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**CHEMICAL THINNING OF PNEUMATICALLY
IMPACTED UO_2 FOR ELECTRON
TRANSMISSION MICROSCOPY**

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MAY, 1967

BATTELLE-NORTHWEST

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CHEMICAL THINNING OF PNEUMATICALLY
IMPACTED UO_2 FOR ELECTRON
TRANSMISSION MICROSCOPY

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May, 1967

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CHEMICAL THINNING OF PNEUMATICALLY
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INTRODUCTION

Procedures for chemical thinning of UO_{2+x} and resulting electron micrographs of thinned areas are presented in this report.

Micron-size UO_{2+x} powders with O:U ratios between 1.90 and 2.15 were densified to about 99% of theoretical density by pneumatic impaction at 250,000 psi and 1200 °C. All of the resulting compacted material contained impaction cracks, but these were not a production problem because the compacted material was crushed for future use.

Such a material should have a higher dislocation density than a material densified by a normal sintering method. It was necessary to thin the material to thin the material to 100 kV electron-beam transparency before dislocation geometry could be observed in an electron microscope.

SUMMARY

Polycrystalline pneumatically impacted UO_{2+x} specimens having O:U ratio ranging between 1.90 and 2.15 were chemically thinned to 100 kV electron transparency. Hypostoichiometric UO_{2-x} was easier to thin than hyperstoichiometric UO_{2+x} ; stacking fault dislocations were easily seen in UO_{2-x} , but seldom seen in UO_{2+x} .

CHEMICAL ETCHANT

The use of nitric or orthophosphoric acid for thinning single crystals of UO_2 was reported as unsuccessful for thinning polycrystalline sintered UO_2 .⁽¹⁾ Nitric acid preferentially attacked the grain boundaries, and orthophosphoric acid roughened the surface.

Whapman and Sheldon⁽²⁾ reported an electropolishing technique for thinning sintered UO_2 based on a mixture of chromic, sulfuric, and phosphoric acids. This technique necessitated vapor-plating metallic silver onto the UO_2 to provide good electrical contact with the chemical solution. This method was not tried because of the excessive amount of handling; also, changes in electrical conductivity caused by changes in stoichiometry often make electropolishing impossible.

A straight chemical method appeared easiest to apply over a wide range of stoichiometry. An attempt was made to use Manley's reported solution,⁽¹⁾ but it attacked the grain boundaries too rapidly and caused the sample to fall apart. Reducing the amount of nitric acid reduced the rate of grain boundary attack. The following modified Manley composition⁽¹⁾ was used as a working mixture for chemical thinning:

Chemical Thinning Solution

10 ml Acetic acid (glacial)
20 ml Saturated chromium trioxide
 solution
5 ml 48% hydrofluoric acid
4 ml Nitric acid

Alterations of the above solution were necessary to give special desired results. For example, it was necessary to reduce the nitric acid content to extend the thinned area during the final seconds of thinning.

PROCEDURE

Individual judgment is required during the thinning process, but reasonable frequency of success was achieved using the following procedure.

Mechanical Thinning

Prepare slices of UO_2 having a final thickness of 0.005 ± 0.0005 in. Prepare these slices by mounting a large piece of UO_2 in Quick-Mount* resin so a minimum number of visible cracks will be perpendicular to the cut surface. Using a diamond saw, cut slices about 0.020 in. thick.

The final mechanical thinning is done in two steps:

1. Mount 0.020 in. slice of UO_2 by using Eastman 910 adhesive on a glass slide. Hand polish on 280, 400 and 600 grit wet polishing paper until surface is approximately parallel to the glass slide and free of deep scratches. Rinse clean and place slide in acetone overnight to release the adhesive.

2. Remove slice from the glass slide and remove all traces of adhesive residue by polishing on 600 grit paper. Remount with polished side next to glass. Reduce thickness to 0.005 in. by repeating polishing procedure of Step 1. The two surfaces should be parallel within 0.0005 in. Remove slice from glass slide as in Step 1.

Sample Sizing

Break the 0.005 in. slices into the chip-size required by the electron microscope specimen holder (usually less than 0.125 or 0.25 in. diam). To do this, place the slice between two concentric glass slides, extend the slice to the required distance from the edge, and break. (Breaking attempted by pressing with a scalpel blade may shatter the slice.)

Masking

With fine-tipped sable brush, paint a coating of protective lacquer* on the edge by slightly overlapping the surface of the chip. This coating forces the chemical attack to take place on the surfaces instead of the edges. An easy method for painting is:

1. Mount the chip in needle-nose tweezers, gently clamping the tweezers with a band of masking tape.
2. Apply an extra amount of protective lacquer in the location where the chip is to be held by the tweezers.

* Quick-Mount, Manufactured by Metallurgical Products Corp., Pittsburgh, Pennsylvania

* Micromask, manufactured by Michigan Chrome and Chemical Company

3. When it is dry, remove the chip from the tweezers and remount with the tips grasping the area painted for holding.
 4. Complete painting of the rim.
- It is important that the painted area extend beyond the tip of the tweezers, otherwise a galvanic cell may develop under the tweezer tips during polishing. Do not paint over the tweezer tips, or removal of the chip from the tweezers will be difficult.

Chemical Thinning

Holding the tweezer-chip assembly, submerge the chip in the acid solution (volume usually less than 10 ml) and stir[†] vigorously until an area develops that transmits red light. (An ordinary flashlight is a good portable light source.) Removal rate of surface will be about 2 μ /min.

Evaluation of Thinning

As soon as the red color is seen in hypostoichiometric and stoichiometric UO₂ (O:U ratios from 1.90 to 2.00), remove all traces of liquids by washing in distilled water and blotting with absorbent paper. The material should be then examined with a 100 X microscope. Grains which are thinning to transparency will be apparent. (Figure 1a) Keep the grains under observation and try to control the thinning rate so that the grain or grain assembly will not be completely removed. The color

changes with thickness for O:U ratios from 1.90 to 2.00 are as follows:

Red - 0.001 in. thick	
Orange	
Orange-yellow	
Light-yellow	} Electron trans-
Almost white	
	mission region

For hyperstoichiometric UO₂ (O:U ratio above 2.0) the red color is missing, and an orange shade is the first indication of approaching thinness. It is easy to over-polish. (Figure 1b) It is a good policy to stop polishing after observing what appears to be a usable area with a 100 X microscope. Don't try to enlarge the area because the probability of successful enlargement is low. Some alteration of the acid solution may be required to give more thinned areas.

Chemical thinning is somewhat of an art; especially during the final phases. The straight edges have few thinned areas.

Figures 1c and 1d show areas having favorable thickness. Rarely does chemical attack produce large, flat, thin regions; instead a grouping of "fingers" are formed. Normally, look at whatever thinned area survives the complete handling procedure. Areas of 1-3 μ wide will give much information.

Conductive Coating Application

Wash the thinned area in distilled water until all acid solution has been removed. Use care in blotting the wash water away from the specimen. When the area is clean, no trace of yellow stain is visible in the

[†] Magnetic stirring or ultra-sonic vibrational methods of agitation have no advantage over hand manipulations.

104X

(a) Polished to Red Color Condition
(Note the small grain structure
within larger grain outline.)

104X

(b) Unsatisfactory Polishing

104X

(c) Typical of Potential Transmission

104X

(d) Typical of Potential Transmission

FIGURE 1. The Progress of Chemical Polishing

absorbent tissue. Do not put the tissue directly on the thinned areas, because the capillary pull of the tissue may break away the thinned areas.

Because of the brittleness of the thinned area, no attempt should be made to remove the protective lacquer by soaking in acetone. Early attempts were made to remove the lacquer, but numerous problems were encountered and the step was omitted. A conductive coating of colloidal graphite, which reduces the electrical charge buildup in the plastic when in the microscope, is brushed over the surface of the protective plastic before removing the tweezers.

Sample Mounting

Carefully remove the chip from the tweezers and place it on a 75 or 100 mesh grid for mounting in the electron microscope holder. The thinned areas are quite brittle, and a small amount of flexing or jarring—such as dropping on the table top—can break away the thinned areas.

After the grid is in the holder, place the holder under a 100X microscope, and position the chip so the thinned areas are not directly on top of grid wires. The sample may be loose on top of the grid, so always keep the specimen holder in a vertical position when handling or storing.

Microscope Observation

Sample contamination from diffusion pump oil vapors must be held to a minimum. In our JEM 6 electron microscope, a cold stage drum, filled with liquid nitrogen was used to reduce the

contamination rate. If a large sample size is used with the heating stage, the column vacuum must be broken each time the sample is changed.

Thinned areas are not easily seen at magnifications below 20,000 but the geometry of the region will indicate whether transparent areas might be present. Locate a possible area, increase magnification to 30,000, and slowly scan the jagged edges.^{††} All work should be done with a double condenser lens system, and as soon as an area is found, adjust the magnification and take a picture. Time is important because information may be lost due to contamination or possible breakage caused by beam heat. Normally, the photographic negative will resolve more details than the fluorescent screen. Remember, the picture is the only evidence to support your observations.

DISCUSSION

Numerous dislocations were easily seen in $\text{UO}_{1.90}$, $\text{UO}_{1.99}$ and $\text{UO}_{2.00}$. The dislocation density is lower or is not as easy to resolve in hyperstoichiometric UO_{2+x} compounds. Occasionally, however, an area of small-size grain structure is found. Use of a tilting stage might be helpful in intensifying the dislocation images.

Most of the large dislocations appear to be of stacking fault origin and similar in geometry to those reported by Ashbee.⁽³⁾

^{††} Occasionally, grains away from the edge will also be transparent.

All of the materials used to evaluate chemical thinning methods for UO_{2+x} were taken from chunks of various pneumatically impacted samples. No information was available as to the location of the sample within the impacted slug. Some typical transmission micrographs are shown in Figures 2, 3, and 4.

A localized small-size grain structure is shown in Figure 2a. The grains are equiaxed and have either received a minimum of impact deformation or have almost completely recovered or recrystallized during the cooling period.

The elongated, worked grain structure of Figure 2b is typical of many samples.

(a)

(b)

(c)

FIGURE 2. *Electron Micrographs of Pneumatically Impacted UO_2*

(a) UO_2

(b) $UO_{1.90}$

(c) $UO_{1.90}$

(d) $UO_{1.90}$

FIGURE 3. Electron Micrographs of Pneumatically Impacted UO_2 and $UO_{1.90}$.

(a) $UO_{1.99}$

(b) $UO_{2.02}$

(c) $UO_{2.05}$

(d) $UO_{2.15}$

FIGURE 4. Electron Micrographs of Pneumatically Impacted Uranium Oxide

Often the grains are more deformed than shown, with dense dislocation tangles darkening the region.

A complete range of chemical polishing results, ranging from very thin to too thick plus surface contamination, is shown in Figure 2c. The spherical balls are residues of chemical-reaction contaminant left because of incomplete washing. Many of the contaminant spheres are located on or near dislocation areas, indicating a possible difference in surface energy surrounding a dislocation region. Tangles formed by the numerous dislocations are apparent.

Figure 3a is an enlarged dislocation area of $\text{UO}_{2.00}$. The dark and light section of a loop is indicative of the dislocation passing through several atomic layers.

The dislocations in $\text{UO}_{1.90}$ (Figure 3b) appear to have a shorter length within the grain and appear to be more concentrated in the grain boundaries than in $\text{UO}_{2.00}$ (particularly in Figure 3c and 3d).

Thinning of $\text{UO}_{1.99}$ was difficult. The grain size was much larger than

other hypostoichiometric materials due to a different heat treatment after impaction. A grain-boundary intersection is shown in Figure 4a.

Good transmission pictures of hyperstoichiometric UO_{2+x} were difficult to obtain by the above procedure. Overpolishing was a problem because it destroyed most of the thinned areas. The dislocations visible in Figure 4b, 4c and 4d are not as intense nor as numerous as those found in the specimen having lower oxygen stoichiometries.

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