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Metallographic preparation techniques for uranium

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Abstract

Existing metallographic preparation techniques for uranium are limited to elucidating specific microstructural characteristics, and some of the techniques are regarded as being environmentally unacceptable. This paper describes a newly developed technique, which is not only more environmentally friendly, but reveals most microstructural features simultaneously. Example microstructures of the various preparation stages are given to highlight the new technique.

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1. Introduction

Historically, metallographic preparation and examination of depleted uranium have been tailored to investigate specific microstructural features [1]. Traditional preparation processes include such techniques as chemical attack polishing and/or oxidation, electropolishing, electroetching, and anodizing. Although these techniques reveal individual microstructural features, a more general technique (which can reveal all aspects of the microstructure simultaneously) has been lacking. Other problems associated with past techniques include etch pitting, loss of inclusions during electro-polishing, and personal and environmental safety concerns. An evaluation of existing techniques has provided the basis for a modification and the subsequent development of a new metallographic preparation technique. This technique defines grain boundaries, sub-grain boundaries, inclusions, impurity segregation and twinning, thus allowing for a broader array of microstructural characteristics to be revealed with a single preparation while minimizing both dangerous chemical mixtures and hazardous waste generation.

2. Specimen preparation

In this section, the specimen preparation steps will be described in some detail. For each stage of the process, the previously recommended procedure will be described, followed by a presentation of the modifications to this procedure in the new technique.

2.1. Sectioning and mounting

2.1.1. Currently recommended [1]

To minimize surface damage, specimens are sectioned with a low speed diamond (or abrasive)

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saw using liberal amounts of non-flammable cutting fluid. The specimens can be mounted in any of the common metallographic mounting materials, such as Bakelite, phenolic, and epoxy. The use of epoxy is discouraged without additional steps (such as nickel plating or coating the specimen with epoxy paint) prior to mounting. The plating or coating step is recommended because the uranium can react with epoxy, which causes a gas evolution problem during curing. However, because uranium surfaces oxidize rapidly when exposed to air, the nickel plating may not adhere. A suggested solution to this problem is to sputter a layer of conductive material onto the oxidized surface prior to the nickel plating process.

2.1.2. New technique

To minimize surface damage and the spread of contamination, specimens are sectioned using low speed diamond or abrasive saw and water as the lubricant. Water is preferred over oil-based lubricants because the residue on the sample quickly evaporates, thereby eliminating solvent cleaning prior to mounting.

While the referenced literature indicates preference for the use of compression mounting, this may not be an acceptable mounting method for material that is fragile or susceptible to phase transformation at or near the molding temperature (180 °C). The mounting method used in this study consists of vacuum impregnation [2] with a slow curing epoxy (10 to 1 ratio of epon 815 resin and diethylenetriamine) followed by pressure curing. This is accomplished using a vacuum chamber with a tilt/pour mechanism to allow simultaneous evacuation of the specimen and epoxy as well as subsequent pouring of the epoxy into the mounting cups. After venting the system, the mounting cups are placed in a pressure vessel to cure at room temperature in a dry nitrogen atmosphere at 5.5–6.9 MPa for a minimum of 5 h, with an overnight cure preferred. This method not only affords excellent penetration of the resin to all surface accessible porosity (making it easier to observe cracking and distinguish between porosity and preparation artifacts) but also eliminates the problem of gas evolution/entrapment in the mounted sample. To further harden the epoxy mounting material, specimens can be final cured for 2 h at approximately 60 °C. This step may be omitted for particularly heat sensitive specimens.

2.2. Grinding and mechanical polishing

2.2.1. Currently recommended [1]

The specimens are sequentially ground through 600 grit (CAMI 14.5) SiC grinding papers using water as a lubricant or 600 (CAMI 14.5) grit aluminum oxide powder in a kerosene vehicle on a cast iron lapping wheel. A uniform 600-grit finish is adequate for subsequent polishing. Coarse polishing is performed using 30-μm diamond abrasive followed by 6-μm diamond abrasive on a nylon lap with a petroleum-base vehicle. These steps are required to remove latent grinding damage. Final mechanical polishing is done on a high-nap cloth with 0.3-μm Al_2O_3 abrasive and a deionized water vehicle on rotating wheels or vibratory polishers (up to 12 h).

2.2.2. New technique

Grinding is accomplished in the manner described above, except that the final grinding step is performed on 800 (CAMI 12.2) grit SiC paper. The final grinding step allows for the elimination of the coarse (30 μm and 6 μm) polishing steps and therefore enhances the ability to retain inclusions in the metallographic sample. Initial mechanical polishing is accomplished on a low nap cloth (Texmet [3] or equivalent) using a 3-μm diamond abrasive, 15 N force, 150 rpm counter rotation, and a propylene glycol lubricant for ~10–15 min. During the final mechanical preparation step, samples are polished on a napped cloth using either of the following methods: (a) 1 μm diamond suspension, 15 N force, 150-rpm counter rotation, and a propylene glycol lubricant for approximately 5–7 min, or (b) 0.3 μm alumina slurry, 15 N force, 150-rpm counter rotation with a water lubricant. Method (a) is preferred because it minimizes oxidation effects during mechanical preparation. Optical examination of the mechanically polished specimen reveals some inclusions, defects (porosity or cracks), and (using polarized light) grain boundaries.

2.3. Electropolishing and electroetching

2.3.1. Currently recommended [1]

To further define microstructural characteristics, specimens are oxidized or chemically prepared using such techniques as electropolishing, electroetching, or anodizing. Some of the more acceptable preparation processes along with their uses and limitations, can be summarized as follows:

(a) *Oxidation* (atmospheric or heat induced – immersion of specimen in hot water).
Used to determine general structure, inclusion distribution, and morphology.
Disadvantages – Some microstructural characteristics not revealed.

(b) *Electro-polishing* (50% H_3PO_4 solution at 20–30 V [4]).
Used to remove vestiges of mechanical polishing induced deformation prior to anodizing.
Disadvantages – high voltages used for this process tend to etch out and/or pit around inclusions.

(c) *Electroetching* (5–10% oxalic at 3–5 V).
Used to determine grain size.
Disadvantages – scratches become more apparent, non-uniform etching (edges attacked while center portions of the sample remain virtually unaffected: etching for longer times increases etched area, but sample edges begin to etch pit).

(d) *Anodizing* (5% NaOH in alcohol solution at 20–60 V 30 s to 2 min [4]).
Used to reveal microstructural contrast due to differences in crystallographic orientation.
Disadvantages – high voltages etch out inclusions and solution must be kept free of water.

While there are many other chemical processes available [1,5], most processes were deemed unsuitable due to safety and/or environmental concerns. For example, such processes include the use of HNO_3, (not recommended for uranium–niobium alloys due to the formation of an explosive surface layer), chromic acid (environmental/waste disposal), ethylene glycol (environmental/waste disposal), acid/organic solvent combination such as phosphoric acid, ethanol, and ethylene glycol (mixed waste), inorganic/organic acid combinations such as chromic and acetic solutions [6] (mixed waste; environmental/waste disposal), 50–50 HNO_3–acetic acid [7] (mixed waste disposal, also not recommended for uranium–niobium alloys due to the formation of an explosive surface layer), and perchloric and glacial acetic acid (mixed waste; special fume hoods required to avoid potentially explosive residue buildup, except when used cold).

2.3.2. New technique

The objective of this process evaluation was to find a technique which: (a) defines/resolves a broad array of microstructural characteristics, (b) retains inclusions, (c) can be universally applied to all uranium/uranium alloys with only slight (if any) process modifications, (d) does not present a waste disposal problem, (e) can be mixed and stored easily, and (f) is user friendly. These criteria narrowed the field of potential chemical processes.

The technique developed during the current study is a modification of methods (b) and (c) above. The surface is electropolished using 3–4 V (reduced from the currently recommended 20–30 V) with either a 5% or 50% H_3PO_4 solution for ~2–3 s. Varying electropolishing solution concentration yields little or no differences in final results. This is followed by electroetching in a 10% oxalic acid solution at 4–5 V for ~3–5 s (method (c) above). All electrolytic steps were conducted with a stainless steel cathode and a tantalum wire anode. The anode was applied to the sample to complete the circuitry. In some cases, the as-electropolished microstructure alone is sufficient to reveal many microstructural features of interest.

Some explanation is called for regarding the designation of the H_3PO_4 electrolytic step as an electropolish. The distinction between electroetching and electropolishing is generally considered to hinge on whether the treatment reveals microstructural features (for the former) or provides a smooth, featureless surface (for the latter). Electroetching is also typically performed at lower voltages than electropolishing. The voltage for the phosphoric acid electrochemical treatment described here has been substantially lowered from that of the referenced procedure [1,5], potentially into the etching regime, and does indeed provide some etching effects. However, this treatment is still referred to as an electropolish, in part to distinguish it from the subsequent oxalic acid etch, but also because it does serve some of the purposes of an electropolish, removing damage layers from mechanical polishing, as well as oxide layers built up during prolonged atmospheric exposure.

3. Results

An as-cast specimen with large uranium carbide (UC) inclusions and relatively coarse grains is shown in Fig. 1. This specimen was final polished on a medium nap cloth with 1 μm diamond for approximately 10 min, then partially masked so that half of the surface could be electropolished. On the as-mechanically polished side (a) the UC inclusions are somewhat visible, while on the electropolished

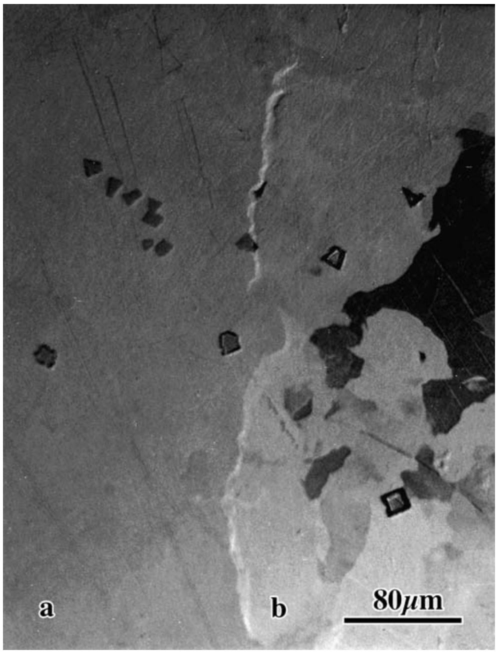

Fig. 1. An as-cast uranium sample which has been final polished (a) on medium nap cloth (Microcloth) using 1 μm diamond abrasive with a propylene glycol lubricant for ∼10 min, followed by (b) electro-polishing using a 5% H_3PO_4 solution at 3 V for ∼2–3 s. After mechanical polishing, the sample was masked with tape on the left side and then electro-polished. The sample was photographed using differential interference contrast (DIC).

side (b), the inclusions are well defined, the scratches are eliminated, and the grain boundaries are partially defined.

Other advantages of electropolishing are evident as specimens (such as the one in Fig. 2) are allowed to oxidize in air. In an oxidized condition differences in the as-mechanically polished and electropolished surfaces become apparent. The surface that has been electropolished/oxidized has more sharply defined grain boundaries and inclusions than the mechanically prepared/oxidized surface. Specimens that have oxidized (in either the mechanical or electropolished condition) may be electropolished without consequence to microstructural features. In some instances oxidation (before electro-polishing) may even be considered beneficial, such as with very small specimens where the completeness of the electropolishing circuitry may be questionable. Electropolishing brightens the oxidized surface, providing the metallographer with confirmation of anode contact. In addition, it was observed that electropolishing prior to etching promotes a more uniform etch and reduces the occurrence of edge pitting noted above for the oxalic solution.

Fig. 2. A DIC micrograph illustrating the differences in microstructural clarity of a cold-rolled uranium specimen for (a) mechanical polished surface (through 1 μm diamond) and (b) subsequently electropolished surface, after allowing the specimen to oxidize in air.

The micrographs in Fig. 3 show the complete mechanically and electrolytically polished and etched microstructure of an as-cast specimen. At lower magnification (Fig. 3(a)), the grains and sub-boundaries are well defined, along with twins and inclusion stringers. The higher magnification micrograph of Fig. 3(b) also shows the retained inclusions.

The micrographs in Figs. 4–6 show mechanically processed microstructures as revealed by the new preparation techniques. The cold-rolled specimen in Fig. 4 has been prepared through the mechanically polished and electropolished steps. The elongated grains and flow lines in this material are clearly defined without a subsequent electroetch. The partially recrystallized specimen in Fig. 5 was similarly prepared. Again, the deformation microstructure is well defined, while inclusions are left intact. In Fig. 6 a fully recrystallized specimen is shown. In this case, subsequent electroetching was used to better define the grain structure.

While the previous examples illustrated the metallographic preparation, it is also important to stress the usefulness of the mounting technique. The specimen in Fig. 7 was subjected to a high energy flat

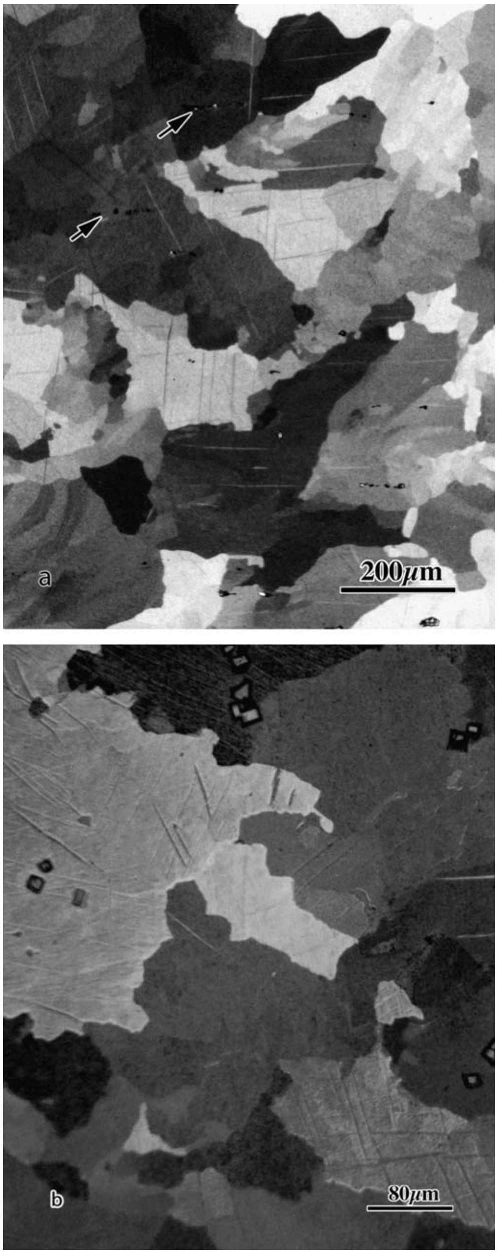

Fig. 3. DIC micrographs of cast uranium showing typical microstructures of fully prepared metallographic samples. (a) A low magnification micrograph showing grains, sub-boundaries and twin definition. The dark lines (indicated by arrows) are uranium carbide stringers. (b) A higher magnification micrograph showing twinning, irregular grains and well defined inclusions. The samples were electro-polished with 5% H_3PO_4 at 3 V for ~4 s and electroetched using 10% oxalic at 4 V for ~4 s.

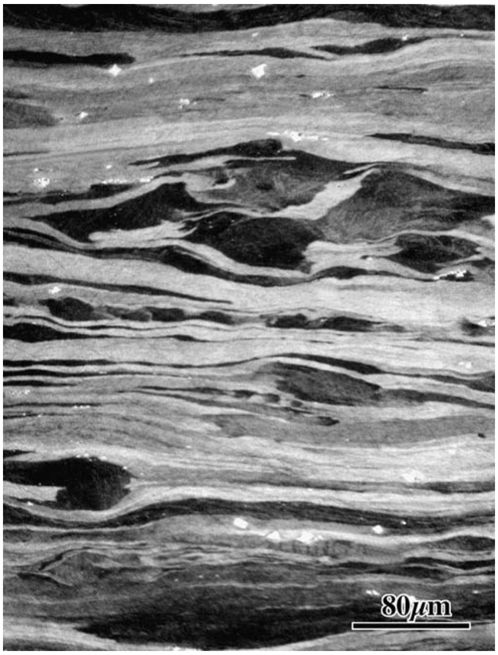

Fig. 4. DIC light micrograph of warm (275 °C) rolled low carbon uranium showing elongated grains and UC inclusions. Electropolished with 5% H_3PO_4 at 3 V for ~4 s.

Fig. 5. DIC light micrograph of warm rolled uranium (275 °C), subsequently annealed at 450 °C for 1 h, showing a partially recrystallized structure. The sample was electropolished with 5% H_3PO_4 at 3 V for ~4 s.

projectile to test the spall characteristics of the material. Metallographic preparation required an evaluation of the damage accumulation in the sample. The vacuum impregnation followed by a pressure curing of the epoxy permits good retention of the damaged structure around cracks. Surface con-

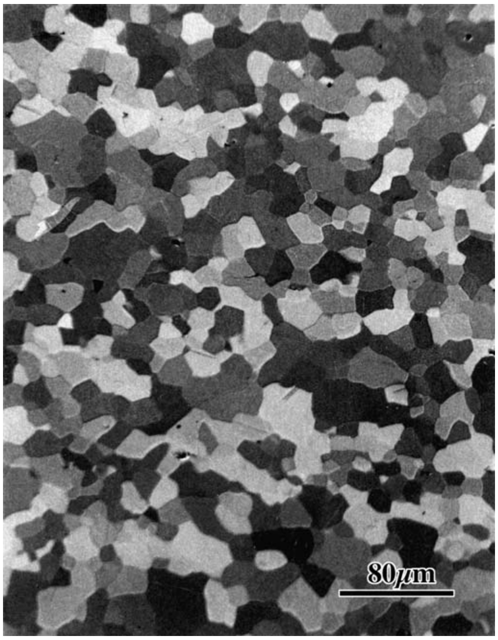

Fig. 6. A DIC light micrograph of warm rolled uranium (275 °C), subsequently annealed at 550 °C for 2 h and slow-cooled, showing a fully recrystallized structure. The sample was electropolished with 5% H_3PO_4 at 3 V for ~4 s and electroetched using 10% oxalic at 4 V for ~4 s.

nected internal cracks have been filled with epoxy, affording good edge retention. Deformation twins are observed extending to the edge of the crack.

Finally, one of the biggest challenges in prior preparation techniques was the retention of inclusions. Carbon is a typical impurity in uranium and can range from 30 to 500 ppm. UC inclusions are always found in uranium samples, but their size and morphology are highly dependent upon the thermo-mechanical history of the sample. Thus the retention of the inclusion provides useful information about the sample.

The micrographs in Figs. 8–10 are higher magnification micrographs showing examples of inclusions. The example shown in Fig. 8 is a UC inclusion in a recrystallized uranium sample (as-electropolished condition). The inclusion is a UC phase containing N and O in addition to carbon; the dark section is a fracture in the inclusion, most probably resulting from the prior work of the sample. The UC inclusion displays a layered structure. Additional details of the internal structures of these inclusions are revealed after electroetching, as shown in Fig. 9.

It is reasonable to ask whether these layered structures represent real microstructural features

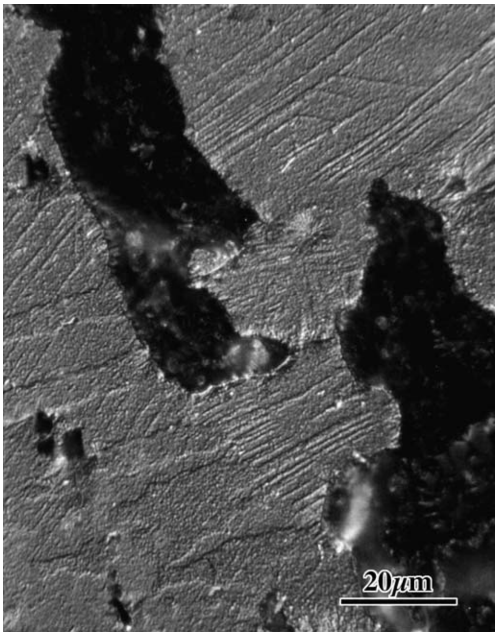

Fig. 7. A specimen mounted via the cold mounting vacuum impregnation system is illustrated in this micrograph. While the epoxy is clear and not discernable in micrographs, it is apparent due to the lack of etchant wicking onto sample surface, and also the flatness at the crack edges. Specimens were electropolished with 5% H_3PO_4 at 3 V for ~4 s, electroetched using 10% oxalic at 4 V for ~5 s.

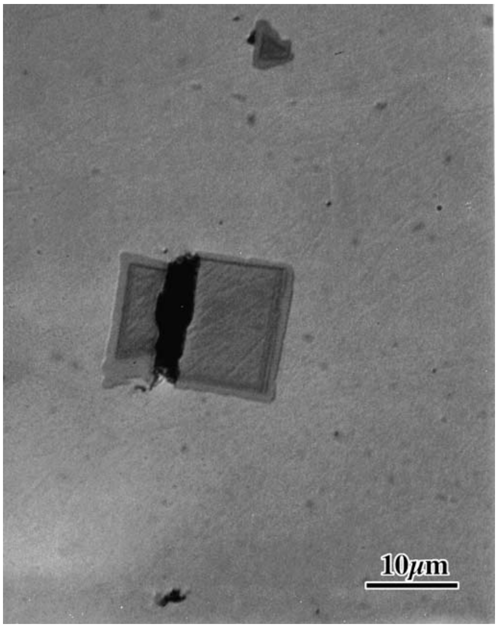

Fig. 8. A DIC light micrograph of a UC inclusion in uranium. The sample was electropolished with 5% H_3PO_4 at 3 V for ~4 s.

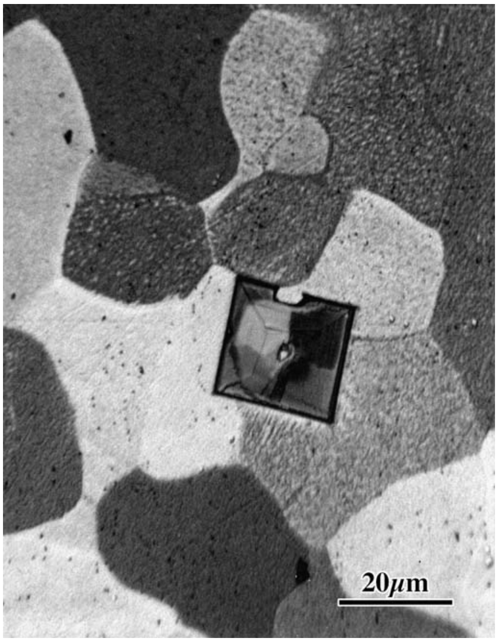

Fig. 9. A DIC light micrograph of uranium showing a typical uranium carbide inclusion in a recrystallized sample. The sample was electropolished with 5% H_3PO_4 at 3 V for ~4 s, electroetched using 10% oxalic at 4 V for ~4 s.

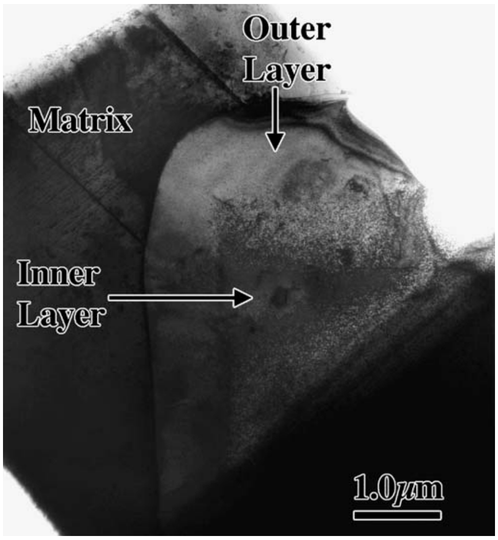

Fig. 10. TEM image of carbide showing layered structure.

or are artifact of the preparation technique. Analysis of similar inclusions in the transmission electron microscope has shown this to be a real feature of these inclusions, caused by a gradation in the composition, particularly with respect to N and O[1]. Fig. 10 is a bright field micrograph taken in a transmission electron microscope (TEM). This foil was removed from an inclusion that displayed a layered morphology, similar to those shown in Figs. 8 and 9, using a focused ion beam (FIB) instrument (FEI DB235). This instrument allows the preparation of TEM foils from specific microstructural features using a Ga ion beam. Since the FIB foil is taken in a plane perpendicular to polishing plane of the optical mount, it is not affected by the optical preparation and therefore is not expected to display artifacts of the preparation technique. The layered structure is clearly visible in the micrograph.

Fig. 11 provides more detail regarding the two layers observed in this inclusion. The inner layer has a mottled appearance (Fig. 11(a)), which is associated with weak satellite reflections in diffraction patterns (Fig. 11(b)). The weak reflections can be seen in the enlargements of two of the reflections, provided in the figure. The main reflections in the patterns are consistent with U(C,N) (NaCl structure, $a \sim 0.49$ nm), while the satellite reflections can be indexed to $U(N,O)_2$ (CaF_2 structure, $a \sim 0.54$ nm), with a cube-on-cube orientation relationship with the U(C,N) matrix. Energy dispersive spectroscopy of X-rays (EDS) in the TEM indicates that the major component on the (C,N) sublattice is C. However, the inner layer is higher in N than the outer layer, while low levels of O are present in both layers. This gradient in composition is believed to result in fine precipitation of the $U(N,O)_2$ phase, giving rise to the extra reflections in the diffraction patterns and the mottled appearance of the inner layer. Dislocations are observed decorating the interface. These could result from small differences in lattice parameter, resulting from the compositional differences between the layers. This effect has been observed in TiC [8].

With longer heat-treatments of uranium samples, the carbides lose the facetted morphology. The sample in Fig. 12 shows two smaller UC inclusions surrounded by a halo of contrast in the matrix. This 'halo' was found to be enriched in Fe by energy dispersive spectroscopy of X-rays (EDS). These small inclusions, along with surrounding features, are particularly difficult to define and retain in the microstructure. The reduced polishing time afforded by this technique allows these features to be observed.

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[1] This analysis, along with other electron microscopy studies of inclusions referred to in this paper, was performed as part of an ongoing detailed investigation of inclusions in uranium alloys, results of which will be published at a future date.

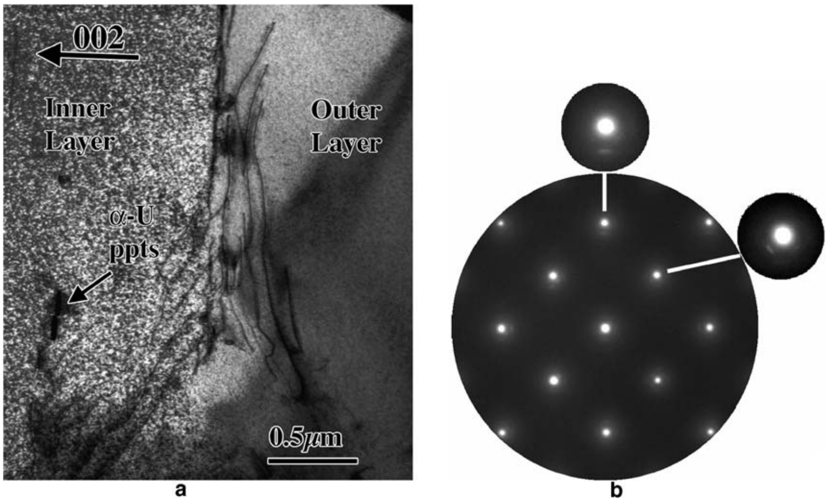

Fig. 11. (a) Higher magnification TEM image of interface between inner and outer layers in U(C,N) inclusion shown in Fig. 10. (b) Selected area diffraction (SAD) pattern from inner layer, taken from [0 0 1] zone axis, showing weak satellite reflections associated with $U(N,O)_2$ precipitates.

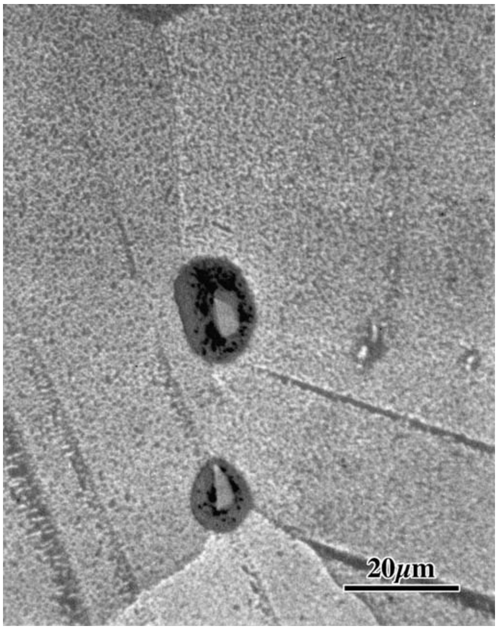

Fig. 12. DIC light micrograph of UC inclusions surrounded by Fe enriched halos in uranium. Electro-polished with 5% H_3PO_4 at 3 V for ~3–4 s.

4. Discussion

Two factors initiated the process of developing new metallographic preparation techniques for uranium: safety/environmental issues and a more general technique to define all microstructural features with one preparation. The two factors are linked owing to the simple notion that one technique that defines all relevant microstructural features minimizes overall preparation time and waste handling. In addition, the new technique offers an alternate mounting method which will not affect microstructural characteristics (found in heat sensitive and fragile materials) and does not require additional steps such as plating or coating prior to mounting. Vacuum impregnation with low viscosity epoxy followed by a pressurized curing cycle fills all surface accessible cracks and porosity and also eliminates the problem of gas evolution/air entrapment. Other benefits are found in the reduction of preparation time simply by extending the grinding sequence to include a finer 800 (CAMI 12.2) grit grinding paper thus eliminating the need for coarse polishing. With the reduction in mechanical preparation time, the possibility of producing preparation artifacts such as inclusion pull out and edge rounding are also reduced. Electropolishing at this low voltage not only removes fine scratches and preserves inclusions, but also provides a slight etching effect proven to be effective for revealing some microstructural characteristics. Other noted advantages of electropolishing are: (1) the sample surface appears to oxidize at a slower rate than strictly mechanically polished surfaces, (2) electropolished surfaces are less likely to pit during the electroetching process. Electroetching, which is also performed using a low voltage, enhances definition of such microstructural features as grain boundaries, twins, inclusions, and sub-grain boundaries. The solutions in the new process, 5% H_3PO_4 (reduced from the previous 50%

concentration) and 10% oxalic, are user friendly, have a long shelf life, are relatively innocuous, can be used universally on all uranium/uranium alloys with only slight (if any) modifications, are straight forward to use (no need to calculate current density), and meet the safety and environmental criteria.

5. Conclusions

A new metallographic preparation technique has been developed for depleted uranium that provides numerous advantages over existing methods. The attributes of the technique include:

- A cold mounting procedure, which
  - reduces thermal/mechanical damage during mounting,
  - provides better edge retention around pores and cracks,
  - eliminates the need for pre-mount coating.
- Reduction of preparation time.
- All microstructural features revealed with single preparation technique.
- Relatively safe and environmentally friendly solutions.
- Better definition of inclusions.

Acknowledgements

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