elevated-temperature metallography can be a useful tool. However, it has rather severe limitations, and one of the conditions stated earlier (volume change or difference in reflectivity) must be met to allow the structure to be revealed.

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Fig. 1 - Hot Stage Furnace with Controls and Accessory Equipment.

Fig. 2 - Hot Stage Furnace in Place Atop Metallograph.

1) pressure screw	10) quartz window
2) cap	11) quartz specimen table
3) gasket	12) base of lower portion
4) furnace terminal	13) water input
5) base of upper portion	14) furnace coils
6) vacuum connection	15) furnace unit
7) thermocouple	16) ceramic furnace lid
8) metal diaphragm	17) cover
9) quartz shutter	18) specimen

Fig. 3 - Cross-section of Hot Stage.

Thermally Etched 350X

Fig. 4 - Pure iron sample which was contaminated during heating, showing precipitate which formed.

Etchant 2% Nital 250X

Fig. 5 - Same sample as Fig. 4, after being removed from the furnace, repolished and etched. Note absence of precipitate.

Thermally Etched

350X

Fig. 6 - Pure iron sample at 780°C. This same structure was present at room temperature, no change had taken place up to this point which is still below the transformation temperature.

Thermally Etched

350X

Fig. 7 - Same as Fig. 6. Photographed at transformation temperature 904°C (measured), 910°C (accepted). Note movement of grain boundary at left as small grain at right was consumed by adjacent grains.

Thermally Etched

350X

Fig. 8 - Same area at 935°C, note fading of old boundaries as new serrated boundaries appear in upper right-hand corner. These new boundaries represent the same structure as in Fig. 5 and are a result of the $\alpha \rightarrow \gamma$ transformation.

Thermally Etched

350X

Fig. 9 - Pure cold-worked copper. This structure persisted from room temperature up to approximately 665°C .

Thermally Etched

350X

Fig. 10 - Cold-worked copper. Photographed at 665°C . Note appearance of grain boundaries.

Thermally Etched

350X

Fig. 11 - Cold-worked copper. Photographed at 675°C . Grain boundaries have become more pronounced.

Thermally Etched 250X

Fig. 12 - Pure copper sample, as removed from furnace.

Etchant: 250X

Fig. 13 - Same sample as Fig. 12 repolished and etched. Note the difference in grain size.

Thermally Etched

350X

Fig. 14 - Ti-16% V alloy heated to 750°C. This mottled structure persisted after cooling to 600°C and holding for three hours at this temperature.

Etchant:

$\text{HNO}_3 + \text{HF} + \text{Glycerin}$

350X

Fig. 15 - Same specimen as Fig. 14, removed from hot-stage, repolished, and etched.

NOVEL METALLOGRAPHIC UTILIZATION OF REPLICAS AND

MICROAUTORADIOGRAPHY

T. K. BIERLEIN - B. MASTEL

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A method for conducting microautoradiography and metallography on radio and chemically active materials is described and illustrated. In the case of intermetallic compound formation between uranium and AlSi, an etched specimen is coated with Saran which, in turn, is coated with NTB liquid emulsion. After suitable exposure and processing, the Saran and adherent emulsion is stripped with Scotch tape from the specimen. Bright field, reflected light examination of this stripped replica reveals the microstructural detail; polarized light examination of the stripped replica, only the tracks, the reduced silver grains in the emulsion. Correlation of the tracks in the emulsion and microstructural features on the replica is simple and unambiguous.

INTRODUCTION

Replicas of opaque specimens are customarily employed for electron microscope examinations, but relatively little use is made of replicas for optical examinations. At the 11th Metallographic Group Meeting, November, 1956 (NMI 4909 - Part 1), the use of replicas as faithful representations of metallographic surfaces, was discussed. Since that time, additional, novel applications of replicas have been made, and these applications constitute the subject of this paper.

EXPERIMENTAL CONSIDERATIONS AND DISCUSSION

The satisfactory use of replicas for microstructural examinations relies in general on the fact that relief structure on a specimen surface will be impregnated onto the replicating medium. In conjunction with development of a "universal" bright field relief etch, namely, etching by ion bombardment, it was found that the replicas very frequently yield enhanced contrast when examined with either transmitted or reflected polarized light illumination. A typical example of this polarization effect is given in Fig. 1. A uranium specimen, etched by ion bombardment, was replicated with cellulose acetate, and the replica surface was made reflecting with an evaporated thin

layer of aluminum. Bright field examination discloses the relief microstructure features, and polarized light examination discloses changes in contrast as a function of specimen stage rotation. Although the cellulose acetate is birefringent and undergoes uniform extinction when rotated under crossed polarizer and analyzer, the extinction and contrast in Fig. 1 is peculiar to the substructure impregnated on the replica surface. The resultant polarization contrast, therefore, must arise from changes in polarization during reflection from the various individual areas on the replica. Since the polarization contrast is appreciable, it must further be concluded that on a micro scale the apparently planar replica actually consists of individual areas having relatively sharp crystallographic facets - the sharper the facets, the greater the polarization change. Such faceting is usually observed by electron microscopy on specimens etched by ion bombardment.

Figure 2 illustrates the use of a "pseudo" replica, NTB emulsion. Uranium metal was contacted with molten, eutectic AlSi, cooled, and then polished, Fig. 2A. It is quite evident that a reaction between the uranium and AlSi has occurred, and that a second phase is present in the AlSi layer. Etching of the specimen removes much of the polishing flow metal, and reveals additional microstructural features, Fig. 2B. But are the narrow bands a uranium intermetallic? Microautoradiography should answer this question.

Bulk NTB emulsion which is liquid at 50 C, available from Eastman Kodak Co., was spread on the specimen, exposed, and then processed in contact with the uranium. Subsequent examination showed that the specimen was severely attacked by the photographic solutions, and that most of the microstructural features had been obliterated. If the specimen is first coated with a thin film of Saran (a single dip in five percent Saran in methyl ethyl ketone suffices), later processing of the NTB emulsion applied over the Saran will yield satisfactory results. Figure 2C shows the alpha tracks in the emulsion as well as the microstructure beneath the double layer of emulsion and Saran protective coat. However, the clarity of the specimen microstructure is reduced considerably by the tracks in the emulsion, and the clarity in the tracks is likewise perturbed by the underlying microstructure. If Scotch tape is placed on the emulsion on the specimen, the emulsion can be readily removed from the Saran coating, and the scotch tape with adherent emulsion can be examined under conditions of favorable contrast. Since the original areas of interest on the specimen were marked with a small micro-character line, and since this discontinuity was apparent on the stripped emulsion, simple comparison of alpha tracks revealed in the stripped emulsion by polarized light, Fig. 2D, can be made with the bright field microstructural features on the etched specimen, Fig. 2B.

A unique adaptation of replication and microautoradiography is illustrated by the results shown in Fig. 3. Figure 3A shows the general bright field microstructure of a specimen of uranium which had contacted molten eutectic AlSi; prior to quenching, the uranium was inserted into a M 388 aluminum can. Several technical features of interest in this micrograph should be

emphasized. Under the specific conditions of temperature, time at temperature, and concentration of eutectic AlSi used, the intermetallic layers that formed contain distinct heterogeneities, and these are the initial sites which revert to a feathery intermetallic phase rather than a relatively smooth, banded intermetallic phase. The uranium rod used, beta heat treated and then machined to proper dimensions, has recrystallized along its external surfaces. As soon as the molten near eutectic AlSi solidifies, large primary aluminum grains form at the aluminum can - AlSi interface, the coldest region, and on further cooling, large primary grains of aluminum also form along the AlSi intermetallic interface. A possible explanation for the latter situation is that silicon is preferentially consumed in the early stages of intermetallic formation, and that the AlSi, depleted in silicon, will, therefore, yield larger primary aluminum grains.

That the intermetallics can indeed spall away from the AlSi intermetallic interface is again verified by use of autoradiography, but in this case the Saran protective coating serves as the replicating medium. The technique used is the following. The specimen, after etching by ion bombardment, is coated with five percent Saran in methyl ethyl ketone, and then coated with a thin layer of Eastman Kodak bulk NTB emulsion. After a suitable exposure, ~ 70 hours, the emulsion in the specimen is processed. The specimen with adherent emulsion and Saran coating is then scribed and a narrow ribbon of the emulsion is stripped from the Saran, adjacent to the scribe cut, by means of a ribbon of scotch tape. Scotch tape is then reapplied over the specimen surface and peeled off in a direction such that the tape adhering to the previously exposed Saran layer will be stripped first. The stripped double layer together with the Scotch tape is placed on a microscopic slide and can be viewed, as was done in Fig. 3B, with bright field vertical illumination. If the illumination is simply changed to polarized light illumination, the image obtained is that given by 3C, for which good contrast of the tracks prevails. Point by point comparison of tracks and microstructural features can be made by interchange from bright field to polarized light illumination. The image contrast of the tracks, black tracks on a white background, obtained with polarized light illumination occurs only if the Scotch tape is present on the clear plastic and emulsion sandwich. That Scotch tape is essential was verified by using a thicker sheet film containing tracks as the specimen on an inverted metallograph, and slowly lowering Scotch tape onto the film. When the tape is on the film, the polarization contrast is markedly increased or decreased, depending upon the stage rotation.

A final application for replicas is given by the example in Fig. 4. At a very early stage in the study of irradiation performance of fuel containing Pu, an alloy of Pu-AlSi was irradiated. Due to lack of sufficient technical information it was not known how the plutonium was distributed in the AlSi. An attempt at determining the location of the Pu in an irradiated specimen by virtue of autoradiography of replicas was therefore made. The following reasoning applied. If the irradiated specimen is etched by

chemical means, a thin oxide layer will undoubtedly form on the specimen, and if the replica is capable of stripping some of this oxide from the specimen, it will contain in addition to the microstructural features, regions of Pu contamination. Such contamination might very likely be highest at specific microstructural regions in the replica and therefore show where the Pu was located. Accordingly, the replica was coated with NTB emulsion, exposed for 20 minutes, and processed. The micrographs of Fig. 4 indicate the extent of this contamination and indicate that Pu contamination is associated primarily with the matrix eutectic microstructure. A logical extension of this technique is to study the contamination on replicas of fracture surfaces or normal metallographic surfaces of a wide variety of irradiated materials to establish whether fission products and the like have migrated to microstructural features, for example, grain and twin boundaries. The degree of reduction in the radioactivity of the replica as compared to that of the specimen permits microautoradiography at practical exposure times.

SUMMARY AND CONCLUSIONS

Some novel features of replicas of metallographic specimens can be used to advantage. Cellulose acetate replicas of specimens etched by ion bombardment frequently show considerable polarization contrast when rotated under crossed polarizer and analyzer. This feature is illustrated for replicas of uranium. Nuclear emulsions placed in contact with a radioactive specimen and properly processed can be stripped from the specimen with Scotch tape and examined with vertical illumination under conditions of crossed polarizer and analyzer; under these illumination conditions, enhanced visual contrast of the tracks in the emulsion is achieved by the Scotch tape on the processed emulsion. Metallographic specimens such as uranium alloys and intermetallics coated with a thin layer of Saran and then coated with NTB "liquid" emulsion can be processed in the photographic solutions and chemical attack on the specimen can be avoided. If the specimen contains a relief etch, the Saran and processed emulsion can be stripped with Scotch tape simultaneously, and the microstructure shown by the replica under bright field illumination can be compared with the tracks in the Saran emulsion double layer shown under polarized light illumination. Replicas of irradiated, radioactive specimens which have "extracted" radioactive sub-microscopic contamination from the specimen can also be studied by successive bright field and polarized light illumination to determine the relationship between major contamination sites and the microstructure of the specimen.

Fig. 1 - Aluminized Cellulose Acetate Replica of Beta Heat Treated, Slow Cooled Dingo
Uranium Etched by Ion Bombardment. 75X

A: Normal bright field; B: Oblique bright field; C: Polarized light, Stage at 60° ;
D: at 80° , E: at 90° ; F: at 110° .

Fig. 2- Intermetallics Formed by Reaction of U and Molten Eutectic Al-Si

A: As polished, B.F.; B: As etched by ion bombardment, B.F.; C: Specimen with thin coat of Saran and processed liquid NTB emulsion, B.F.; D: NTB emulsion, stripped with Scotch Tape.

250X Polarized Light

Fig. 3 - Intermetallics Formed by Reaction of U and Molten Eutectic Alsi.

- A: Microstructure of a specimen showing layered and feathery intermetallics, B.F.
- B: Microstructure of a different field as revealed by a Saran protective film (the replica) and adhering NTB emulsion stripped from specimen with Scotch Tape, B.F.
- C: Appearance of the Scotch Tape stripped NTB emulsion and Saran replica shown in B under polarized light.

Etching: Ion bombardment; Magnification: 250X

Fig. 4 - Replica of Irradiated Pu-Alsi Alloy on which Liquid NTB Emulsion Has been Exposed and Processed
B. F.; 250X. HF etch.

DECREASING THE ELECTROPOLISHING TIME FOR URANIUM

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The behavior of mechanically polished uranium was studied during electropolishing to determine the times for preparing satisfactory metallographic samples. Specimens suitable for preferred orientation and microstructural examinations were obtained after 10-minutes in an orthophosphoric acid-ethyl alcohol-ethylene glycol solution, and after about 1.0 minute in a chromic-acetic acid solution. Evaluations were based on X-ray diffractometric and microscopic observations.

INTRODUCTION

A comparison of the minimum times to remove the cold-worked surface layer from mechanically polished uranium by electropolishing in (a) orthophosphoric acid-ethyl alcohol-ethylene glycol solution (usually referred to as MIT solution) and (b) chromic-acetic acid solution was desired. The chromic-acetic acid solution is under consideration as a possible time-saving substitute for the commonly employed MIT solution.

A large number of specimens are metallographically prepared at the Havens Research Laboratory of the Bridgeport Brass Co. in the course of the uranium extrusion development programs for the AEC. It was anticipated that certain planned experiments for the production of uranium slugs with improved properties for reactor service would increase the number of specimens required above the normal load. Therefore a considerable saving in metallographic preparation time could be achieved by a significant reduction in electropolishing time.

Electropolishing times of between 10-min. and 20-min. are employed for surface preparation with the MIT solution currently used at the Havens Laboratory. Mr. R. N. Thudium of the National Lead Co. of Ohio mentioned at a recent meeting that they can electropolish uranium in 1-min. or less by using a chromic-acetic acid solution. This solution has also previously been successfully employed at several laboratories for electropolishing uranium alloys.

On this basis a comparison was made of the time to electropolish uranium in (a) the MIT solution, and (b) the chromic-acetic acid solution, as described

in the following report. The electropolished surfaces were evaluated on the basis of X-ray diffraction and micrographic analyses. The X-rays penetrate only a tiny distance below the surface due to the high absorption of the rays by uranium. This results in diffraction patterns highly indicative of only the actual surface. Other solutions and techniques (e.g. interrupted electropolishing), which have been employed in attempts to reduce the electropolishing time, are not included in this investigation.

OBJECT

To determine the minimum time required to satisfactorily prepare uranium for X-ray diffraction and microstructural studies by electropolishing in (a) MIT solution and (b) chromic-acetic acid solution.

PROCEDURE

A 1.0-in. diam. extruded uranium specimen was employed throughout the investigation. The specimen had been electropolished to remove the cold-worked surface layer from previous sawing, grinding, and polishing operations. The specimen was then mechanically polished through 600-grit SiC paper, using water as a coolant, before electropolishing in each solution. The two solutions employed were as follows:

1. 5-parts orthophosphoric acid, 8-parts ethyl alcohol, 5-parts ethylene glycol. (This solution will be referred to as MIT solution). Twenty-volts and one-amp were employed with an anode-to-cathode distance of 0.5-in.
2. 1-part chromic acid (118-gms. chromic oxide, 100-ml. water), 4-parts glacial acetic acid. Twenty-volts and two amps were employed with an anode-to-cathode distance of 0.25-in. The bath was maintained at about 45° F by cooling with ice water.

Electropolishing was periodically interrupted to make the following evaluations:

1. Measurement of the amount of metal removed, employing a "ten-thousandths" micrometer caliper.
2. Microscopic examination of the surface. Photomicrographs were taken of the same grain area after each removal from the solutions.
3. Diffraction line intensity and $\text{Cu } K\alpha_1 - K\alpha_2$ doublet resolution data were obtained from a partial X-ray pattern. The diffraction lines covered were in the range, up to $105^\circ (2\theta)$, presently employed in our preferred orientation studies. The lines studied and their 2θ values were (111)- 39.6° , (040)- 63.4° , (023)- 64.8° , (200)- 65.4° , and (152)- 101.6° .

A Geiger-counter X-ray diffractometer, copper target tube (at 35-KV and 20 MA), Ni filter, and a rotating flat specimen holder were employed to obtain the X-ray patterns. The scanning speed was $1^\circ (2\theta)/\text{min}$.

DISCUSSION OF RESULTS

The effects of electropolishing time in the two solutions were as follows (the data is listed in Table I):

Metal Removal Rate

The rate of uranium removal was nearly twice as fast in the chromic-acetic acid as in the MIT solution. This is based on a comparison of the slope of the curves in Fig. 1. The initial rate for the MIT solution was relatively constant for about 15- to 20-min., and then decreased.

Metallographic Surface Quality

For the MIT solution, evidence of mechanical polishing, in the form of faint traces of directional furrows, remained on the surface after 5-min. This is illustrated in Fig. 2b (a mechanically polished surface is shown, for the purpose of comparison, in Fig. 2a). No polishing marks were apparent at 7.5-min. (Fig. 2c), where the evidence of mechanical polishing had been removed. The photomicrographs indicated no significant change in surface quality from 7.5 through 30-min.

For the chromic-acetic acid solution, an outline of the grain structure was clearly visible at 10-sec. The directional comet-tail streaks, shown at 20-sec. (Fig. 3a), were still present after 45-sec. All polishing marks were essentially removed at 60-sec. (Fig. 3b). Little further change occurred for electropolishing times up through 4-min. The quality of the photomicrographs were satisfactory in the range from 1- to 4-min., but the surface appearance after 6-min. indicates that overetching occurred (Fig. 3c).

Diffraction Line Profiles

The lattice distortion resulting from cold working is shown by the line-broadening and lack of $\text{Cu } K\alpha_1 - \alpha_2$ doublet resolution for the as-mechanically polished specimen (Fig. 4a, 4b).²

The effect of electropolishing time in MIT solution on $K\alpha_1 - \alpha_2$ doublet resolution is illustrated in Fig. 4a. Doublet resolution was fully developed in between 2.5- and 10-min. for some peaks. The (152) and (023) peaks became completely resolved at between 2.5- min. and 5-min. The (200) peak, however, was not resolved until 10-min. The depth of metal removed in the 10-min interval was 0.0005-in.

Doublet resolution commenced at between 20- and 30-sec. in the chromic-acetic acid solution (Fig. 4b). At 30-sec. the (023) peak was fully resolved while the (152) peak was partially resolved. The doublet for the (200) peak, the last peak to be resolved, was completely developed in about 45- to 60-sec.

Intensity of Diffracted X-Rays

The initial rapid increase in diffraction peak height with electropolishing time terminates in approximately 5-min. for the MIT solution, and in 1.0- to 1.5-min. for the chromic-acetic acid (Fig. 5). The initial increases in intensity, attributed to the removal of the cold-worked surface layer, are of the order of 100-pct. The smaller variations in intensity, noted after longer times, may be due to the factors such as a change in preferred orientation, and the error in recording intensity counts for the medium-coarse grain sized specimen employed. It is expected that very long electropolishing times would decrease in the intensities if excessive pitting occurred.

The minimum time for satisfactory surface preparation varied somewhat according to the criterion employed to evaluate the condition of the surface. This effect was most marked in the case of the MIT solution where an electropolishing time of 5-min. was sufficient time to remove the cold-worked layer according to the diffraction line intensity data, while 10-min. was required on the basis of α_1 - α_2 doublet resolution. Similarly, the relative change in minimum electropolishing time for the two solutions differed according to the evaluation test. The rate of metal attack appeared to be twice as fast in the chromic-acetic acid solution as in the MIT solution. However the cold-worked surface was apparently removed about five times faster according to the diffraction line intensity data (1-to 1.5-min./5-min.), and ten times faster on the basis of α_1 - α_2 doublet resolution (1-min./10-min.). In addition, all surface markings from mechanical polishing were removed almost ten times faster (1-min./7.5-min.).

Thus, substitution of the chromic-acetic acid for the MIT solution presently employed at the Havens Laboratory is recommended when a large group of metallographic specimens are to be prepared. The former requires about one-tenth the time needed with the MIT solution to satisfactorily electropolish uranium samples for preferred orientation analysis and microstructural examination. The minimum electropolishing times are based on the X-ray diffraction line intensity and $K\alpha_1$ - α_2 doublet resolution evidence for removal of the cold-worked surface layer, for the polishing conditions employed.

CONCLUSIONS

The minimum electropolishing time to satisfactorily prepare uranium for preferred orientation studies is about 1.0-min. in a chromic-acetic acid solution and 10-min. in the orthophosphoric acid-ethyl alcohol-ethylene glycol solution. The surfaces are also suitable for grain structure examination in these lengths of time.

FUTURE WORK

In relation to the data presented from the preliminary work, the accuracy of data obtained in future experiments may be improved in the following manner: employment of a slower 2θ scanning speed, higher-angled diffraction lines (in the back-reflection region), integrated intensities, and finer-grained extruded material to increase the statistical accuracy of the intensity measurements. Quantitative line-width and α_1 - α_2 doublet resolution measurements could be used to determine the amount of cold-work introduced into the surface, the depth of penetration, and the attainment of a strain-free surface.

TABLE I - METAL REMOVAL AND X-RAY DIFFRACTION DATA OBTAINED DURING THE ELECTRO-POLISHING OF MECHANICALLY-POLISHED URANIUM

A. In orthophosphoric acid-ethyl alcohol-ethylene glycol solution.

Total Electropolishing time, min.	Specimen Height, in.	Intensity of Diffraction Lines for Planes (hkl) *				
		(111)	(040)	(023)	(200)	(152)
0	0.2621	28	4.5	13	5	8
2.5	.2620	41	6	23	8	10
5	.2618	43	7	32.5	9	9.5
7.5	.2617+	42	7	30	9.5	10
10	.2616	43	7	31	10	10
15	.2613	44.5	6	28.5	9.5	11
20	.2612	45	7.5	33	9	11.5
30	.2610	48	6.5	31.5	10	12

B. In chromic-acetic acid solution.

Total Electropolishing time, min.	Specimen Height, in.	Intensity of Diffraction Lines for Planes (hkl) *				
		(111)	(040)	(023)	(200)	(152)
0	0.2595 +	37	6	17	6	6
0.17	.2595 +	43.5	8	25	6	7
.33	.2595	47	7.5	30	8.5	8
.50	.2595	50	8	32	10	8
.67	.2594 +	49	8	34.5	11.5	8
1.0	.2594 +	52	8	33	13	9.5
1.33	.2594	55.5	9.5	38	12	8
1.67	.2594	54	9	36	13	8
2.0	.2593+	51.5	9.5	36.5	12	8.5
2.5	.2593	52	7	34.5	12	9
3.0	.2593	52.5	8	33	13	8.5
4.0	.2592	56	8	34	13	9
6.0	.2590 +	58	8.5	35	11	8

*Intensity was measured as the peak height above background.

Slits: Divergence and scatter, 1° ; receiving, .003-in.

$\lambda = 1.5405 \text{ \AA}$.

Fig. 1 - Thickness of metal removed from the surface during the electro-polishing of uranium with various electrolytes.

(a) As-mechanically-polished.
U964 - A.

(b) Electropolished for 2.5-min.
U964 B-a.

(c) Electropolished for 7.5-min.
U964 B-c.

Fig. 2 - Mechanically polished uranium after electropolishing for various times in orthophosphoric acid-ethyl alcohol-ethylene glycol solution. The same grain areas are shown in each photomicrograph. 100X Polarized light.

(a) Electropolished for 0.33 min.
U964 A-b.

(b) Electropolished for 1.0 min.
U964 A-c.

(c) Electropolished for 6-min.
U964 A-n.

Fig. 3 - Mechanically polished uranium after electropolishing for various times in chromic-acetic acid solution. The same grain areas are shown in the photomicrographs of Figs. 2 and 3.
100X Polarized light.

Fig. 4a - Diffraction line profiles for electropolished uranium.

Fig. 4b - Diffraction line profiles for electropolished uranium.

METALLOGRAPHY OF BERYLLIUM OXIDE *

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This is a preliminary report on the metallographic examination of beryllia samples produced at GE-ANPD. The metallographic procedures used for preparing metallic samples can be used for BeO samples

Porosity is a major problem in microstructure interpretation. Mechanical porosity can, however, be distinguished from natural porosity. Impurities are mainly metallic.

The ultimate grain size of hot-pressed samples and sintered samples could not be correlated to fabrication times, temperatures, or pressures.

Beryllia samples nearly always have equiaxed grains; however, several samples had rod-shaped grains. In an isothermal (1500°C) test conducted in 25 hour increments, the grain sized tripled in 100 hours.

INTRODUCTION

Beryllium oxide is becoming more prominent in high-temperature reactor applications, and the need for standardized metallographic procedures for evaluating beryllia bodies is of immediate value. Therefore, this paper on metallographic preparation procedures and microstructural interpretations is submitted.

In the past year the metallographic laboratory has examined the microstructures of BeO specimens which have been produced only on a pilot plant or laboratory scale. This report represents a preliminary summary of the metallographic techniques developed to date. Methods of sample preparation and microstructural interpretations are stressed, preceded by a brief description of the prior history of the samples studied.

In view of the nature of this report, many of its conclusions are necessarily tentative. With the evaluation of more samples, some concepts may be changed. It is believed, however, that at the present state of knowledge, this report should serve as a useful guide.

* GE-ANPD Report DC 59-2-133

Fig. 5 - Variation in diffraction line intensity (peak height above background) with electropolishing time for uranium.

PRIOR HISTORY

The specimens discussed were fabricated by one of three methods, depending upon shape or ultimate density desired. The three methods are:

1. Hot pressing
2. Cold-pressing and sintering
3. Extrusion and sintering

The methods listed above are described as follows:

1. Hot pressing: The dried powder is loaded into a graphite die; then hot pressed at 3000 psi and 1700°C for one-half hour in an inert (argon) atmosphere.
2. Cold-pressing and sintering:
 - a. Powder is coated with lubricant and/or plasticizer.
 - b. Coated powder is loaded into steel die and pressed to 20,000 psi.
 - c. Piece from (b) may be recrushed to powder and (b) repeated.
 - d. Pellet of (b) or (c) is prefired in air at 900°C for 1 to 2 hours (depending on size of specimen), heating at a rate of 150°C/hr. Pellet then cooled to room temperature.
 - e. Pellet from (d) is then sintered in air or hydrogen at 1650°C for two hours.
3. Extrusion and sintering:
 - a. Powder is mixed with starch, glycerin, and water.
 - b. Mixture is extruded and vacuum (or air) dried at 110°C.
 - c. Piece is prefired in air to temperature range of 760 to 980°C.
 - d. Prefired piece is then sintered in hydrogen at 1650°C for 2 hours.

In addition to the "as-fabricated" condition, samples were studied after subsequent heat-treatments. Generally, the specimens were subjected to either or both of the following types of treatments:

1. Extended heatings at various temperatures and atmospheres to ascertain the effects on microstructure.
2. A normalizing (annealing) treatment performed by heating in air at 1370°C for one hour.

SAMPLE-PREPARATION TECHNIQUES

The metallographic procedures used for preparing metallic samples were found to be applicable to beryllia samples. The basic preparation steps,

however, required a longer time for the latter samples. The technique which has proven to be the most efficient of the various methods tried is described in the following section.

If the specimen to be examined is 100 mils or more thick, a thermo-setting phenolic resin (commercial Bakelite) is the mounting material used. If the specimen is less than 100 mils thick, the pressure required to polymerize the Bakelite will crack or shatter the sample; so a room-temperature curing epoxy resin, which requires no pressure, is used.

All grinding and polishing is done using maximum pressure on a Buehler "Automet" automatic polishing wheel. The samples are taken successively through 280-grit, 400-grit, and 600-grit silicon carbide papers using water as a lubricant. The samples are ground on each grit size twice to assure the optimum surface finish. Using water as a lubricant is of little consequence on the final surface condition of the beryllia, but it does tend to keep airborne dust to a minimum. (The entire procedure to this point takes a maximum of thirty minutes.) A very rough surface results from the grinding operations because the amount of smooth cutting is small while a considerable amount of chipping occurs.

Initial polishing is done with three-micron diamond paste on a cashmere cloth using kerosene as a lubricant. Polishing with diamond paste should be continued until all angular voids are removed.

Polishing is completed with 0.3-micron levigated alumina on a cashmere cloth using water as a lubricant. (This step requires 5-10 minutes.) With this surface finish the grains are visible, because of a slight relief polishing effect due to the difference in orientation of the beryllia grains. This surface is ready for etching.

Grinding and polishing can be done by hand using the same technique as used in the automatic polishing procedure, but requiring at least twice the time for each step.

The etchant used to bring out grain boundaries is concentrated (47%) hydro-fluoric acid. The sample is immersed in the etchant for 1-2 minutes.

MICROSTRUCTURE

For purposes of clarity, the basic microstructure will be discussed under the headings of specific and general characteristics. Specific characteristics, which include voids and impurities, are those which will be considered independent of basic fabrication methods. General characteristics, which include grain size, grain shape, and grain growth, are those which are reported in conjunction with fabrication and heat-treating conditions.

Specific Characteristics

Voids in BeO are a major problem in microstructure interpretation, since porosity can be mechanically induced. These mechanical voids are inherently angular in shape. To minimize confusion between natural and mechanical voids, continued polishing can be performed until all angular voids have been removed. (This procedure is unnecessary when the objective is to determine grain size or similar characteristics of the sample. The use of an extended polishing operation may also be limited by a low-density sample.) Natural porosity occurs, in practically all instances, as small spherical voids within the BeO grains. This criterion may be used to distinguish between natural and mechanical porosity, since mechanically-induced porosity occurs at grain junctions (sometime entire grains chip out). Figure 1 shows a poorly polished beryllia sample with a large amount of mechanical porosity, which is characterized by its angular shape. Figure 2 shows a polished surface with virtually no mechanical porosity. Figure 3 shows a sample with a large amount of angular porosity which is mechanically induced, but, due to incomplete sintering, continued polishing to improve the sample was impossible.

Metallic particles are the major impurities, or inclusions, which occur in BeO samples. These are easily distinguished from voids and matrix because of their metallic luster. Examples of metallic inclusions are seen in Figs. 4 and 5.

General Characteristics

Examination of samples which were hot-pressed by identical methods revealed that the ultimate grain size could not be correlated to hot-pressing conditions. The average grain diameter of these hot-pressed samples ranged from 14 to 72 microns. Figure 6 is a hot-pressed sample with an average grain diameter of approximately 20 microns. Figure 7 is a hot-pressed sample with an average grain diameter of approximately 75 microns. It would appear that the parent compound of the beryllia used, the calcining conditions, and the resultant particle size range of the BeO powder may be correlated with the ultimate grain size.

As with hot-pressing, sintering in the temperature range of 1600 to 1650°C produced a wide range in the average grain diameters: from 30 to 80 microns. Figure 8 is a sample sintered at 1600°C having an average grain diameter of 60 microns. In contrast to the grain size variations of samples sintered at the higher temperatures (1600 - 1650°C), samples sintered in the temperature range of 1500 - 1550°C consistently had an average grain size of 10-15 microns. These samples, however, also showed considerable porosity. This would indicate incomplete sintering at these lower temperatures. Figure 9 is a sample sintered at 1500°C, having an average

grain diameter of 10 microns. The shape of the grains in hot-pressed and sintered samples is almost always equiaxed. However, several samples observed had rod-shaped grains. The presence of rod-shaped grains could not be correlated to fabrication techniques. For example, rod-shaped grains have been noted in a sample sintered in air at 1500°C, Figure 10, a sample sintered in hydrogen at 1620°C, and a sample sintered in air at 1760°C.

To establish a grain growth trend, an isothermal test was conducted on beryllia pellets. The samples were prepared by extrusion and sintering for two hours in hydrogen at 1620°C. They were then heated at 1500°C, for 25, 50, 75, and 100 hours. The results are shown in Figures 11 through 15 and are tabulated in the following table.

EFFECT OF HEATING SINTERED BeO
AT 1500°C

<u>Time at</u> <u>Temperature</u>	<u>Grain Size</u>
0 Hrs.	36 microns
25 Hrs.	42 "
50 Hrs.	51 "
75 Hrs.	72 "
100 Hrs.	100 "

Grain growth within a sample may be non-uniform. This may be attributed to either non-uniform heating, variation in particle size, or impurity segregation. An illustration of this is shown in Figure 16.

The normalizing treatment did not appear to alter either the grain size or grain shape from the "as-fabricated" condition.

SUMMARY

Fabrication techniques for the samples examined are (1) hot-pressing, (2) cold-pressing and sintering, and (3) extrusion and sintering.

Heat-treated samples were also examined

The metallographic procedures used for preparing metallic samples can be used for BeO samples by extending the length of time for each operation. Grinding is done on silicon carbide papers, polishing with 3 micron diamond paste and 0.3 micron levigated alumina, and etching with concentrated (47%) hydrofluoric acid. All polishing and grinding is carried out on a Buehler "Automet" automatic polishing wheel.

Mechanically induced porosity can be distinguished from natural porosity since natural porosity is nearly always spherical in shape and occurs within

the grains, whereas mechanically induced porosity is always angular in shape and occurs at grain junctions. Impurities are mainly metallic and, by nature, easily distinguished from voids and matrix.

The ultimate grain size of hot-pressed samples could not be directly correlated to hot-pressing techniques. The same is true for samples sintered in the temperature range of 1600 - 1650°C. The grain size of hot-pressed samples ranged from 14 to 75 microns. Samples sintered from 1600 - 1650°C had a grain size from 30 to 80 microns. Sintering in the temperature range of 1500 - 1550°C produced incomplete fusion of BeO particles. These samples consistently had a grain size of 10-15 microns.

Hot-pressing and sintering nearly always produce equiaxed grains, however, several samples had rod shaped grains. There is no correlation between fabrication data and rod shaped grains.

In an isothermal (1500°C) test conducted in 25 hour increments, the grain size tripled in 100 hours. Also noted is the fact that grain growth is not always consistent within each sample.

The author wishes to acknowledge the assistance of Dr. R. Cooperstein and Mr. K. Lacefield in the preparation of this report.

100X

(Neg. 10524)

Etchant: HF

Fig. 1 - Illustration of a poorly polished BeO sample; cold-pressed and sintered two hours in hydrogen at 1650°C.

100X

(Neg. 12849)

Etchant: HF

Fig. 2 - A polished surface with virtually no porosity; cold-pressed and sintered two hours in air at 1600°C.

250X (Neg. 11731) Etchant: HF

Fig. 3 - A polished surface which cannot be improved; as received from Brush Beryllium Corp. (As hot-pressed).

100X (Neg. 11530) Etchant: HF

Fig 4 - A large metallic inclusion in BeO:
Cold-pressed and sintered two hours in
air at 1650°C ; normallized one hour
at 1870°C .

100X (Neg. 12986) As Polished

Fig. 5 - Numerous small metallic inclusions in BeO; Hot-pressed at 3000 psi and 1700°C for one hour.

100X (Neg. 12845) Etchant: HF

Fig. 6 - BeO with a grain size of approximately 20 microns; Hot-pressed at 2300 psi and 1700°C for one-half hour.

100X (Neg. 10508) Etchant: HF

Fig. 7 - BeO with a grain size of approximately 75 microns; Hot-pressed at 2000 psi and 1700°C for one-half hour.

100X (Neg. 12235) Etchant: HF

Fig. 8 - BeO with a grain size of approximately 60 microns; cold-pressed and sintered two hours in hydrogen at 1600°C.

100X (Neg. 10521) Etchant: HF

Fig. 9 - BeO with a grain size of approximately 10 microns; cold-pressed and sintered two hours in hydrogen at 1500°C.

250X (Neg. 12492) Etchant: HF

Fig. 10 - Rod-shaped grains in BeO; cold-pressed and sintered two hours in air at 1500°C.

100X (Neg. 10512) Etchant: HF
Fig. 11 - Original sample for isothermal test,
grain size: 36 microns; extruded and
sintered two hours in hydrogen at
1620°C.

100X (Neg. 10513) Etchant: HF
Fig. 12 - Twenty-five hour grain growth test;
grain size: 42 microns; 25 hrs. at
1500°C in air.

100X (Neg. 10514) Etchant: HF

Fig. 13 - Fifty hour grain growth test, grain size: 51 microns; 50 hrs. at 1500°C in air.

100X (Neg. 10515) Etchant: HF

Fig. 14 - Seventy-five hour grain growth test, grain size: 72 microns, 75 hrs. at 1500°C in air.

100X (Neg. 10516) Etchant: HF
Fig. 15 - One hundred hour grain growth test,
grain size: 100 microns, 100 hrs.
at 1500°C in air.

100X (Neg. 12644) Etchant: HF
Fig. 16 - Non-uniform grain size in BeO;
150 hrs. at 1500°C.

ELECTRON MICROSCOPE STUDIES OF BERYLLIUM OXIDE POWDERS

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This report describes the electron microscope investigations of beryllium oxide powders and relates their contribution to the advancement of beryllium oxide technology pertinent to the application of the General Electric Company, Aircraft Nuclear Propulsion Department.

Results are presented to characterize the physical and morphological features of various beryllium oxide powders in relation to parent compounds, calcination conditions, fabricated density and chemical purity.

Electron microscope particle size data have been tabulated and the results are compared with X-ray diffraction, line-broadening and surface area measurements to facilitate a complete particle size perspective.

INTRODUCTION

There is quite an accumulation of literature on various phases of particle size determination and the behavior of particles above the colloidal range. Unfortunately, there has been no comprehensive treatment of the behavior and physical properties of the very minute particles we currently find of interest. Certain distinctions must be made with regard to the meaning of the ambiguous term, particle size. Since we are attempting to delineate the smallest subdivision of beryllium oxide powders, we have ascribed appropriate terms to the various boundaries of subdivision which are crystallites, ultimate particles and agglomerates. These subdivisions are quite often directly related to the method of evaluation. A crystallite can be defined as the smallest subdivision of matter containing atoms or molecules in a continuous ordered arrangement. The ultimate particle is one which has definite physical boundaries. An ultimate particle may or may not be polycrystalline. Agglomerates are the grouping together of these crystallites or ultimate particles.

Various methods of particle size and surface area determinations have been utilized in our study of beryllium oxide powders. These are: X-ray line-broadening, small-angle scattering, nitrogen gas adsorption, air permeability, water adsorption, petrographic analysis and electron microscopy. In this way, data from many parameters can be compared and an intelligent interpretation

of particular data can be ascertained. Our contention has been that the range and variation of BeO was so extreme as to make impractical the assigning of specific values to average particle size and distribution from electron microscope studies. We have thus attempted to integrate these other methods, which often produce more expedient, accurate and reproducible analyses, with the electron microscope studies. Each method contributes its own specific information, and the sum total is complementary to a realistic particle size evaluation.

Many aspects of beryllium oxide technology are currently being investigated utilizing advantages afforded by electron microscopy. The electron microscope provides the only means for direct observation of particles throughout the colloidal range. In this particular application, the information obtainable is threefold: determination of ultimate particle range and size within the limits of resolution and sampling techniques; shape and morphological features of the particle; and evidence regarding the state of aggregation.

In respect to nuclear application, density and purity are primary considerations of fabricated beryllium oxide. With the realization that the raw material inconsistencies, as well as fabrication variables, have a contributing effect on sinterability and subsequent density, an investigation of the various beryllium oxide powders is essential. The objective of such an endeavor has been to characterize the oxide powders by their physical appearance and to correlate the particular crystal habits to parent compounds, calcining conditions, fabricated density, and chemical purity.

A comprehensive investigation was initiated to establish applicable electron microscopy techniques for examination of beryllium oxide powders. Simplified techniques were deemed paramount due to our inexperience in the electron microscope field, the toxicity of the material, and the large number of anticipated specimens. The finely divided beryllium oxide powders were considered to consist of ultimate particles joined in groups or agglomerates with varying forces of cohesion. These particles were studied, where applicable, in the condition submitted, although the material may be subjected to future operations which may tend to break the agglomerates apart or even fragment the ultimate particles. The techniques utilized were intended to preserve, without distortion, the actual agglomerate and ultimate particle characteristics.

EXPERIMENTAL METHODS

The sample preparation for electron microscope examination is initiated by making an aqueous suspension of the powder. The appropriate quantity of material dispersed is determined by trial to ensure a well populated grid that is assumed to be representative of the specimen. The aqueous suspension is allowed to settle for a brief period to enable the large agglomerates to precipitate and thus prevent clogging of the sampling

micropipette. A drop of the suspension is placed on a filmed grid and allowed to evaporate to dryness. Two types of filmed grids or substrates, parlodion and carbon, are employed. Each has its own particular advantages. The carbon substrates are superior from the standpoint of stability, higher contrast, and increased resolution; however, they are more difficult to prepare.

Shadow-casting techniques are used to essentially produce a third dimension, so as to better establish structures and shapes of particles and agglomerates. To study the morphological features of the powders, the surface structures of the particles are replicated.¹ This replication is accomplished by shadow-casting the particles dispersed on a parlodion substrate. A film of carbon is then deposited normal to the surface. This carbon film produces the replica which is strong and resistant to the reagents used for dissolution. A suitable solvent is used to remove the parlodion, and hydrofluoric acid was employed to leach out the beryllium oxide. The final replica is washed and dried. Utilizing this combined method, manipulation is kept to a minimum and the same specimen can be observed before and after shadow-casting, and after replication.

The other methods of particle size analyses, as previously noted, have contributed so much to our electron microscope studies, we feel they are worthy of mention. BeO average crystallite₂ size was determined with the X-ray diffractometer and the powder camera.² In practice, the maximum limit of crystallite size which can be measured accurately by diffraction line-broadening techniques is about 1000 Å. With refined diffractometer methods, this limit can be increased to 2000 Å, with quite rough approximations of crystallite size being possible up to 10,000 Å. Just as there is a maximum limit, there is also a minimum limit which can be determined by line-broadening measurements. In practice, the minimum crystallite size producing measurable diffraction lines is about 40 Å. From this study of measured crystallite sizes and observed powder patterns and electron micrographs, a set of calibrated powder diffraction patterns of BeO has been obtained which are used to estimate unknown BeO crystallite sizes from 40 Å to 10,000 Å merely by comparison of the powder pattern of the unknown with the calibrated standard patterns. This method of estimating crystallite size from powder film has proved quite accurate and time-saving in what is now considered routine analysis of BeO powders.

Ultimate particle size and the distribution has been estimated by analysis of the small-angle scattering of X-rays.³ The important factor in this method is that the scattering is produced by the difference in density between the particles and the surrounding medium. Small-angle scattering data have not always correlated well with other data. This may be partly because we have not determined if we are measuring particles containing closed pores or particles surrounded by voids, or it may be that better instrumentation would provide data at lower angles to detect scattering from the larger particles. This type of analysis

in conjunction with electron micrographs has verified the fact that a large portion of the small particles are present in calcined material. Surface areas of BeO powders by the B.E.T. nitrogen adsorption method was reported by the Oak Ridge National Laboratory.⁴ Air permeability, a simplified method of determining the specific surface area by measuring the resistance of a column of packed particles to a gas flow,⁵ was also investigated. This method has shown good correlation with other surface area measurements, except with the finer particles where compacting the material to the appropriate porosity is difficult. A uniquely simplified method of surface area measurement was developed which utilized the particular water adsorption characteristics of BeO powder.

DISCUSSION OF RESULTS

It is well to keep in mind that we are essentially concerned with single phase beryllium oxide and that the changes in characteristics are due to intentional or often unintentional variations in the methods of beryllium oxide preparation. Material produced in our own development labs and from all known vendors has been examined. It became apparent at once that the only consistent feature about beryllium oxide was its inconsistency. However, we have found BeO powder can be characterized in relation to the various parent compounds from which it is formed. (Fig. 1 to 4) The four parent compounds covered in our study are beryllium hydroxide, beryllium sulfate, beryllium basic acetate and beryllium oxalate. Fig. 5 to 8 illustrate some of the variations in BeO produced from beryllium hydroxide. The distinct spherical manner in which the particles agglomerate and the extreme range of ultimate particles is readily visualized. The upper size range of the ultimate particles from high temperature calcination is so large that petrographic techniques were used to measure the size.

Supplementary petrographic examination has proved to be quite useful in this respect. The electron micrographs of the ultimate particle we believe are commensurate with the average crystallite size determined by X-ray line-broadening. The limitations of the two methods are graphically illustrated in these micrographs. Line-broadening from the large crystallites in the high temperature calcined material becomes negligible compared to the observed instrumental broadening. The low temperature calcined powder has a substantial portion of material that is below the resolution limit of our electron microscope. BeO from beryllium sulfate is not so distinctive as with the other parent compounds but is included for comparison. Beryllium basic acetate also has been included for completeness. Through necessity, considerable study has been placed on investigation of GEOM (General Electric Oxalate Material) - Fig. 9 to 12. BeO from beryllium oxalate has been particularly characterized by its often exhibited prismatic dihexagonal, pyramidal shaped crystals which are similar to the mineral bromellite as described by Dana.⁶ Its mode of lath-like aggregation probably results from the prismatic nature of the crystals and contributes to the extreme range of ultimate particle size.

The beryllia-bearing salts are converted to the oxide by a calcination process. There are a number of phase transformations as well as physical changes which take place during calcination. These changes are dependent on the temperature, time and atmosphere of calcination and initial material used. The calcination is accomplished by thermal decomposition of the hydrated beryllium compounds, at a temperature sufficient to drive off the water and other volatiles, and produces the final beryllium oxide product. Calcination above the decomposition temperature produces varying degrees of crystallite growth and agglomerate formation. Since particle size is an important factor affecting sinterability, it was desired to also characterize calcining conditions that would contribute an optimum particle size for maximum densification.

A typical GEOM calcination series denotes the physical changes and characteristic features of BeO in relation to specific calcining environment. The characteristic features of GEOM calcined for two hours in air at 500, 900, 1200, and 1500°C are illustrated in Fig. 13 to 16. The development of initially formed anhedral BeO crystallites at 500°C to the large euhedral crystals developed at 1500°C is readily visualized. The data obtained from electron microscopy, X-ray line-broadening and various surface area investigations of this calcination series are presented in Table I and Fig. 17. It is thought that if the limitations of the measuring media are known and the nature of the physical changes that occur are defined, all the results are in reasonably good agreement.

The relation of BeO particle size to fabricated density has proved to be quite difficult, due to the inconsistent and irreproducible density data. Consequently, we have attempted to correlate the physical features of BeO powder with the ceramographic microstructures of BeO fabricated solids that measure in excess of 99% of theoretical density, Fig. 18-23. This evaluation is also necessarily limited because deleterious effects of mechanical polishing and the nature of artifacts introduced in other preparation methods are not completely understood.

BeO utilized in our studies generally contain impurities in such minute amounts that they are not detectable by X-ray diffraction methods. However, Fig. 24 to 27 illustrate various anomalous shapes that exist in material that did not meet the Department's purity specifications.

SUMMARY

We have defined selected, complementary parameters of investigation, namely electron microscopy, calibrated X-ray powder films, small-angle scattering and water adsorption, which can be utilized to resolve the finest particulate character and physical features of BeO powder to ascertain their relationship in regard to parent compounds, calcination, density and purity. An understanding of specific aspects of beryllium oxide technology has been attained and, with continued effort, the objectives pertinent to our development program will be achieved.

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TABLE I

INTERRELATION OF PARTICLE SIZE MEASUREMENTS ON GEOM CALCINED
FOR TWO HOURS IN AIR AT VARIOUS TEMPERATURES

Calcination Temperature °C	Estimated Observed Ultimate Part Size _μ	X-Ray Line-Broadening Crystallite Size Å	B.E.T. Nitrogen Adsorption		Air Permeability M ² /gm	Water Adsorption M ² /gm	Small-Angle Scattering		
			M ² /gm	Å ² / _—			M ² /gm ³	Distribution	
								Wt. %	Mean Diameter Å
400 ¹	---	50	314	60	157	294	404	---	-----
500	.01	75	190	104	103	197	307	22.4 27.2 14.6 35.8	23.2 46.0 65.8 92.8
600	.02	120	127	156	72.4	131	201	17.6 30.2 41.2 11.0	24.4 48.4 84.2 123.2
900	.01 - 0.75	1,500	16.3	1,200	12.5	14.6	22.2		
1000	.01 - 1.0	1,500	14.1	1400	10.3	9.8	24.7		
1200	.1 - 1.5	2,800	8.0	2480	5.8	--	11.1		
1500 slow cooled	.05 - 8.0	10,000	2.8	7100	2.15	--			

¹ - Incompletely calcined beryllium oxalate.

² - $S = 6/\rho d$ relation between surface area and average spherical diameter of particles $\rho = 3.00$ gm/cc.

³ - Surface calculated assuming spherical shape.

FIG. 1 - BeO FORMED BY CALCINATION OF THE HYDROXIDE AT 1000°C

FIG. 2 - BeO FORMED BY CALCINATION OF THE SULFATE AT 1000°C

FIG. 3 - BeO FORMED FROM THE BASIC ACETATE

FIG. 4 - BeO FORMED BY CALCINATION OF THE OXALATE AT 900°C

FIG. 5 - BeO FROM HIGH TEMPERATURE CALCINED HYDROXIDE
X-RAY CRYSTALLITE SIZE 10,000 Å

FIG. 6 - BeO FROM LOW TEMPERATURE CALCINED HYDROXIDE
X-RAY CRYSTALLITE SIZE 85 Å

FIG. 7 - BeO FORMED BY CALCINATION OF THE HYDROXIDE AT 1000°C

FIG. 8 - SURFACE REPLICA OF BeO FORMED BY CALCINATION OF THE
HYDROXIDE AT 900°C - X-RAY CRYSTALLITE SIZE 300 Å

FIG. 10 - SURFACE REPLICA OF BeO FORMED BY CALCINATION OF GEOM
AT 900°C for 8 HOURS - X-RAY CRYSTALLITE SIZE 4000 Å

FIG. 11 - GEOM CALCINED FOR 8 HOURS AT 900°C

FIG. 12 - GEOM CALCINED FOR 8 HOURS AT 900°C
X-RAY CRYSTALLITE SIZE 1200 Å

FIG. 13 - GEOM CALCINED FOR 2 HOURS AT 500°C

FIG. 14 - GEOM CALCINED FOR 2 HOURS AT 900°C

FIG. 15 - GEOM CALCINED FOR 2 HOURS AT 1200°C

FIG. 16 - GEOM CALCINED FOR 2 HOURS AT 1500°C

Fig. 17 - GEOM calcined for 2 hours in air at various temperatures - maximum deviation of average BeO particle size as measured by:
 X-Ray Line Broadening
 Nitrogen Adsorption
 Air Permeability (Data Omitted Below 900°C)
 Water Adsorption
 Small - Angle Scattering (Data Omitted Above 600°C)

FIG. 18 - BERYLLIUM CORPORATION'S "GRADE I" BeO

FIG. 19 - ATOMICS INTERNATIONAL'S TRANSLUCENT BeO FABRICATED BY HOT-PRESSING "GRADE I" - MATERIAL MECHANICAL POLISH, HF ETCHANT, LIGHT MICROGRAPH

FIG. 20 - TYPICAL GEOM BeO

FIG. 21 - GEOM BeO FABRICATED BY HOT-PRESSING-MECHANICAL POLISH,
FLAME ETCHED, ELECTRON MICROGRAPH

FIG. 22 - BRUSH BERYLLIUM COMPANY'S "UOX" GRADE BeO

FIG. 23 - BeO FABRICATED BY EXTRUSION AND SINTERING "UOX" MATERIAL
MECHANICAL POLISH, HF ETCHANT, LIGHT MICROGRAPH

FIG. 24 - ANOMOLOUS SHAPES ATTRIBUTED TO IMPURITIES

FIG. 25 - ANOMOLOUS SHAPES ATTRIBUTED TO IMPURITIES

FIG. 26 - ANOMOLOUS SHAPES ATTRIBUTED TO IMPURITIES

FIG. 27 - ANOMOLOUS SHAPES ATTRIBUTED TO IMPURITIES

METALLOGRAPHIC PREPARATION OF IRRADIATED URANIUM CARBIDE

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Uranium carbide is extremely susceptible to corrosive attack by water and moist air. This creates a problem in the hot-cell metallographic preparation of irradiated material, since water alone cannot be used as the abrasive vehicle in vibratory polishing. A solution of 2 per cent chromium trioxide in water was found to provide a satisfactory suspension and polishing medium, although its use for badly cracked specimens is not recommended. Water formed during preparation of plastic replicas also presents a problem in the hot cell. This can be overcome by using methyl acetate as the solvent in preparing cellulose acetate replicas and by desiccating the specimen and replica immediately after application.

INTRODUCTION

Recently Battelle has been engaged in fairly intensive studies of uranium carbide as a fuel material. As is the case with most materials, metallography has played an important role in these studies.

Metallographic techniques very similar to those reported by R. J. Gray ⁽¹⁾ were used initially and found satisfactory in the cold metallographic laboratory at Battelle. However, modifications have since been adopted. These modifications were necessary because of the problems encountered during metallographic preparation of uranium carbide on vibratory polishers in the hot cell. All techniques used in the hot cell were initially investigated in the BMI cold metallographic laboratory. While many materials behave quite differently after irradiation than before, this problem has not been encountered with UC.

The major problems encountered in the handling and preparation of uranium carbide arise from its reactivity with water and water vapor. Thus, cast ingots of UC will spall and crack when exposed to normal air as a result of reaction with moisture in the air. For this reason it is necessary to store UC specimens in a dry atmosphere; a desiccator containing Drierite is satisfactory for this purpose.

(1) Gray, R. J., Thurber, W. C., and DuBose, C. K. H., "Preparation of Arc-Melted Uranium Carbide", Metal Progress (July, 1958).

Despite the reactivity of UC with water, metallographic polishing techniques have been developed in which water or water solutions are employed. No detrimental effects to UC have been observed as a result of this use. A discussion of metallographic techniques, primarily as applied in the hot cell, is given below. Replication techniques are also discussed.

METALLOGRAPHIC TECHNIQUES

All specimens are mounted in Bakelite to which Bakelite resinoid has been added to fill cracks if any are present as a result of irradiation. This method of mounting was adopted after carefully checking a number of specimens to make certain that mounting temperature and pressure did not produce cracks in the irradiated material. This precaution was taken since cracks are one of the major defects introduced by irradiation, and it is important to know that any cracks present can be correctly attributed to irradiation and not to any subsequent handling procedures.

Mounted specimens are ground on silicon carbide papers, through 600 grit, with kerosene as the lubricant.

All polishing in the Battelle Hot-Cell Facility is done on Microcloth in Syntron Model LP-01 vibratory polishers. Originally, slurries of 1-micron alumina and Linde A were used as abrasives with kerosene being used as a lubricant. These abrasives were then replaced by Linde B and kerosene. However, kerosene does not wet the abrasive well, and in the vibrator the abrasive tends to agglomerate and the mixture becomes gummy. This slows the polishing action considerably which, besides lengthening the time of the operation, leads to considerable scratching of the specimen surface.

Consequently, other vehicles for suspension of the abrasive in the vibrators were investigated in the cold metallographic laboratory. Water was found to attack the carbide structure. The results obtained by polishing with Linde B and water are shown in Fig. 1 and 2. Cracks, holes, and pits resulting from the removal of UC₂ particles can be seen in these photomicrographs.

A solution of 2 per cent chromium trioxide in water with Linde B was found to provide satisfactory results in the vibrator. This solution appears to act as an etch-polish solution, although no etching of the structure is observed. The polishing action is faster than in water alone, and a very clean work-free surface is produced. The addition of the chromium trioxide to water also apparently eliminates the tendency toward the preferential attack of UC₂ observed in water alone.

Figs. 3 and 4 show the as-polished surface and as-etched structure of UC specimens prepared by vibratory polishing in the BMI cold metallographic laboratory using the chromic solution. The cracks shown in Fig. 3 were present in the specimen before polishing, and this particular photo-

micrograph was taken to show the cracks. However, its purpose here is to illustrate the good clean surface obtained. The etchant used to develop the structure in Fig. 4 is the same as that reported by Gray, a solution of equal parts of nitric acid, acetic acid, and water.

While no evidence of cracking has been observed either in the hot cell or in the cold metallographic laboratory as a result of polishing with the chromic solution, its use is not recommended for a badly cracked specimen where these cracks cannot be filled by the mounting material. If the solution were to enter the cracks, additional cracking would undoubtedly result. For such specimens, kerosene and Linde B are employed at the hot cell.

After polishing with the chromic solution at the hot cell, in some instances it has been found that the specimen will not etch. Apparently the polishing solution produces a passive protective layer on the surface of the specimen. To remove this layer the specimen is given a brief polish on kerosene and Linde B in a vibrator.

After polishing, the specimens are cleaned in alcohol. The alcohol rinse usually produces stain markings on the surface of the specimens which are cleaned off by a short rinse in water. The specimens are dried with a hot-air hair dryer.

Some of the metallographic results achieved in the hot cell on irradiated UC are shown in Figs. 5 through 8.

Fig. 5 shows the as-polished surface of a badly cracked uranium carbide sample. No damage attributable to the chromic polishing solution was noted on the sample, which exhibits a very bright and clean surface. Fig. 6 shows this same specimen after etching. Of particular interest is the absence of visible preferential attack of UC_2 particles either by the polishing medium or the etchant. This is also evident in Fig. 7. An interesting facet of the irradiation behavior of uranium carbide containing excess carbon is illustrated in Fig. 6. Clean grains containing no UC_2 are observed in the center of the specimen. Apparently either the UC_2 goes into solution as a result of neutron damage or bombardment or else the excess carbon diffuses under the influence of the thermal gradient to the colder portions of the specimen. Fig. 8 shows the center area of another specimen from which the UC_2 plates have disappeared.

Since they may be of interest, the standard techniques used for polishing UC in the BMI cold metallographic laboratory will also be given. The specimen, after mounting and rough grinding on silicon carbide papers and kerosene, is first polished on a silk wheel with Linde A abrasive and a 50 per cent water-alcohol solution. This is followed by a polish on Forstmann's cloth with blue diamond abrasive. The specimen

is then etched unless it contains too many scratches. In this event, the specimen is given a final polish on Microcloth with Linde B and the 50 per cent water-alcohol solution at slow speed.

REPLICATION TECHNIQUES

Plastics replicas are normally obtained in the BMI Hot-Cell Facility by using cellulose acetate sheets with acetone as the solvent. However, when attempts were made to replicate UC specimens in the same manner, a problem was encountered due to water formation. The nature of the problem is illustrated in Fig. 9. Water either forms by condensation during drying of the replica or else is left as a residue from the solvent. This water reacts with the UC and UC_2 needles to form CH_4 and CH_2 , respectively, which produce bubbles in the replica. The reaction with the UC_2 is more pronounced than with the UC, and bubble artifacts, lined up with the UC_2 particles, can be seen in the electron micrograph. Dioxane when used as the solvent gives the same result.

Methyl acetate, which is extremely volatile, was finally chosen as the solvent, and a modified procedure was adopted. Again, the procedure was developed initially on cold material before application in the hot cell. The specimen surface is flooded with methyl acetate, and then then the cellulose acetate sheet is placed down slowly to iron out any bubbles.

The specimen is then immediately placed in an airtight box containing barite as the desiccant. The replica is generally allowed to dry overnight and is then stripped from the specimen.

Positive replicas are taken of the master replica with cellulose nitrate dissolved in lacquer thinner. A platinum-shadowed carbon replica is then prepared after which the cellulose nitrate is dissolved in amyl acetate.

Electron micrographs of UC are shown in Fig. 10, 11, and 12. The specimens were polished with Linde B and the 2 per cent chromic solution on Microcloth in vibratory polishers prior to etching with a solution containing equal parts of nitric acid, acetic acid, and water.

The unirradiated structure of UC is shown in Fig. 10. The UC_2 particles are very sharp and quite straight. By comparison, the UC_2 particles in the irradiated structure shown in Fig. 11 show some curvature and appear to be breaking up or changing shape. This particular sample was irradiated at a maximum temperature of about 660 F. The change in shape of the UC_2 needles was not observed at higher irradiation temperatures.

An electron micrograph of a specimen which exhibited a disappearance of UC_2 in its center after irradiation is shown in Fig. 12. What may be remnants of UC_2 are seen in the matrix. An explanation for the changes in structure observed has not been developed as yet.

CONCLUSIONS

A satisfactory method for the vibratory polishing of irradiated UC has been developed. While the use of water leads to rapid attack of UC, Linde B suspended in a 2 per cent solution of chromium trioxide in water produces a clean, work-free surface.

A satisfactory method for the replication of UC has also been developed. It involves the use of a highly volatile solvent in preparing the plastic replica, followed by desiccation of the replica during the drying period. This is necessary to prevent formation of water which attacks the UC and UC₂ particles.

100X RM15262
Fig. 1-U-5.0 w/o C as-polished in
vibrator on Linde B with water

500X RM15263
Fig. 2-U-5.0 w/o as-polished in
vibrator on Linde B with water

100X RM15264
Fig. 3 - U-5.0 w/o C as-polished in
vibrator on Linde B with 2 per cent
chromic solution

250X RM15261
Fig. 4 - As-etched U-5.0 w/o C
structure after polishing in
vibrator on Linde B with 2 per
cent chromic solution.

100X HC4008
Fig. 5 - As-polished structure of U-5.0 w/o C irradiated to A 0.61 a/o burnup at an average maximum temperature of 1375°F

100X HC4007
Fig. 6 - As-etched structure of U-5.0 w/o C irradiated to a 0.61 a/o burnup at an average maximum temperature of 1375°F

250X HC4010
Fig. 7 - As-etched structure of U-5.0 w/o C irradiated to A 0.13 a/o burnup at a maximum temperature of 880°F

100X HC4184
Fig. 8 - As-etched structure of U-5.0 w/o C irradiated to A 1.34 a/o burnup at an average maximum temperature of 1178°F

15,000X

E-6710C

Fig. 9 - Electron micrograph of unirradiated U-5
w/o C sample replicated with acetone as solvent
Bubble artifacts appear in the replica.

13,000X

J-65

Fig. 10 - Electron micrograph of unirradiated U-5
w/o C sample replicated with methyl acetate as the
solvent.

15,000X J-140
Fig. 11 - Electron Micrograph of U-5 w/o C sample
irradiated at a maximum temperature of 660°F to
A 0.094 a/o burnup. Note distortion of UC₂ needles.

15,000X J-223
Fig. 12 - Electron micrograph of center of U-5 w/o
sample irradiated at average maximum temperature of
1086°F to 1.4 a/o burnup. Note absence of UC₂
needles.

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SWELLING IN URANIUM AS A FUNCTION OF
POST-IRRADIATION ANNEALING

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Specimens from two cylindrical rods of restrained uranium irradiated to burnups of 0.29 and 0.41 ^a/o at temperatures of 500°C in the core and 350°C on the periphery have been annealed for 100 hours at 600, 650, 700, and 880°C. The resultant swelling in the unrestrained specimens has been studied by optical and electron metallographic techniques. Problems associated with the statistical determination of fission gas pore diameters and their distribution are discussed. The results obtained permit qualitative observations on fission gas mobility and the nucleation and growth of fission gas pores. The effect of temperature and burnup on swelling in uranium is illustrated by representative micrographs.

INTRODUCTION

Swelling, the increase in volume of uranium due to fission gas accumulation and agglomeration during irradiation, imposes serious limitations on the use of metallic uranium as reactor fuel. Although the phenomenon of swelling is not clearly understood, it is reasonable to expect that such factors as temperature of irradiation, total burnup, burnup rate, external pressure, and the microstructural state of the uranium can singly and collectively influence the nature and extent of swelling in uranium.

Evaluation of the relative importance of the above listed parameters is complex. Few irradiation experiments have been conducted under controlled conditions for which important parameters and variables are known or are constant. Changes in burnup rate, fission gas and fission product concentrations, and temperature gradients are difficult to minimize. Irradiated uranium is known to be dimensionally unstable; cracking on a macro and microscale can occur as a result of rapid thermal cycling, especially through the transformation temperatures. Little wonder, therefore, that the problem of characterizing radiation effects in uranium is complex. A study of swelling in uranium, however, can be appreciably simplified if specimens are irradiated under semi-controlled

conditions, that is, at prescribed constant temperatures, to particular burnups, and in particular neutron fluxes. Results from such irradiations should avoid much of the ambiguity inherent in the interpretation of observations and measurements. The minimum number of distinctly unique "controlled" irradiations requires expenditure of considerable time and money. It is imperative, therefore, to extract as much qualitative information as is practical from the variety of irradiated uranium specimens which have been studied in the past, and to use the available information as a guide in designing "controlled" irradiation experiments. Accordingly, this report presents microscopic data and observations on swelling in two types of specimens which have been annealed for 100 hours at 600, 650, 700, and 880°C. Although ex-reactor induced swelling is undoubtedly quite different from in-reactor swelling, that is nucleation and subsequent growth is different, the annealed specimens provide a means for studying the effect of time at temperature on gas porosity in uranium, and should yield information on the diffusivity of fission gases in uranium and the restraint on the growth of gaseous pores by the surface tension and the plastic properties of the uranium. Just as dislocations can be studied by virtue of selective internal decoration or by etch pit attack of the free surface, gas pores normally too small to be observable, may become large enough during post-irradiation annealing to be discernable. The possibility of such "decoration" constitutes an additional justification for post-irradiation annealing studies.

EXPERIMENTAL CONSIDERATIONS

The value of microscopy as a tool for studying swelling depends upon the reliability of pore diameter measurements. Possible sources of error are: (1) small pores can only be examined in the electron microscope, and the size measurement obtained is influenced by the faithfulness of the replication process used; (2) small pores on a mechanically polished surface are generally filled with flowed metal, and unless the surface is properly etched they will not be apparent; (3) etching of the polished surface may reveal pores, but if the rate of removal of uranium during etching is highest at the pores, the shapes and volumes of the original pores may be considerably altered. Analysis of the magnitude of the above listed potential errors has progressed to a point which warrants the description and clarification contained in this paper.

SPECIMEN PREPARATION AND MICROSCOPY TECHNIQUES

The basis metallographic preparation procedure for specimens involves sectioning, grinding, polishing and etching. Prior work on irradiated uranium had established the utility of etching by ion bombardment as a means for removal of surface metal which had flowed as a result of the mechanical polishing process, and for revealing the true microstructure. Since a surface etched in this fashion is clean and shows microstructural relief, a negative plastic replica of the surface can be studied extensively in a standard optical and electron microscope laboratory. Several

advantages in the study of gas pores in uranium arise from use of this procedure of specimen preparation and examination. Pitting or selective attack at impurity inclusions by the common electrolytic or chemical etchants is avoided; the negative replica depicts holes on the specimen as mounds which if small can be studied more easily than holes or depressions on positive replicas; the replica provides a permanent record of the specimen microstructure.

A description of the radiometallurgy facilities and procedures used has been described elsewhere. (1) Replicas of a specimen are shadowed with a thin layer of uranium dioxide and backed with amorphous carbon. For optical examination of replicas, the universal goniometer shown in Fig. 1 is employed. Such a goniometer is necessary for orienting fracture facets or features in a replica which deviates from a plane perpendicular to the microscope axis.

DENSITY MEASUREMENTS

Density measurements on irradiated uranium specimens are routinely obtained from determinations of the weight of the specimen in air and the reduced weight of the specimen submerged in water of known density. One of the major sources of error in such determinations arises from incomplete wetting of the specimen (this is reduced by small additions of detergent to the water) or due to partial wetting of open porosity and cracks on and within the specimen. As specimen size becomes smaller, the resultant accuracy and related precision of individual measurements becomes poorer. Accordingly the reliability of measured density values is a function of the type of specimen used, and in many instances provides only a qualitative, relative gauge for evaluating the extent of swelling that has occurred in a bulk specimen.

RESULTS AND DISCUSSION

As indicated previously, the interpretation of the microstructure of irradiated uranium requires knowledge of the irradiation history of the specimen under study. In the event that such important parameters such as irradiation temperature, microscopic temperature gradients, number and degree of in-reactor thermal cycles, restraint of cladding, differential and integrated burnup rates, impurity concentration, grain size, preferred orientation, and perhaps others are now known, only qualitative observations can be made. Such observations, however, provide a simple criterion for assessing the combined overall extent of swelling under conditions employed and may answer such questions as: (1) Has gas agglomeration occurred? (2) Is gas porosity associated with microstructural features, such as twin, grain, or impurity interfaces? (3) Is swelling more pronounced (relative size and number of pores of given size) near the axis of a cylindrical specimen, where the temperature during irradiation was highest, or near the periphery, where the temperature was lowest? (4) Is there any indication of differences in the shapes of pores in two directions,

on sections cut parallel and perpendicular to the axis of a cylindrical specimen? (5) Is there any difference in pore size and frequency in a particular temperature range in cases of high burnup rates (enriched versus natural isotopic composition)?

Fig. 2 shows typical optical micrographs of negative replicas of uranium. The original rod specimen, clad mechanically with Zircaloy-2 was irradiated to a burnup of $0.29 \frac{\text{a}}{\text{o}}$; irradiation temperatures in the core and periphery were 500°C and 350°C , respectively, and decreased 100°C during irradiation as a consequence of improved thermal conductance of the uranium-clad interface. Essentially no "normal" microstructure exists in the as-irradiated state. Wafers from the declad rod were subjected to 100 hour anneals at 600°C , 650°C , 700°C , and 880°C and were then polished, etched, and replicated. Fig. 2 also contains micrographs which illustrate the microstructure resulting from the annealing treatment. Some change in microstructure as a consequence of beta and of gamma phase annealing has occurred. After the beta phase anneal, adjoining grains are recognizable only by virtue of a difference in "pepper"; grain boundaries are indistinct. The gamma anneal, however, shows some annealing twins and grain boundaries. After the high temperature anneal many cracks are present. Porosity is extremely difficult to resolve on an optical scale, and can very easily be confused with impurities. The electron micrographs of Figs. 3, 4, and 5, prepared from the same replica from which the optical micrographs were taken, clearly disclose changes in the extent and distribution of pores after the 600°C and 800°C annealing treatments. In the as-irradiated state, Fig. 3, the largest pores are $3000 \text{ \AA}$ in diameter, and the smallest observable ones are $300 \text{ \AA}$. No significant change in the total volume of pores nor the number of pores per unit volume is disclosed from comparison of the core and peripheral region of the specimen. Fig. 4 illustrates that a fine-grained recrystallized structure and growth in pore size has occurred as a consequence of the 600°C anneal. Although most of the pores appear to be located at the boundaries of the recrystallized grains, it is not possible to establish whether these pores result from sweeping of gas atoms during growth of the grains, or whether growth of grains has terminated at the site of the larger, pre-existing and growing pores. After the 100 hour anneal at 880°C , considerable increase in pore size has occurred, Fig. 5. The resultant pores appear to be spherical in shape and are distributed quite uniformly over the specimen. No indication of preferential location of pores at impurity inclusions is indicated.

But how can pores, their size, and their size distribution be described from micrographs such as given in Figs. 3, 4 and 5? A method of quantitative electron metallography for porosity is required, and such a method is currently being developed. (2)

On the supposition that pores in uranium are spherical, that etching of a specimen causes no change in pore size, that replication is faithful even for pores sectioned considerable distances above their centers, and that

pore centers are randomly distributed throughout a specimen, the total void fraction of pores in a matrix, V. F., may be derived from the individual void fractions v. f. (r_i) corresponding to pores of radii r_i . Thus,

$$V. F. = \frac{\text{Total Void Volume}}{\text{Total Volume}} ,$$

$$= \frac{\int_0^{\infty} dV(r)}{V} ,$$

$$= \int_0^{\infty} dV. F. (r) ,$$

where

$V(r)$ is the total void volume for all pores of radius - r ,
 V is the total volume, and
 $V. F. (r)$ is the void fraction for all pores of radius - r .

For a finite number of pores,

$$V. F. = \sum_{i=1}^k v. f. (r_i),$$

where

$v. f. (r_i)$ is the void fraction for all pores of radius r_i ,
 and $r_1, r_2, \dots r_k$ are the k recognizable radii.

To obtain an estimate of $v. f. (r_i)$ for the total volume V under consideration, consider the partial volume $A \times 2r_i$ determined by the cross sectional area A .

All pores of radius r_i whose centers lie in this volume $A \times 2r_i$, will be intersected by A . If there are n_i such pores and they are spherical so that each volume $= 4/3\pi r_i^3$, then an estimate of v. f. (r_i), computed from the partial volume, is

$$\begin{aligned}\widehat{\text{v. f.}}(r_i) &= \frac{\left(\frac{4}{3}\pi r_i^3\right) n_i}{A \cdot 2r_i}, \\ &= \frac{2}{3} \frac{\pi}{A} r_i^2 n_i.\end{aligned}$$

Then, an estimate of the total void fraction is

$$\begin{aligned}\widehat{\text{V. F.}} &= \sum_{i=1}^k \widehat{\text{v. f.}}(r_i), \\ &= \frac{2\pi}{3A} \sum_{i=1}^k r_i^2 n_i, \\ &= \frac{2\pi}{3A} \sum r^2,\end{aligned}$$

where the sum extends over all pores intersected by A .

Similarly, for the pore density:

$$\begin{aligned}\text{Pore Density} &= \frac{\text{Total Number of pores}}{\text{Total Volume}}, \\ &= \int_0^{\infty} d \text{ P. D. } (r), \\ &= \sum_{i=1}^k \text{p.d.}(r_i).\end{aligned}$$

An estimate for the partial volume $A \times 2r_i$ pore density is

$$\widehat{\text{p.d.}}(r_i) = \frac{n_i}{A \cdot 2r_i}.$$

And, therefore,

$$\begin{aligned}
 \text{P.D.} &= \sum_{i=1}^k \widehat{\text{p.d.}}(r_i), \\
 &= \sum_{i=1}^k \frac{n_i}{A \cdot 2r_i}, \\
 &= \frac{1}{2A} \sum \frac{1}{r},
 \end{aligned}$$

where, as above, the summation extends over all pores intersected by A. Both the pore volume and pore density formulas involve true radii, while the only data obtainable are radii observed on the electron micrographs of preshadowed negative cellulose acetate replicas. If it can be assumed that half of these observable radii represent pores cut at or above their centers and half represent pores cut at or below their centers, then it is possible to obtain estimates of the true radii, expressed as functions of the observed radii. If r is the true radius, r_p is the interface radius, and r_o is the observed radius, then the following relationships apply. Fig. 6 identifies the various parameters.

$r_o = r$, when the pore $> 1/2$ out on the negative replica

$r_o = r_p$ " " " $\leq 1/2$ " " " " "

To estimate r only from r_o the relationship between r_p and r must be established. It can be shown that for any n

$$E\left(\frac{r_p}{r}\right)^n = \frac{1}{2} B\left(\frac{n+2}{2}, \frac{1}{2}\right).$$

Here, E is the expected value operator, and $B(x,y)$ is the complete beta function defined by

$$B(x,y) = \int_0^1 t^{x-1} (1-t)^{y-1} dt.$$

Ref.: Sokolnikoff, High Mathematics for Engineers and Physicists

For $n = 2$

$$E\left(\frac{r_p^2}{r^2}\right) = \frac{2}{3},$$

or

$$E(r_p)^2 = \frac{2}{3} r^2.$$

Using the calculus of conditional expectations,

$$E(r_o^2) = E \left\{ E(r_o^2 \mid \text{position of pore center}) \right\}.$$

Assuming an even split of pore centers above and below the interface A,

$$\begin{aligned} E(r_o^2) &= 1/2 E(r_o^2 \mid r_o = r_p) + 1/2 E(r_o^2 \mid r_o = r), \\ &= 1/2 E(r_p^2) + 1/2 E(r^2), \\ &= 1/2 \cdot \frac{2}{3} r^2 + 1/2 r^2, \\ &= \frac{5}{6} r^2. \end{aligned}$$

Thus, an unbiased estimate of r^2 is $\frac{6}{5} r_o^2$. Substitution gives as an unbiased void fraction formula,

$$\begin{aligned} \widehat{V.F.} &= \frac{2\pi}{3A} \sum \frac{6}{5} r_o^2, \\ &= \frac{4}{5} \frac{\pi}{A} \sum r_o^2. \end{aligned}$$

The relative standard error of the estimate $\widehat{V.F.}$ is approximated by

$$S_{\widehat{V.F.}} = \frac{\sqrt{\sum r_o^4}}{\sum r_o^2}.$$

Thus, a 95% confidence interval estimate of V. F. is given by

$$V.F. (1 \pm 2S_{\widehat{V.F.}}).$$

Similarly, for the pore density,

$$\begin{aligned} P.D. &= \frac{1}{2A} \sum \frac{1}{r}, \\ E\left(\frac{r_p}{r}\right)^{-1} &= \frac{\pi}{2}, \\ E\left(\frac{1}{r_p}\right) &= \frac{\pi}{2r}. \end{aligned}$$

Hence,

$$\begin{aligned}
 E\left(\frac{1}{r_o}\right) &= E\left\{E\left(\frac{1}{r_o} \mid \text{position of pore center}\right)\right\}, \\
 &= \frac{1}{2} E\left(\frac{1}{r_o} \mid r_o = r_p\right) + \frac{1}{2} E\left(\frac{1}{r_o} \mid r_o = r\right), \\
 &= \frac{1}{2} \frac{\pi}{2r} + \frac{1}{2} \cdot \frac{1}{r}, \\
 &= \frac{1}{r} \left(\frac{2+\pi}{4}\right).
 \end{aligned}$$

So, an unbiased estimate is

$$\begin{aligned}
 \widehat{P.D.} &= \frac{1}{2A} \sum \left(\frac{4}{2+\pi}\right) \frac{1}{r_o} \\
 &= \frac{2}{(2+\pi)A} \sum \frac{1}{r_o};
 \end{aligned}$$

the relative standard error is

$$S_{\widehat{P.D.}} = \frac{\sqrt{\sum \left(\frac{1}{r_o}\right)^2}}{\sum \frac{1}{r_o}},$$

Thus, a 95% confidence interval estimate of P. D. is given by

$$\widehat{P.D.} (1 \pm 2 S_{\widehat{P.D.}})$$

Several micrographs of the negative replica for the center and edge of the specimen with a burnup of 0.29 a/o in the as-irradiated state and after a 100 hour anneal at 800C have been carefully analyzed. Fig. 6 shows a plot of cumulative fraction of total number of pores, $F_n(S/d)$, versus measured S/d values. The quantity, S/d , is independent of pore sizes. Each experimental curve represents at least 250 pores measured in an area of 200 square microns. Since such plots do not agree with the theoretical $F_n(S/d)$ versus S/d curves, a distortion must arise. If the pores or voids are not spherical, but are cylindrically elongated in the direction perpendicular to the specimen surface, as a result of extrusion of the replica during stripping, a higher percentage of pores will appear to have large S/d values; if, on the other hand, pore diameters are increased and the pore depth is unaltered, a possible consequence of the etching process, a

smaller percentage of pores will appear to have large S/d values. If such experimentally determined curves are compared with the theoretical, it is apparent that a general yet similar distortion prevails. The data for uranium irradiated at the lowest temperature and then annealed yields a distortion noticeably less than is the case for higher temperatures of irradiation. As can be seen in Fig. 7, in which the cumulative fraction of pores with apparent diameters $\leq d$ is plotted against apparent diameters, this specimen history also yields the largest sizes pores. It is probable, therefore, that distortion is a function of the pore size, becoming less as the pores get larger. The calculated void fractions and pore densities which pertain to the four specimen histories of Figs. 6 and 7 are listed in Table I.

The calculated void fraction increase due to annealing at 880C compares quite satisfactorily with the per cent change in macroscopic density, 1.8% after irradiation, and 8.2% after irradiation and the 880C anneal. From the data in Table I and Figs. 6 and 7, it would appear that (1) very little swelling (increase in void fraction)

THE INFLUENCE OF IRRADIATION TEMPERATURE AND POST-IRRADIATION ANNEALING ON PORE VOID FRACTION AND DENSITIES IN URANIUM WITH A BURNUP OF 0.29 a/o

<u>Temperature of Irradiation, °C</u>	<u>Post-irradiation Annealing History</u>	<u>Pore Void Fraction</u> $\frac{4\pi}{5A} \sum r_o^2$	<u>Pore Density, Pores/μ^3</u> $\frac{2}{(2+\pi)A} \sum \frac{1}{r_o}$
~ 300C	None	0.020	2.81
~ 300C	100 hours at 880C	0.105	1.50
~ 500C	None	0.018	3.31
~ 500C	100 hours at 880C	0.039	5.41

occurs during irradiation at temperatures below 500C in restrained specimens; (2) there is no significant difference in either pore size or distribution for the two irradiation temperatures; (3) post-irradiation annealing causes a slight decrease in the number of observable pores per unit volume in uranium irradiated at low temperatures, approximately 300C, and causes an increase in the number of pores formed in uranium irradiated at high temperatures, approximately 500C. It must, however, be re-emphasized that the data refers only to several hundred pores revealed on a 350 sq. micron area on each sample. Additional data is required to determine the extent of variations from point to point and grain to grain before statistical significance can be placed on these conclusions.

The deviation of experimental points from the theoretical curve can arise from three possibilities: (1) the model from which the theoretical curve was constructed deviates drastically from the actual or true model;

(2) extrusion of the plastic replicating material occurs in cases where the pores have been cut above their centers; and (3) distortion of the pores results as a consequence of the specimen preparation treatment, polishing and etching. Two experimental approaches are being utilized to evaluate the magnitude of the second and third possibilities, and results are being used to refine the reference physical model.

Since the pores in uranium are of various sizes and can be affected differently by the etching process, a synthetic specimen containing spherical pores of constant and known size, and which does not require etching was developed to avoid ambiguities in interpretation. Polystyrene latex spheres of constant and known size, obtainable from Dow Chemical Company, were embedded in various plastics. After solidification a flat interface on the specimen through some of the polystyrene spheres was prepared by mechanical polishing and by microtoming. Dissolution of the polystyrene spheres exposed on the prepared surface was accomplished by suitable solvents. Of the many synthetic specimens prepared from various types of plastic materials and solvents, the best specimens were produced by successive evaporation of drops of a dispersion of polystyrene in an aqueous solution saturated with polyvinyl alcohol. The solidified plastic was built up to a thickness of 1/4 inch on a rod of aluminum. Mechanical polishing resulted in considerable smearing and flow of the plastic; microtoming with a Jung Metals Microtome, however, yielded a satisfactory flat interface. Benzene was a satisfactory, specific solvent for solution of the polystyrene spheres; two hours total immersion time was required. Fig. 8 depicts the appearance of shadowed negative replicas of two synthetic specimens having pores with diameters of 1.18 and 0.55 microns, respectively. From measurements of shadow lengths and measured apparent diameters of 200 such pores, it is possible to isolate and characterize the extent of extrusion or distortion associated with the replication of small pores. Fig. 9 shows the disagreement of the ratio of shadow length to apparent radii for given apparent diameter values from the theoretical curve. As indicated by the disagreement and by the micrographs of the synthetic pores, extrusion of the replicating medium occurs when the pore has been cut above its center. The extent of the extrusion in many cases appears to be a function of interface area and pore size; in the extreme case, breakage of a partially extruded conical mound on the replica can occur. If the model for pores cut above their centers as revealed by the replica is changed from a spherical shape to a cylindrical shape, included in Fig. 9, a new theoretical curve can be constructed. Such a curve, also shown in Fig. 9, agrees more closely to the experimentally determined curve. If the theoretical curve or model is corrected for a lower observable detection limit and an upper "break point" limit, the error associated with distortion due to replication can be further reduced. One of the major consequences of this study of distortion is that the mathematically exact void fraction estimate for pores derived previously must be changed. The true pore radius is always greater than the observed maximum interface or observed pore radius. Since pores are revealed on negative replicas as mounds having in addition to a cross sectional area, a depth, an improvement over standard quantitative metallography, can, however, be realized.

But how does etching influence the original pore configurations in irradiated uranium? The extent of this source of error is currently being analyzed from pore size and shadow length measurements on specimens which have been etched for different periods of time. From a consideration of the micrographs in Fig. 10 it is quite obvious that mechanical polishing with no etching yields an irradiated uranium surface which shows essentially no pores, but that a short 20 minute etch discloses pores. If the specimen is subjected to an additional 70 minute etch, considerable metal is removed. Comparison of the identical areas on the specimen surface shows similar "macro" features, impurity inclusions and cracks, but the original pores have been etched away and new pores are now disclosed. Pore sizes and pore size distributions, however, appear quite similar, and it must be concluded that etching does not distort the pores to an appreciable extent. The crack which appears after 20 minutes etching consists of a combination of finer cracks and a second phase after the additional etch; the second phase has a much slower etching rate than the matrix uranium. After the short etch it is impossible to recognize grain structure or boundaries, whereas after the prolonged etch, fine twin lines clearly terminate at a boundary which contains the second phase constituent. Pore densities and void fractions determined from identical 350 square micron areas in the 20 minute and 90 minute etched specimen have been determined by the idealized relationship derived previously (not corrected for replication distortion, etc.). The pore density values are 9.9 and 12.6 pores per cubic micron, respectively; the void fractions are 0.046 and 0.079, respectively. The differences must arise from incomplete removal of polishing flow metal on the specimen surface. Studies of X-ray diffraction line breadths of non-irradiated uranium metallography specimens versus etching time have revealed that a one minute electropolish in phosphoric acid-ethylene glycol-ethyl alcohol solution followed by a 20 minute etch will not remove all of the cold worked surface structure. A longer etching period, however, does remove the flow metal completely.

For purposes of comparison, metallographic results obtained on a rod specimen irradiated to a higher burnup, 0.41 a/o are included. As a consequence of an increase in thermal conductance at the clad-uranium interface and a decrease in burnup rate during the irradiation, the core temperature and peripheral temperatures decreased from 500 to 380C, and 400 to 190C, respectively.

Fig. 11 illustrates the microstructure which resulted from a 100 hour anneal at 600, 650, 700, and 880C in wafer specimens cut from the rod specimen. Porosity develops much more extensively than was the case for specimens irradiated to a lower burnup, Fig. 2. Extensive open porosity and cracking has resulted during the lower temperature anneals, and this porosity appears to be associated as a lattice network around relatively dense regions containing impurity inclusions. At the high annealing temperature, 880C, however, the porosity has changed to isolated,

irregular shaped large pores, and no impurity inclusions are evident. The specimen subjected to the 880C anneal was repolished and etched several times, but inclusions were never observed. Two explanations for the absence of the inclusions can be advanced: (1) the inclusions go into solution by virtue of a chemical reaction with the fission gas impurity atoms, or (2) the high temperature anneal causes porosity to envelope impurity inclusions, and the inclusions fall out or are not observable within the large pores.

Figs. 12, 13 and 14 illustrate the electron microscope appearance of the replicas of the specimens in the as-irradiated, 600C, and 880C annealed states. It is quite apparent that the microporosity changes drastically as a consequence of the annealing treatment. Recrystallization has occurred at 600C, and pores are associated with grain boundaries. For the specimen with the higher annealing temperature, the large pores are too large to be examined in the electron microscope and only the smaller pores can be examined. In this case, only a small number of medium sized pores with large interpore spacings are observed. Careful scrutiny in the electron microscope failed to reveal impurity inclusions.

SUMMARY AND CONCLUSIONS

Optical and electron microscope examination of fission gas pores in irradiated uranium as a function of material history and irradiation conditions should provide a relatively simple means for studying the nature of swelling in uranium. The size and density distribution of pores in irradiated uranium changes markedly during post-irradiation annealing treatments. Since the number of gas nuclei and the growth of such nuclei into perceptible pores is of extreme interest in understanding the mechanism of gas migration and agglomeration, a semi-quantitative metallographic procedure which yields pore void fraction and pore void density values has been developed and is being refined. Errors associated with the replication of pores and errors associated with etching of pores have been investigated, and a theoretical model to be used as a reference for quantitative metallography of pores in uranium is being developed.

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Fig. 1 - Universal Goniometer With X, Y and Z Translations, and Perpendicular Rotations For Optical Viewing of Irregular Surfaces

Fig. 2 - Microstructure of Natural Uranium Irradiated in the α Phase to 0.29 ^a/o Burnup after a 100 hour Anneal at 600, 650, 700, and 880 C, Respectively

Fig. 3 - Pores Present in Uranium Irradiated to 0.29 ^a/o Burnup

Fig. 4 - Pores Present in Uranium Irradiated to 0.29 ^a/o Burnup after 100 hour Anneal
at 600°C

Fig. 5 - Pores Present in Uranium Irradiated to 0.29 ^a/o Burnup after 100 hour Anneal
at 880°C

Fig 6 - Comparison of $F_\phi(S/d)$ versus S/d for Uranium Irradiated to a Burnup of 0.29 ^a/o, Before and After 100 hour Anneal at 880°C

Fig. 7 - The Effect of Temperature of Irradiation and Post Irradiation Annealing on Pore Size Distribution in Uranium with a Burnup of 0.29 a/o.

0.57 μ diameter

1.17 μ diameter

Fig. 8 - Electron Micrographs of Plastic Specimen Containing Spherical Pores of Known Sizes.

Fig. 9 - Analysis of the Distortion Associated with the Replication of Synthetic Pores with a Known Diameter of 1.17 Microns.

As-polished

20-Minute C.V.E.

90-Minute C.V.E.

Fig. 10 - Electron Micrographs Illustrating the Effect of Surface Preparation on the Porosity in Irradiated Uranium.

Fig. 11

Microstructure of 1.3 ^a/o Enriched Uranium Irradiated in the α Phase to 0.41 ^a/o Burnup after a 100 hour Anneal at 600, 650, 700, and 880°C, Respectively

Fig. 12 - Pores Present in Uranium Irradiated to 0.41 ^a/o Burnup

Fig. 13 - Pores Present in Uranium Irradiated to 0.41 ^a/o Burnup after 100 hour
Anneal at 600°C

Fig. 14 - Pores Present in Uranium Irradiated to 0.41 ^a/o Burnup after
100 hour Anneal at 880°C

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METALLOGRAPHIC CHARACTERISTICS OF OXIDES, NITRIDES, AND CARBIDES
IN ALPHA TANTALUM *

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Tantalum, with controlled additions of oxygen, nitrogen, and carbon, was studied metallographically. It is shown that the characteristics of the resulting compounds in alpha tantalum are dependent on the temperature at which they are formed.

INTRODUCTION

As part of the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) materials program, a study was conducted to obtain a better understanding of metallographic characteristics of oxides, nitrides, and carbides in alpha tantalum. Tantalum with controlled additions of the respective elements was heat-treated at various temperatures between room temperature and 1600°C to allow the formation of possible phases. The resulting structures were analysed by metallographic and X-ray diffraction techniques. Tantalum tubing fabricated by Metallwerk Plansee was used as the base material. The chemical analysis of the tantalum is given in Table I.

Metallographic preparation of the specimens included rough polishing on graded silicon carbide papers and final polishing with 6 and 1 micron diamond abrasive. A solution of one part HF (48%), one part HNO₃ (70%), and two parts lactic acid (85%) was used as the etchant.

Tantalum Oxides

Tantalum specimens, previously degassed for two hours at 2600°C in vacuum, were gassed in pure dry oxygen at 1600°C to give an approximate gas concentration of 4500 ppm by weight. The gassed specimens were then reheated in vacuum at various temperatures to allow precipitation.

Tantalum, as oxidized at 1600°C, formed a discontinuous grey grain-boundary oxide when the solubility limit was exceeded (Figs. 1 and 2). The oxide was identified by X-ray diffraction analysis to be the high temperature modification of Ta₂O₅. No oxide formed within the grains of the specimen when it was cooled rapidly. The Ta₂O₅ phase was not optically active in polarized light.

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

Subsequent vacuum heat-treatment of the gassed specimens between 600 and 1000°C resulted in the precipitation of a grey, semitransparent Widmanstätten structure (Fig.3). The precipitate, β oxide, is characterized by its light blue color when examined in polarized light (Figs. 4 and 5). No β oxide was observed to form in the grain boundaries. A crystallographically oriented structure was observed within the precipitated β oxide platelets, most probably the result of a lower temperature phase transformation (Fig.6). The β oxide structure and composition have not been determined. X-ray diffraction analysis gave no indication of the presence of the low temperature modification of Ta_2O_5 after the 600-1000°C heat-treatments.

It has been reported by Gebhardt¹ that 1200°C is the lower limit of formation of the intergranular Ta_2O_5 . Below 1200°C, β oxide only is formed intragranularly along the cubic planes of the Ta.

A vacuum heat-treatment at 300°C of the as-oxidized tantalum resulted in the formation of a fine white precipitate within the grains unlike the β oxide formed at higher temperatures (Fig.7). This oxide, previously not reported, will be referred to as γ oxide. The γ oxide was not active in polarized light. The structure and composition of the γ oxide has not been determined.

Tantalum Nitrides

Tantalum specimens previously vacuum-degassed at 2600°C were gassed in dry spectrographic grade nitrogen at 1600°C to give an approximate gas concentration of 5000 ppm by weight. The gassed specimens were then reheated in vacuum to allow precipitation.

Tantalum as nitrided at 1600°C formed a grey grain-boundary nitride phase when the solubility limit was exceeded (Fig.8). The phase was identified by X-ray analysis to be TaN. No nitrides were observed to precipitate in specimens rapidly cooled. Subsequent vacuum heat-treatment at 1000°C and 800°C caused a fine white nitride to precipitate along crystallographic directions, outlining grain boundaries and sub-boundaries (Figs. 9, 10, and 11). The nitride phase was identified as Ta_2N by X-ray analysis. The Ta_2N phase was not optically active in polarized light.

Vacuum heat-treatment of an as-gassed specimen at 600°C resulted in an extremely fine crystallographically oriented precipitate of unknown composition (Fig. 12). It was determined by X-ray analysis that this nitride was not TaN or Ta_2N .

Vacuum heat-treatment of as-gassed tantalum at 200°C caused no precipitation, but etch pits outlined sub-boundaries, indicative of incipient precipitation (fig. 13).

It has been reported in the literature² that a relatively coarse nitride phase could be formed by nitriding tantalum at 750°C. The reported phase appeared to be similar in form and in reaction in polarized light to the previously mentioned β oxide. A phase of that type was not observed by either precipitation from supersaturated α Ta, or by nitriding in the 700-800°C range.

Tantalum Carbides

Degassed tantalum was carbided by holding a molten cerium-carbon alloy in a Ta crucible at 900°C for 5 hours in vacuum. This treatment resulted in the formation of a white surface carbide layer as well as a discontinuous white intergranular carbide phase (Fig. 14). X-ray diffraction analysis detected only the α Ta and TaC phases. The hardnesses of the surface carbide and of the intergranular carbide were similar (approximately 1000 DPH units, as measured with a 5 gram load). It is therefore assumed that both the surface carbide and the intergranular carbide is TaC. The TaC phase was not active in polarized light. It should be noted that there is no evidence of the Ta_2C phase between the α Ta and the TaC as would be predicted by the phase diagram.³ Apparently the diffusion rate of carbon at this temperature is significantly greater along the grain boundaries than it is transgranularly.

An arc-cast tantalum alloy, containing 310 ppm by weight of carbon, was cold rolled and annealed at 1400°C for 1/2 hour. The resulting metallographic structure (Fig. 15) is believed to be incipient precipitation of the Ta_2C phase along sub-boundaries and grain boundaries. No second phase could be detected by microbeam X-ray analysis. The same alloy, when examined in the as welded condition (Fig. 16), contained a fine particulate phase in the grain boundaries and sub-boundaries in addition to the background structure as shown in Fig. 15. Microbeam X-ray analysis detected a small amount of the Ta_2C phase in the α Ta; no other phases were observed. Therefore, it is assumed that the carbon in α Ta tends to collect at boundaries, and by means of heat treatment, the Ta_2C phase can be precipitated in the boundaries.

Summary

1. It has been observed that Ta_2O_5 , β oxide, and γ oxide can be formed in α Ta. The occurrence of a particular phase in a Ta-O system is dependent on the thermal history of the system. The oxide phases have been identified metallographically by their color, manner of formation, and by their reaction in polarized light.
2. It has been observed that TaN, Ta_2N , and an unidentified nitride phase (a modification of Ta_2N) can be formed in α Ta. The occurrence of a particular phase in a Ta-N system is dependent on the thermal history of the system. The nitride phases have been identified metallographically by their color and manner of formation.
3. It has been observed that the Ta_2C phase can be formed in α Ta under certain thermal conditions as predicted by the Ta-C phase diagram, and that the TaC phase can be observed in α Ta under certain non-equilibrium conditions.

Acknowledgements

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TABLE IChemical Analysis of Metallwerk Plansee Tantalum Tubing

Ti	5 ppm	W	300 ppm
Fe	80	Ni	20
Cu	1	Si	10
Cb	1000	Al	10
Mo	200	C	40

Fig. 1 150X Etched
Ta + 4500 ppm O₂. As gassed at
1600°C.

Fig. 2 2000X Etched.
Ta + 4500 ppm O₂. As gassed at
1600°C.

Fig. 3 300X Etched.
Ta + 4500 ppm O₂. Gassed at
1600°C + H. T. at 800°C, 24 hr.

Fig. 4 1000X Etched.
Ta + 4500 ppm O₂. Gassed at 1600°C
+ H. T. at 800°C, 24 hr.

Fig. 5 1000X Etched.
Polarized Light. Same as Fig. 4.

Fig. 6 2600X Etched.
Polarized Light. Platelet at
 β oxide precipitated at 600°C.

Fig. 7 1000X Unetched.
Ta + 4500 ppm O_2 . Gassed at 1600°C
+ H. T. at 300°C, 200 hr.

Fig. 8 1000X Etched.
Ta + 5000 ppm N_2 . As gassed at
1600°C.

Fig. 9 2000X Etched
Ta + 5000 ppm N_2 . Gassed at $1600^{\circ}C$ +
H. T. at $1000^{\circ}C$, 24 hr.

Fig. 10 1000X Etched
Ta + 5000 ppm N_2 . Gassed at $1600^{\circ}C$
+ H. T. at $800^{\circ}C$, 24 hr.

Fig. 11 2000X Etched.
Ta + 5000 ppm N_2 . Gassed at $1600^{\circ}C$
+ H. T. at $800^{\circ}C$, 24 hr.

Fig. 12 1000X Etched.
Ta + 5000 ppm N_2 . Gassed at $1600^{\circ}C$
+ H. T. at $600^{\circ}C$, 24 hr.

Fig. 13 1000X Etched
Ta + 5000 ppm N_2 . Gassed at
 $1600^{\circ}C$ β H.T. at $200^{\circ}C$ 24 hr.

Fig. 14 600X Etched.
Ta carbided by a molten Ce-C alloy
at $900^{\circ}C$, 5 hr.

Fig. 15 300X Etched
Ta + 310 ppm C. Cold rolled and
annealed at $1400^{\circ}C$, 1/2 hr.

Fig. 16 1000X
Ta + 310 ppm C. As welded.

OBSERVATIONS ON THE MICROSTRUCTURE OF PLUTONIUM

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The procedure and technique of metallographic examination of plutonium and plutonium alloys at the Hanford Atomic Products Operation are discussed. Metallographic studies were made on plutonium buttons reduced from plutonium fluoride; on plutonium ingots recast from buttons; on several plutonium alloys; on the effect of tension and compression in the alpha, beta, gamma and delta phases on the microstructure of recast ingots; on the formation of voids in thermally-cycled plutonium and a plutonium uranium alloy; and on the effect of different casting and heat-treating conditions.

INTRODUCTION

A knowledge of the metallographic characteristics of a metal are essential for metal quality, fabrication and heat treatment evaluations. In addition, microstructural variations in grain structure and inclusion size, shape and distribution can have significant effects on the properties of a metal.

Since plutonium has six allotropic modifications in the solid state it is apparent that large variations in metallographic appearance could be present. Therefore it was decided to study the microstructure of both calcium reduced and calcium reduced-re-cast plutonium in order to characterize them from a metallographic standpoint. In addition some preliminary work on the effect of heat treatment on microstructure is presented.

It is hoped that the observations presented herein will to a large degree provide the basis for a more detailed study of plutonium microstructures; eventually leading to complete identification of the inclusions observed and to an explanation of the most prominent microstructural characteristics.

SUMMARY

Photomicrographs are presented which illustrate the various configurations of the Pu-Pu₆Fe eutectic, PuN, PuC, and Pu_xMg_y inclusions in both as-reduced and re-cast plutonium. Several variations in the microstructure

were observed with respect to inclusion distribution, size, and shape. These variations, which occurred as a result of heat treating and casting conditions, are illustrated.

The average re-cast grain size was 0.040 mm. Preliminary investigation of the effect of the beta-alpha transformation rate on the alpha grain size showed that decreasing the isothermal quench temperature from 73C to -23C after holding one hour at 175C resulted in a decrease in grain size from 0.023 to 0.006 mm.

Extensive microcracking was observed in plutonium having less than 500 ppm iron. The presence of 500 to 1500 ppm iron appeared to inhibit microcracking.

MATERIALS AND SPECIMEN PREPARATION PROCEDURE

Materials

Plutonium is reduced to the metallic state during the bomb reduction of plutonium fluoride with calcium. To ascertain the quality of the as-reduced plutonium buttons, representative sections were taken for metallographic study. In addition, to determine the effect of a remelting operation, as-reduced buttons were melted at 950C in vacuo and poured into a MgO coated graphite mold which had been heated to 300C. Sections of these castings were also taken for metallographic observation.

Specimen Preparation Procedure

All specimens were mounted in Thalco polyester resin which sets up slightly above room temperature. This kept the specimen temperature below the 112C beta-to-alpha transformation temperature during mounting. The mounted specimens were rough polished by hand on wet-or-dry emery paper of 180 through 600 grit. A liberal amount of carbon tetrachloride was used as a lubricant and coolant during this operation.

Fine polishing was accomplished in a two step process on Syntron vibratory polishers. The first step consisted of a two hour polish on billiard cloth using a Linde A emulsion in carbon tetrachloride. The second step, on a different Syntron, consisted of a five to fifteen minute polishing period on Buehler microcloth again using Linde A and carbon tetrachloride. This procedure resulted in a non-oxidized scratch free surface which will be termed "as-polished" in the remainder of the report.

Electrolytic etching for inclusion studies and for grain structure were accomplished in a solution of 20 parts tetraphosphoric acid, 30 parts water, and 50 parts 2-ethoxy-ethanol. To study grain structure the specimens were electrolytically etched for 60 seconds at 23 volts and

0.15-0.30 amperes and then allowed to oxidize for two to fifteen hours at room temperature. Electrolytic etching times for inclusion studies varied between one and ten seconds at 15-23 volts. All photomicrographs with the exception of those containing grain structure were taken under bright field illumination. Grain structures were taken under polarized illumination.

Because of the hazards involved in working with plutonium, all operations involving plutonium or its alloys were conducted in glove boxes. This complicated most metallographic operations and tended to lower the overall quality of the surface finish. In addition, all metallographic samples were viewed through a sealed 0.015 inch thick clear plastic bag since a glove box enclosed metallograph was not available. Thus imperfections in the plastic frequently lowered the quality of the photomicrographs, especially at magnifications greater than 250X. A photograph of the metallographic glove box train is illustrated in Fig. 1.

RESULTS AND DISCUSSION

Pu-Pu₆Fe Eutectic

One of the most common microconstituents occurring in both as-reduced and re-cast plutonium was the Pu-Pu₆Fe eutectic. It appeared as a network which outlined the grains which were present during the eutectic solidification at 410C, Fig. 2. When the iron content of re-cast plutonium was greater than 600 ppm (by weight) the network was continuous and outlined a grain size ranging from 0.080 to 0.160 mm with an average of 0.120 mm. Generally the Pu-Pu₆Fe eutectic network was relatively equiaxed as illustrated in Fig. 2, however in some samples the unusual configurations illustrated in Figs. 3 and 4 were observed. Figure 5 illustrates the substructure present in the Pu-Pu₆Fe eutectic.

Plutonium Nitride Inclusions

Plutonium nitride inclusions were common in as-reduced plutonium, Fig. 6. They frequently occurred in clusters, around gas pockets, or along cold shuts, Fig. 7 and 8.

Since PuN inclusions float to the top of the melt during a remelting operation, they were not commonly observed in re-cast plutonium if a 30 second slagging period was provided prior to pulling the mold plug. The segregation of nitrides to the top of an ingot during casting in place is illustrated in Fig. 9.

It is interesting to note that some nitride inclusions had angular shapes as illustrated in Fig. 10 while others were somewhat spherical. This can possibly be attributed to the solution of other impurities in the PuN inclusions.

Plutonium Carbide Inclusions

Plutonium carbide inclusions in the form of long thin platelets were also numerous in as-reduced plutonium, Figs. 11 and 12. They were infrequent in re-cast metal, again because they floated off during remelting. Note that a separation sometimes occurred between the inclusions and the plutonium matrix, Fig. 12. This was probably caused by the nine percent decrease in volume associated with the beta-to-alpha transformation. An inclusion believed to be a plutonium carbide compound formed by casting in place in graphite at 950C is illustrated in Figs. 13 and 14.

Other Inclusions

What was believed to be a plutonium magnesium compound in as-reduced plutonium is illustrated in Fig. 15. Inclusions of this type either slagged off or volatilized during re-casting and did not appear in re-cast metal. Note the numerous PuN inclusions at the periphery of the Pu_xMg_y inclusion.

The somewhat spherical inclusions illustrated in Figs. 16 and 17 have not been identified. They were common in both as-reduced and re-cast plutonium; however, they were considerably larger in as-reduced plutonium.

Microcracking in Re-Cast Plutonium

Microcracks were found to be quite prevalent in normally re-cast plutonium with low iron content. It has been determined that the presence of Pu-Pu₆Fe eutectic, corresponding to 500 to 1500 ppm iron has an inhibiting effect on the formation of microcracks in re-cast plutonium. ⁽¹⁾ When the iron content was less than 500 ppm, extensive microcracking was observed, Fig. 18. As the iron content was increased above this level the number of microcracks decreased. Plutonium containing more than 1000-1500 ppm iron revealed virtually no microcracks.

The transverse cross sectional distribution of microcracks in low iron plutonium cylinders was not always uniform. In some castings microcracks were located primarily near the periphery, Fig. 19, while in others, one-half of the cross section would have extensive microcracking and the other half would have practically none. These observations strongly suggested that the rate of cooling to room temperature may have had a great effect on microcracking. Thus it was probable that casting technique had an effect on microcrack formation. It was observed that when metal of low impurity content was cooled very slowly through the beta-to-alpha transformation after casting, little or no microcrack formation was observed.

- (1) Gardner, H. R. and Mann, I. B., "Mechanical Property and Formability Studies on Unalloyed Plutonium", Proceedings of the 2nd International Conference on Plutonium at Grenoble, France, April 1960.

Grain Structure

Both as-reduced and re-cast plutonium had non-equiaxed subgrained structures, Figs. 20 and 21. Average grain sizes ranged from 0.016 to 0.070 mm with an overall average of 0.040 mm. In some cases, large individual grains were observed with an average grain size of 0.30 mm, Fig. 22. Subgraining in plutonium is illustrated in Fig. 23. Note the effect of metallographic stage rotation on grain structure.

A columnar grain structure has been observed at the periphery of re-cast plutonium cylinders, Fig. 24. It is suggested that during cooling through the beta-alpha transformation, nuclei form at the periphery first and grow in a columnar fashion until the nucleation rate becomes higher in the interior resulting in a random grain alignment.

The effect of quench bath temperature after a beta phase anneal at 175C for one hour is illustrated in Fig. 25. The cooling rate during the beta-alpha transformation had a marked effect on the resultant alpha grain size. Decreasing the quench bath temperature, i.e. increasing the cooling rate, resulted in a decrease in grain size from 0.023 to 0.006 mm. The maximum rate of transformation of Beta to alpha occurred at approximately -20C. A more rapid quench, particularly from the gamma, delta, or epsilon phases produced a finer grain size than 0.006 mm. An extremely slow cool produced a more coarse microstructure.

ACKNOWLEDGEMENTS

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Fig. 1 - Hanford Metallographic Glovebox Train

50X

Fig. 2 - Pu-Pu₆Fe eutectic network.
As-polished.

50X

Fig. 3 - Pu-Pu₆Fe eutectic network.
Etched 10 seconds.

50X

Fig. 4 - Pu-Pu₆Fe eutectic network.
Etched 10 seconds.

250X

Fig. 5 - Pu-Pu₆Fe eutectic.
As-polished.

250X

Fig. 6 - Plutonium nitride inclusions in fluoride reduced metal. As-polished.

100X

Fig. 7 - Plutonium nitride inclusions segregated at gas pockets in as-cast plutonium. As-polished.

100X

Fig. 8 - Plutonium nitride inclusions segregated at a cold shut. As-polished.

50X

Fig. 9 - Plutonium nitride inclusions near the top of an ingot cast in place. As-polished.

Fig. 14

Plutonium carbide inclusions with
unusual configurations.
As-polished, 100X.

Fig. 15

Plutonium-magnesium inclusion in fluoride reduced metal.
Note PuN inclusion at periphery. As-polished. 250X.

250X

Fig. 10 - Plutonium nitride inclusions with an angular shape. As-polished.

100X

Fig. 11 - Plutonium carbide, etched 10 seconds.

250X

Fig. 12 - Plutonium carbide inclusions. Note the separation at the interface between the large carbide and the base metal. As-polished.

250X

Fig. 13 - Plutonium carbide inclusions with unusual configurations. As-polished.

Fig. 16 250X
Unidentified spherical shaped in-
clusions in as-cast plutonium.
As polished.

Fig. 17 250X
Unidentified spherical shaped
inclusions in fluoride reduced
metal. As-polished.

100X

250X

Fig. 18 - Microcracks occurring in as-cast purity
plutonium with less than 500 ppm Fe. As polished.

Fig. 19
Microcracks occurring near the periphery of a casting. As-polished.

Fig. 20
Microstructure of fluoride reduced plutonium. Electropolished.

Fig. 21
As-cast grain structure with an average grain size of 0.04 mm, electropolished.

Fig. 22
Very large grains, 0.2 x 0.4 mm in as-cast plutonium. Electropolished.

90.6°

120.7°

149.7°

Fig. 23 - Photomicrographs taken under polarized illumination at the indicated metallograph stage rotations to illustrate sub-graining in plutonium. Electropolished. 250X.

Fig. 24 50X
Columnar grain growth at the periphery of a casting. Electropolished.

-21C

26C

73C

Fig. 25 - Effect of an isothermal quench at the indicated temperatures on the alpha grain size after an anneal at 175 C for 1 hour. Electropolished, 300X.

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SOME PRELIMINARY METALLOGRAPHIC STUDIES
OF MATERIALS FOR USE ABOVE 2500°C

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Nuclear rocket engines require materials capable of operating at temperatures in excess of 2500°C. Little is known of such materials, including their metallography. A few preliminary studies of materials such as the refractory metal carbides and other high melting materials are presented in this paper, including metallographic preparation, examination and microhardness determinations.

This paper is not the result of an organized research program, but rather a potpourri of the almost limitless variety of requests which come through this metallographic laboratory. This is, however, a very fertile field for research. It is limited on one side only by the elements in the periodic table, on the other side by the cost, on the bottom by a very arbitrary temperature of 2500°C, and is without any well defined top. This defines a very large area, sufficiently large for a tremendous amount of study, yet only the high spots have been touched so far.

The metal carbides have attracted the most attention up to this time, for the most part in the hot pressed or sintered condition. Today one is not only hot pressing carbides, one is forming them "in situ" by carbiding the metal parts, and one is also melting them, including tantalum carbide, which melts at about 4100°K. Carbiding of metals produces some most unusual microstructures and it is suspected may produce some hitherto unknown compounds.

In connection with carbides formed by carbiding of metals, there is an extremely interesting series for metallographic study, namely eutectics and triple points. By a judicious selection of metal wires enclosed in graphite capsules, and subsequent metallographic examination, one can determine fairly well what the temperature of a given body has been. For instance, one may place a capsule containing tungsten and a capsule with tantalum in a body which attains a high temperature. If one later finds evidence of W-W₂C eutectic but no evidence of any

eutectic with the Ta, one may say the temperature has been over 2730°C but less than 2900°C.

Metal nitrides, borides and silicides are also being examined to some extent, though the interest is some orders of magnitude less than that shown for the carbides.

Yet a third area in this field is other intermetallic compounds. The interest in this area so far amounts largely to the gleam in the metallurgist's eye. This paper touches all three of these areas, though rather lightly in spots.

Almost without exception these materials are very hard compared with most materials a metallographer may encounter. Because of this fact, this Laboratory has developed one standard technique for polishing which appears to work well for almost all materials encountered. This technique is essentially as follows:

1. The sample is cut with an American Instrument Company cut-off wheel using an Aminco 5-2211 abrasive wheel, which works very well for most hard materials, though occasionally it is necessary to resort to a diamond saw.
2. Mounting is usually done in Epon resin with a light gauge cotter pin gripping the sample to make electrical contact when necessary.
3. Rough grinding is done on the conventional horizontal wheel with wet "Wet-or-Dry" silicon carbide paper. Some of the very hard materials require a number of papers of each grit size, since the silicon carbide is worn down so rapidly. Grinding on a "dull" paper is poor economy and has a strong tendency toward "smeared" surface material. The successive grit sizes may be like 100, 250, 400 and 600.
4. The penultimate polishing operation is on Metcloth or its equivalent with a 6 micron Diamet-Hyprez compound with kerosene.
5. The final polish is on a Forstmann Woolen high nap broadcloth using 1 micron diamond paste.

The two final polishing operations take about one to two minutes each and result in a very satisfactory polish with relatively little relief polishing considering the large hardness variations encountered, as in a partially carbided tantalum wire. Occasionally on a very brittle material, it is necessary to spend much more time on the 6 micron cloth because the large SiC grits have shattered the surface leaving a very rough surface. The diamond paste, however, cuts and polishes without shattering the very brittle constituents.

Etching was done either chemically or electrolytically as the case may be. The cotter pin connection to the sample through the plastic

made it possible to have only the sample in electrical contact with the electrolyte. While it is desirable not to have any anode composed of more than one metal or compound because of the variation in decomposition potential, it is extremely important in some cases such as Rhodium, where the current density is very high.

The hardness readings were taken with a Leitz Miniload hardness tester. No trouble was experienced in obtaining hardness checks within the limits of the test block, $970 \pm 30 \text{ Kg/mm}^2$. Normally a load of 100 g was used with occasional checks up to 500 g.

X-ray phase identification was accomplished in one of two ways, a Norelco Debye-Sherrer outfit using nickel filtered copper radiation or by a Hilger micro-beam unit for polished metallographic samples.

The two most used etchants for this report are:

No. 1	3- HNO_3	No. 2	10% NaOH at 0.5 A/in^2
	1- HF		
	5- H_2O		

The other etchants are given with each photomicrograph.

Acknowledgements

C. E. Olsen - microbeam X-ray work.

C. P. Kempter - Debye-Sherrer work.

R. J. Dietz - work with temperature measuring system.

Others who submitted samples for metallographic examination.

Fig. 1
Etch No. 1
Melted Mo_2C ; DPH-1700

250X

Fig. 2
Etch No. 1
 Mo_2C penetrating Mo foil during
carbiding at 1800°C
Gamma MoC at crystal planes

500X

Fig. 3
Etch No. 1
 Mo_2C at grain boundaries of Mo
by carbiding Mo rod at 1800°C
DPH-130 and 1800

200X

Fig. 4
Etch No. 1
Eutectic of Mo- Mo_2C
DPH 250-500

500X

Fig. 5
Etch No. 1
Eutectic plus Mo_2C at grain
boundaries of Mo. 1500X

Fig. 6
Etch No. 1
Eutectic plus Mo at grain
boundaries of Mo_2C . 1500X

Fig. 7
Etch No. 1
Mo- Mo_2C eutectic plus MoC with
not enough Mo to form eutectic
and melt. 200X

Fig. 8
Etch No. 1
Gamma MoC major phase with some
Gamma prime MoC, similar to larger
striated particles in Fig. 7. 500X

Fig. 9
Etch No. 1
Gamma MoC, almost pure, multiple
twinning. 1740 DPH

Fig. 10
Etch No. 1
Similar to Fig. 9 but also contains
graphite or some unknown carbide.

Fig. 11
Etch No. 1
MoC-C eutectic with excess
graphite

Fig. 12
Etch No. 2
WC melted; DPH-2100

Fig. 13 500X
Etch No. 2
Hot pressed W_2C 1800 DPH

Fig. 14 500X
Etch No. 2
 W_2C on W metal by carbiding at
1600°C

Fig. 15 500X
Etch No. 2
W- W_2C eutectic 2730°C

Fig. 16 500X
Etch No. 2
 $W_2C + W$ 2730°C but not proper
composition to melt.

Fig. 17
Etch No. 2
500X
 W_2C and an unknown carbide,
probably some graphite
needles.

Fig. 18
Etch No. 2
1500X
Similar to Fig. 17 with unknown
carbide at grain boundaries.

Fig. 19
Etch No. 2
500X
VC melted
DPH 2460

Fig. 20
Etch No. 1
6X
Nb in graphite capsule has melted
and run up sides of capsule. Two
zones of carbiding are visible
 $2750^{\circ}C$.

Fig. 21
Etch No. 1
NbC melted DPH-2600

500X

Fig. 22
Etch No. 1
Center of capsule seen in Fig. 20
Nb₂C plus some NbC with high carbon
in each case.

250X

Fig. 23
Etch 3-HNO₃: 1-HF
Melted Zeta³ phase TaC
DPH 3100

500X

Fig. 24
Ta₂C on surface and at G.B. of Ta
metal, carbided at 2000°C 15 min.
DPH 3060.

500X

Fig. 25
Etch - 3 HNO₃ : 1 HF
Ta carbided at 2000°C Zeta TaC
(major) with some Ta₂C 2000X

Fig. 26
Etch - 10% H₂SiF₆ 200 A/in²
Eutectic of Rh-C 100X

Fig. 27
Etch: 10% H₂SiF₆ 200 A/in²
Shows Rh-C eutectic plus the graphite.
Note deficiency of C around graphite
needles. 500X

Fig. 28
Etch: 10% H₂SiF₆; 200 A/in²
Re + C eutectic plus carbon needles 500X

Fig. 29
No etch
Carbon precipitated from Pt-C melt

100X

Fig. 30
Etch - 3 HNO₃: 1 HF: 4 H₂O
ZrC melted; DPH-2500

500X

Fig. 31
Etch: 2 HF: 8 HNO₃: 15 H₂O
ZrB₂ melted, second phase probably
oxide. DPH 2100.

250X

Fig. 32
Etch: 2 HF: 8 HNO₃: 15 H₂O
TiB₂ melted, some cracking, very
brittle. DPH 2900.

250X

Fig. 33
Etch: 1 HF; 3 HNO₃; 9 H₂O
TaB₂ pressed and sintered
DPH 2400 500X

Fig. 34
Etch: 1 HF; 3 HNO₃; 5 H₂O
TiN pressed and sintered
DPH 1970 500X

Fig. 35
Etch: 5 HF; 3 HNO₃; 6 H₂O
ZrRe₂ - arc melted
DPH 1400 500X

Fig. 36
Etch: 5 HF; 3 HNO₃; 6 H₂O
HfRe₂ - arc melted. Polarized Light.
DPH 1400 500X

X-RAY FILM DEFECTS AND AUTORADIOGRAPHY OF FUEL ELEMENTS
FOR CLADDING THICKNESS MEASUREMENT

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Radiography of fuel element cladding can be performed by using the natural radioactivity of the core material as the source of exposure. X-ray film is placed in close contact with the surface of the cladding for several hours and the film is exposed by rays from the uranium which penetrate the cladding. The resulting density of the processed film at any specific location is related to the thickness of the cladding at the same location on the fuel element. By measuring photographic film density and comparing it with that of a standard film, which has been exposed and processed at the same time as the subject film, one can determine cladding thickness. The degree of accuracy depends upon carefulness in control of the entire autoradiographic procedure. Plus or minus 10 percent accuracy is normal for cladding below 20-mils in thickness. This method is not suitable for measuring more than 30-mils of Zircaloy or 50-mils of aluminum.

There is a certain defect which is sometimes encountered in photographic supplies "as purchased" and which can be detrimental to fuel element inspection, particularly if these defects are not readily recognized by the testing laboratory. A considerable number of these defects have been observed recently during autoradiographic analysis and a few samples of them are shown with this paper. Knowledge of their characteristic appearance and occurrence is sufficient to permit them to be distinguished as separate from metallurgical or fabrication defects in fuel elements in about 80 percent of all cases.

It is of considerable importance that a certain type of defect known as RA spots be more generally recognized in photographic film supplies. It is perhaps most important to those people who might use autoradiography as a means for measurement of fuel element cladding thickness.

This type of defect appears as small dark spots on photographic film after development. They are known as Radioactivity Spots, hence RA spots. Each source is an extremely tiny particle of radioactive substance lodged inside the box of film during manufacture and packaging. Their nature and occurrence in photosensitive supplies as the user receives them is recognized by

every film manufacturer. One of the leading makers of film in the United States has published data stating that they have spent over a million dollars trying to eliminate the spots. The particles are so small that some of the finest of them get past extensive filtering systems for all the water and air in the film manufacturing areas. Employees are thoroughly "screened" before entering work areas, having to change clothing and having to pass through inspection by counting device for detection of any radioactive contamination. It was believed that the emulsion did not contain the particles and that they were in the film base material or more likely in the paper leaflets which separate the individual sheets of film. The same manufacturer had taken over the making of the leaflet paper in order to have better control in the RA spot problem.

The few minute particles which get by are especially damaging because, of course, it is their nature to radiate in all directions and create fogged spots in the emulsion which are far bigger than themselves. The resultant spots in developed film can be as large as 1/8-inch in diameter. They have a very black, dense center, surrounded by a continuous halo, fading in density toward the periphery and having an appearance like the sun on a hazy day. Each particle damages more than one sheet of film. More nearly ten sheets are affected by every particle. The film nearest the source receives the heaviest radiation and accordingly shows the most dense spot after development. About four adjacent films on each side of the source become fogged at precisely the same location on the film but to a lesser degree. The density decrease outwardly in the package as the radioactivity becomes absorbed and attenuated by distance and the intervening material. Actually 19 to 25 layers of material are penetrated by one radioactive particle as follows: 7 to 9 films and 12 to 16 sheets of interleaving paper. Each spot in a batch is directly superimposable over the next like the hole a worm bores through an apple. This is the main feature which makes the spots recognizable, if the operator consistently uses the film consecutively from one end of the box.

On further examination it becomes obvious that the worst RA spots are not the dense ones. They are the easiest to recognize because they contain a lot of blackness at the center. Whether one is familiar with RA spots or not, he will probably recognize the excessive blackness and the roundness as a defect that is not related to the specimen. It might be mistaken for chemical spatter. One might guess that a contaminating spot of developer may have reached the film and been there far longer than the normal developing period.

The more diffuse spots may seldom attract attention in industrial X-ray films since very large portions of film area are often so dense as to mask them out. The latter fact could lead to errors in evaluation and possible product rejects. The spots could be misinterpreted as voids or less dense areas in the subject if they occurred in likely locations. The same is true for medical films. The film we use for our autoradiography is a different brand and type from that used for our medical X-ray work. Both have RA spots. The implication is that other brands of film probably

have them, also. The spots might not be too critical in many other kinds of photography. But they might be of considerable nuisance in tracer work, back reflection Laue patterns, sun-spot pictures, etc. The knowledge of their existence and appearance should be sufficient to prevent serious trouble from them. Why are they easier to detect, perhaps, in autoradiographic film than in most other photographs produced in the metallurgical laboratory?

(a) The entire area of such film is usually of fairly low density.

(b) The film is usually inspected with a densitometer. This is certainly true for fuel element cladding measurement. The fairly rigid measurements produce density numbers which will be converted to metal thickness. All maxima and minima of densities are of particular concern since these determine whether the product is within specifications. This brings any film defect to question until it has been rectified or until it is adjudged a known defect directly related to the autoradiographic process and which is either rectifiable or tolerable. In the inspection of metal cladding by autoradiography, a small dark spot the size of RA spots in the film would indicate the presence of a cladding hole up to several thousandths of an inch in diameter or a thin spot in the cladding.

The autoradiographic test is a fairly sensitive one. The exposure source is always more consistent than the test materials or the people using them. Accordingly, numerous difficulties were recognized during development of this test procedure in 1957 and recommendations for overcoming them have been accumulated since then while applying the process in practice.

There are several refinements of technique which are vital to the success of the autoradiographic method for nondestructive testing. The purpose here is to present the technique and necessary refinements rather than to evaluate the process. There is considerable interest expressed for other nondestructive tests such as ultrasonic testing or eddy current testing mainly because of the desirable time limits. Each method has good points as well as disadvantages and resultant uncertainties. We find autoradiography the most reliable and consistently reproducible method to date although we utilize other tests in conjunction with it. Furthermore, it provides a photographic image which is a permanent map of the entire product.

AUTORADIOGRAPHIC TECHNIQUE

It is fairly well known that photographic emulsions are affected by radioactive materials such as by X-rays or by visible light. When a piece of uranium is placed in contact with photographic emulsion in a dark room and allowed to remain less than a half hour, the radiation from the uranium exposes the emulsion closest to it so that a very dark area appears on the film after photographic processing. It is somewhat larger than the region of contact because of scatter in all directions. The total time of

required exposure does not appear to change from day to day because the half-life of uranium is very long. Normal uranium has been known to darken film faster than slightly enriched or so-called "hot" uranium.

It is possible to avoid the use of a darkroom to make useful exposures. To protect the photographic emulsion from visible light exposure, the film can be wrapped in a single layer of household aluminum foil (usually about .005 inch thick) or a similar total thickness of opaque plastic sheeting. We use plastic sheeting which is more pliable and durable than aluminum foil. Rays in the particular range of wavelength emitted by the uranium can penetrate wrapping as X-rays would. The rays penetrate slightly thicker or denser layers and it is this feature which is employed in autoradiography. They travel short distances and intensity falls off rapidly. Accordingly, the amount of metal foil or cladding thickness which can be penetrated is limited. We can use autoradiography as an inspection tool for measuring zirconium or Zircaloy cladding accurately up to about .030 inch and aluminum cladding up to about .050 inch. With greater thicknesses, the penetration falls off to such an extent that darkening of the film is barely perceptible. The slight differences of film densities due to very large differences in exposure time or in clad thicknesses are not sufficient to allow accurate measurement.

The film must be in close contact with the subject to get an image dense enough and clear enough to be meaningful. For a cylindrical rod the film in its holder is wrapped snugly around the entire circumference of the rod and taped firmly in position as sketched in Fig. 1. Normal activity of the core material creates radiation which proceeds in all directions and most of it is absorbed by the dense uranium itself. That which radiates outward through the cladding produces a picture of the cladding on the film. For metal tubing, the inside cladding can be measured by inserting narrow film within the tube and pressing it firmly against the metal. The film should be wide enough to cover the entire inside circumference and overlap slightly.

During autoradiography of a fuel element tube 17-inch films are applied end-to-end to cover the entire length. Some tubes, when examined, are over 10 feet long. The films are carefully coded by marking each at one end and loading systematically with the numbered ends pointing to the forward end of the tube. An identification system is essential to know the relationship of each film to the tube, to determine the location of the core ending and to pinpoint possible flaws.

It is necessary to expose film to a known standard and to process one of these standard films in the same photographic chemical tank with each batch of exposed autoradiographs. We use a metal standard of our own manufacture which was designed to simulate the range of products being tested. We made several types of experimental standards and now use one consisting of a short length of uranium tube with known clad thickness coupons attached to the exterior. Several Zircaloy strips of different thickness were

attached so that we could determine the resultant film density for each corresponding thickness of cladding. Also, "standard" films serve as controls for photographic processing. By processing an exposed standard film with every batch, which means every tankful of films, one can be assured that any variation associated with the photographic processing will be cancelled out.

Each coupon on the standard represents a certain thickness of cladding within the range from the expected maximum to the expected minimum of the product and well beyond the range. The areas around the coupons are blocked out with lead foil. A photographic film exposed to this standard is similar to a step-wedge or gray-scale. Figure 2 is a standard film for which the exposure time was 3-1/4 hours. It includes a wedge step for every two mils of cladding from eight to twenty-two mils. From twenty-two mils it increases in one step to thirty-two mils which is represented by the last and barely discernable strip at the bottom. Several density measurements are recorded at the right of the film.

The density of each step on the standard film, after photographic processing and drying, can be measured and plotted into a curve as in Figure 3. Each point represents a different thickness. The first one at the top of the curve represents a cladding which allowed considerable radiation to reach the film during exposure and the film is accordingly quite black. The density of the film in the blackened area measured about 1.88.

Results and interpretation are clear cut in this range because considerable change in density occurs with a change of two mils of cladding. Density of the second point is only 1.64. As the rectangular patches of film get thinner, or lighter, the density gets lower, until at 22 mils the density is only .88. The curve begins to straighten out here so that this value differs very little from the one to the left although it represents material of two mils difference in thickness. It is more difficult in this range to detect accurately the variation in density and therefore in cladding. This allows for very little deviation in the entire test procedure. Particularly close darkroom control is required in order to achieve consistency in all steps of the procedure.

For measuring film density, we use a Photovolt densitometer, Model 501A shown in Figure 4. It is reasonably stable after proper warm-up period. A good feature of this particular model is the long arm which holds the probe. It allows sufficient room for insertion of a large film and permits the probe to reach all areas including the center. There are other commercial densitometers of which some might provide greater ease of operation than others. The price seems to vary accordingly.

FILM DEFECTS

There is a faint RA spot in the original film from which Figure 2 was reproduced. The spot is located at the right, immediately above the

density digits (.088). It is difficult to see and therefore difficult to print for reproduction. There are also some crescents or crimp marks at the top of Figure 2. Crescents are fairly well known defects which can be produced during the handling of heavy X-ray films. Examples of crimp marks and precautions for avoiding them can be found in publications such as Eastman Kodak's guide book "Radiography in Modern Industry". For instance, if a narrow film like this one which was 17 inches long is held with one hand at one end, usually there is a tendency to flip it to hold it horizontally. No more than two fingers should be used to grasp the film during cutting and loading operations. To avoid bending the film, gravity should be employed to advantage. The film should be held at the top by thumb and one finger only so that its entire weight hangs freely. The ends of the film in Figure 2 were particularly susceptible to bending and crimping during application and removal because the film was longer than the metal standard. In applying film to tubes and rods before exposure it must be taped firmly in position. During the taping of the film shown in Figure 2 it became dented and crimped only at the ends where the excess film projected beyond the tube without benefit of support.

The type of film we use for the entire process is Eastman Kodak Industrial X-ray Film, Type KK. It was chosen mainly for its fast speed to keep exposure time to a minimum. It has emulsion on both sides of the base, as does most X-ray film unless otherwise specified. The emulsion is necessarily heavier than that of slower films and is fairly susceptible to abrasion. It is pliable enough to wrap around large objects but is more difficult to manipulate when wrapped around objects of small diameter. If bent to a radius less than 1/2 inch it may break.

Figure 2 represents an OD (outside diameter) film. Actual size of all films shown here and in the other figures is 17 inches long by 4 inches or more in width. Since the 4-inch dimension applies to the complete circumference with slight overlap, it indicates a fairly small tube radius.

Figure 5 shows typical autoradiographs of two tubular fuel elements at locations where the radioactive core ends. One represents a tube made by earlier coextrusion techniques and the other represents newer and improved techniques.

The films in Figure 6 illustrate RA spots in four radiographs selected from the same batch of tests resulting from a "production" fuel element tube. They are ID (inside diameter) films of which there were nine developed in one batch including seven from the tube length, one from the standard and one unexposed film. The unexposed film is developed as a measure of inherent fog level. This is a requirement because extra high speeds in photographic emulsion ordinarily are accompanied by attendant fog difficulties which indicate short shelf life of film stock

even in refrigerated storage. About three months supply is as much as the consumer should stock. One must test the film from time to time for fog density; meanwhile the expiration date printed on the outside of the package is used only as an indication of which box to open first. Film as fast as KK can have a fog density as high as 0.5 at time of purchase although it generally does not. If a density of 0.5 were added to film levels, and evaluated according to the curve shown in Figure 3, it could easily indicate a cladding difference of two to five mils depending on its position in the thickness range.

There is possible usefulness in prefogging film under carefully controlled conditions to arrive at certain exposure thresholds but no attempt was made to employ a prefogging method in our autoradiographic experiments. In Figure 6 the extrusion direction is vertical and parallel to the length of the film. An entire circumference is shown in each film. A narrow light strip at one long edge of a film is caused by overlapping of the film holder.

The encircled areas in Figure 6 illustrate RA spots which are located almost identically from film to film and which decrease in intensity toward the right. This array does not constitute one entire half of a series of RA spots as they usually are found but it serves to illustrate their typical appearance and manner of occurrence. The first and densest spot of all in this series is missing from the figure. It would be located beyond the far left of this group. The first film at the right contains two spots. Ordinarily, there would be about five films to the left of spot No. 2, all of which would display both spots. The film shown here on the right actually came from the far left hand side showing a spot considerably decreased in density from the first source spot so that it is hardly visible. It would be difficult for an inspector to identify such a spot without knowledge of adjacent film appearance.

PROCESS DETAILS

The films are processed vertically in deep tanks of chemicals controlled by temperature regulators. Baths are thoroughly stirred before use and all films in a batch are fully immersed at once. There should be little temperature or chemical variation from top to bottom and intermittent agitation is essential. Gaseous burst development might help in providing more uniformity but it is also possible that it might give small localized variations.

Industrial film as fast as Type KK differs from almost all others in the speed with which it depletes chemicals. Manufacturers' instructions should be observed and followed closely. For maximum density and speed the film is developed 8 minutes instead of 5 minutes. Acid shortstop should be used and the films agitated thoroughly. They remain in the shortstop from 1/2 to 2 minutes depending on whether a water rinse precedes it. To rinse with clear water without using shortstop is not sufficient unless water floods both sides of the film and flows rapidly for two

minutes before immersion of the film in hypo. Some agitation upon immersion in hypo is also desirable to promote uniform fixing and prevent films from sticking together. The highly alkaline developer remains in the emulsion and continues to work and stain unless films are well spaced to permit adequate fixation. The entire film process is not difficult providing the operator controls it rather than the reverse. It would be a major error to assume that general photographic procedures apply to this type of film without regard for its special instructions. Darkroom light must be kept at low levels with the lights at ample distance. Conditions for processing without danger of fogging from excessive illumination are best determined by testing. One method for testing is as follows: A sheet of the unexposed film with a portion of it covered is placed on the bench at normal handling height and allowed to remain for three or four minutes. After processing, it should be possible to detect the difference between the covered area and the exposed area of the film if any fogging has taken place. To rectify fogging, the bulbs in the darkroom safelights can be changed for lower wattage bulbs or replaced by 220 to 230 volt bulbs. Higher voltage bulbs in 110 to 115 volt lines will burn with a dull red glow so that there is much less white light from which to protect the film.

Covers of film containers should be replaced at once since fogging can result at the top of a 14 by 17 inch box of film if allowed to stand open and upright during loading operations. Time may be too long and distance to the safelights too short.

Good exposure holders for the O.D. are not available as standard commercial items and there are none available for the I.D. films. We use a pliable, black sheeting, 5 mils thick, for wrapping the I.D. films. Plastic sheeting is seldom manufactured so as to be absolutely free of pinholes. An exception is the heavy type for weather balloons and this is not necessarily manufactured so as to be opaque to light. Black sheeting can be inspected by placing it against an X-ray viewer at highest light intensity with all extraneous light carefully blocked out. Three layers of plastic for I.D. holders should minimize the possibility of superimposed pinholes and resultant light leaks.

Lead foil is used for backing the film to intensify the image and absorb undesirable radiation. Wrinkles are avoided so that the foil can be as close to the film as possible and so that intensification of the image is uniform.

Our I.D. holders are made with 17" lengths of pipe used for mandrels, each of which has a single layer of lead foil permanently affixed to the outside surface. The lead foil should be of the quality furnished by X-ray supply dealers and it can be applied most easily with double-faced pressure sensitive tape. The photographic film is wrapped around the lead covered mandrel and held in place by one sheet of black plastic

large enough to permit three circumferential windings and some excess to tuck inside the ends of the pipe.

The autoradiographic technique is not useful for measuring the thickness of the uranium core and any major increase in core material is not recorded on the film except where it physically affects the dimensions of the cladding. Only that radiation from the uppermost or outermost atoms of the core material penetrates the cladding to affect the photosensitive material. The remaining radiation of the core is absorbed within itself.

Fig. 1 - Cross-section of co-extruded tubular fuel element with photographic film applied to the outer surface.

Fig. 2 - Film Standard - The value at left of each gray patch is thickness in inches of each Zircaloy step wedge. Approx. 1/4 size. RF 7403

Fig. 3 - Sample plot - clad thickness vs. film density.
Drawing No. RA-2683.

RF 7409
Fig. 4 - Photograph of Densitometer

RF 8/54

"A"

RF 8753

"B"

TYPICAL AUTORADIOGRAPHS

Fig. 5 - Positive duplicates of autoradiographs reduced to one half actual size. Each film was wrapped around the outside of an extruded fuel element tube and represents the complete circumference. "A" reveals straiations in the cladding and irregular taper and wandering of the uranium core end. "B" shows a tube with considerable improvement in fabrication design and technique to correct for extrusion flow.

RF 7405

Fig. 6 - Typical RA Spots

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SOME METALLOGRAPHIC OBSERVATIONS ON THORIUM METAL *

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The occurrence of extensive twinning is a prominent feature of the microstructures of arc-melted thorium. The twin boundaries and subgrain boundaries may influence the mechanical properties of thorium. A new electropolishing technique promises to simplify the examination of minor phases in thorium and may reveal details of the mechanism of deformation.

INTRODUCTION

For several years an investigation of the physical properties of thorium and methods of preparing higher purity thorium metal has been conducted at the Ames Laboratory of the U. S. Atomic Energy Commission. In the metallographic examination of high purity thorium, an electropolishing procedure which did not obliterate the inclusions was desired. The mechanical polishing of thorium to reveal small inclusions is difficult and slow, and becomes more difficult as the hardness of the metal decreases with higher purity. In addition, a number of tensile specimens were to be examined to determine the grain size, and a convenient method of revealing the grain structure was needed. A previous study of the electropolishing of thorium had shown that a solution of hydrochloric and hydriodic acids in formic acid had some promise as an electropolishing solution. A more extensive study of electropolishing solutions which used formic acid as the solvent was undertaken to see if a satisfactory solution and procedure could be evolved. The results are incomplete and the solutions used are not recommended for general use but some very interesting observations have been made on thorium metal.

* Report No. IS-155, Contract W-7405 eng-82., TID 4500.

RESULTS AND DISCUSSION

Variation in Electrolyte Composition - The composition of the electrolytic solution could be varied considerably without losing the electropolishing action on thorium metal. The solution containing 2% hydrochloric acid in formic acid had a high resistance which required high voltages to obtain the necessary current density. Ammonium chloride was added to the solution to increase the conductivity and enabled polishing currents to be reached at approximately 20 volts. However, the hydrochloric acid in this solution reacted chemically with the thorium surface and pitted the samples badly. A solution containing two grams of ammonium chloride per 100 ml of formic, but no hydrochloric acid had approximately the same conductivity as a similar solution containing 2% hydrochloric acid. Thorium went into solution at the anode but no polishing of the metal surface was observed. However, the addition of 6% by volume of water resulted in excellent polishing and smoothing action by this electrolyte. Apparently a small amount of water was necessary to obtain polishing and this had been supplied by the hydrochloric acid.

This solution (2 grams ammonium chloride, 100 ml formic acid and 6 ml water) at 20 volts produced a smooth scratch free surface in 60 seconds on thorium samples which had been ground through 600 mesh silicon carbide paper. The principal disadvantages of this solution were that a thin soft blue film was left on the specimen and the grain boundaries were not revealed. This film was epitoxic and under polarized light often gave contrast between grains. The surface film could be easily removed by swabbing with a dilute nitric acid solution but the swab dislodged particles of thorium oxide and scratched the surface. A number of other organic and inorganic compounds containing ionizable chloride were substituted for ammonium chloride. This included methylamine hydrochloride, aniline hydrochloride, guanidine hydrochloride and tetramethylamine hydrochloride. The polishing action of all of these solutions was nearly the same as that of the ammonium chloride solution. The last two compounds are the salts of strong organic bases and consequently sodium chloride was used and found to work quite well. Apparently the necessary constituents of a thorium polishing solution based on formic acid are a compound which ionizes to provide chloride ions and a small amount of water or glycerine. The successful use of salts of an acid rather than the acid in electropolishing has also been reported for perchloric acid by Tegart.*

Observations on Thorium Microstructure - The major portion of this investigation was made with specimens of arc-melted thorium which had been prepared by the magnesium reduction of thorium tetrachloride. This thorium was comparable to crystal bar thorium in purity and had microstructures similar to crystal bar thorium. The most prominent feature of the microstructure of thorium in the arc-melted condition is very extensive twinning. The twin boundaries were revealed by almost all electropolishing or etching procedures before other details of the microstructure became evident. A photomicrograph of a specimen of crystal bar thorium heated at 1200°C and furnace cooled which has been repeatedly electropolished is

* W. J. McG. Tegart, The Electrolytic and Chemical Polishing of Metals (1959) Pergamon Press, Inc., New York, N. Y.

shown in Fig. 1. The twin boundary is deeply etched but the grain boundaries are imperfectly delineated although the severe polishing conditions have produced pitting and surface undulations. A heavily twinned area in an arc-melted specimen is shown in Fig. 2. A portion of the structure apparently consists of straight parallel twinned lamellae. Although the twinned areas are clearly visible, the grain boundaries are not revealed. The microstructure of arc-melted thorium resembles that of other metals which have undergone an allotropic transformation. Large grains formed by crystallization of the high temperature phase transform to areas which are extensively twinned and fragmented by subgraining. A fairly typical microstructure photographed under polarized light is shown in Figs. 3 and 4. The same area is shown in both figures but was rotated slightly for Fig. 4. The twinning and subgrain formation probably result from the transformation from the body-centered-cubic form to the face-centered modification but this has not been verified by quenching experiments.

Thorium oxide is often found in the microstructure of thorium metal. If present in amounts greater than about 200 ppm it occurs as dendrites or large angular inclusions which may be readily seen in mechanically polished specimens. In the arc-melted magnesium-reduced thorium a much smaller thorium oxide inclusion was found in addition to the dendritic form. These particles were not observed in the mechanically polished specimens, probably because of the tendency of thorium to smear during polishing. These particles ranged in size from 1 micron to 6 microns. In Fig. 5 are shown these particles in crystal bar thorium under bright field illumination. The size of these particles is about 4 microns and the shape was typical of this kind of inclusion. The particles are slightly larger and more numerous in the specimen of magnesium-reduced thorium shown under dark field illumination in Fig. 6. These particles may be responsible for the extensive pitting of thorium by perchloric acid electropolishing solutions. Perchloric acid electropolishing solutions produce pitting around the larger oxide particles and would likewise be expected to cause small pits at these very small inclusions.

Fig. 1 50X
Crystal bar thorium heated to
1200°C and furnace cooled.
Bright field.

Fig. 2 200X
Mg-reduced thorium as arc-melted.
Polarized light.

Fig. 3 200X
Mg-reduced thorium as arc-
melted. Polarized light.

Fig. 4 200X
Mg-reduced thorium as arc-
melted. Polarized light.
Rotated several degrees.

Fig. 5 500X
Crystal bar thorium.
Bright field

Fig. 6 900X
Mg-reduced thorium.
Dark field.