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MACROEXAMINATION OF URANIUM ALLOYS

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MACROEXAMINATION OF URANIUM ALLOYS

Ross J. Jackson, Robert L. Lucas, and Arthur E. Calabra

Abstract. Two procedures for macroetching uranium-base alloys are described. The first procedure consists of electropolishing followed by immersion etching in a HNO_3 -HAc solution. This procedure is ideal for large nonflat specimens. The second procedure is one of mechanical grinding followed by a vibratory polish-attack macroetch. This procedure is ideal for macropatterns that are difficult to develop. Photomacrographs of uranium alloy castings and forgings prepared in this manner are presented as are the limitations of the procedures.

INTRODUCTION

Microscopic examination of a metal or alloy is often not representative of the entire part, owing to the heterogeneous nature of metals on a macroscale. Rather, such examinations may represent the characteristics of the metal only at the particular location observed. As examples, localized observations may not indicate the general distribution and variation in size of nonmetallic inclusions; the uniformity of structure; the location and extent of segregation; the presence of fabricating defects, such as seams or hammer bursts, and residual ingot defects, such as pipes. These factors profoundly influence the over-all properties of a given section, and consequently are determining circumstances with respect to serviceability.

The nature of inhomogeneities in a metal, and their extent therein, are best determined by macroetching a representative piece and subsequently examining the conditions thereby revealed with the unaided eye or with the aid of a low-powered microscope or magnifying glass. Such an examination is referred to as a macroscopic, or macro examination. It is distinguished from a conventional metallographic examination by the low magnifications used — usually less than 10X; and by the fact that large areas of the specimen are examined. The primary interest is in defects, segregation, etc., over the entire part rather than microscopic areas at one or more locations. Macroetching and subsequent examination of the etched sections are widely used as control methods in the fabrication of metals and alloys. By macroetching appropriately selected sections at different stages in a forming process, for example, defective material can readily be detected early in the sequence of operations, and thereby the expense of continuing fabrication only to produce, finally, an inferior and low-quality product is avoided.

The Rocky Flats Plant is engaged in a development program on uranium alloys. This program encompasses the casting and forging of U-Mo, U-Nb, U-Re, and U-Ti alloys. Macroexamination is a valuable tool in development programs involving castings and forgings. A limited literature survey was conducted to find a procedure for macroetching of uranium alloys, but no references were found. Undoubtedly, workers have developed etchants for this purpose; however, the results are apparently discussed in reports centering on other aspects of the study. It was therefore necessary to develop and report macroetch procedures for uranium alloys.

EXPERIMENTAL

The entire process of macroexamination of a uranium alloy consists of several steps:

1. Sampling and Sectioning. Obtaining a representative sample of the alloy appropriate for the purpose of examination. When the finished section is small the entire piece may be used. When the finished part is large it may be necessary to observe several representative sections.
2. Surface Preparation. Preparation of the surface that is to be etched. In some instances a properly machined surface is satisfactory, whereas in other instances electropolishing or mechanical grinding-polishing is necessary.
3. Macroetching. Appropriately etching the prepared or unprepared section of interest by controlled chemical reactions for macro-observation is referred to as macroetching. The macroheterogeneities are revealed by macroetching because of the variance of reaction rate with structure-composition.
4. Recording the Macroetching. Conventional photographic methods are probably the best available for recording details of macroetched specimens.
5. Interpretation. The correct interpretation of photomacrographs is often very straight forward. However, keep in mind that during macroetching the areas occupied originally by certain small heterogeneities will increase in size far beyond their original dimensions and eventually reach a size that will be visible to the unaided eye. Unless full cognizance is taken of this enlargement effect during

macroetching, considerable confusion may arise, in some cases, when attempting to interpret the results. Since this paper is primarily concerned with describing macroetching techniques, the photomicrographs shown are interpreted only from a technique point-of-view.

Sampling and Sectioning

The selection of a representative sample for macroetching, to be removed from the whole, should be made with proper consideration for the aim of the test. Frequently, the piece may be of so convenient a size that it may itself, in its entirety, serve as the sample. Large sections should be avoided whenever possible, as they are difficult and cumbersome to handle, as well as requiring an unnecessary excess of electropolishing or etching reagent. As a general rule, thin slabs and disks are the most convenient to handle and manipulate during the macroetching process. Because of the high density of uranium alloys, the sections should not exceed, if possible, dimensions greater than about 10 by 10 by 0.25 inches.

As an example of a typical macro-sampling procedure, a U-6.3 wt% Nb alloy arc-casting would be sectioned as shown in Figure 1a. A typical arc-cast ingot has the shape of a right cylinder with dimensions of 22 by 6 inches and weighs about 145 kg. While vertical cross-sections weighing about 70 kg have been successfully macroetched, they can cause hernias, etc. Three slab and two disk samples taken from positions shown in Figure 1a give a representative picture of the total ingot. Also, these slab and disk samples are ideal sizes for subsequent X-ray radiographic studies. A typical macro-sampling procedure for a 500 kg U-4.2 wt% Nb induction cast ingot in the form of hollow right cylinder is shown in Figure 1b.

Whatever method is used to section the sample, it is important that during the operation the specimen be kept sufficiently cool to prevent heating the surface to an excessively high temperature. Unless such precautions are taken, the frictional heat evolved may cause structural changes to occur to such a depth, and may, after etching, lead to misinterpretation of the macrostructure. For example, sectioning small samples with a water cooled Si-C cut-off wheel commonly produces temperatures of 700°C at a depth of $\frac{1}{32}$ inch from the sectioned surface. Therefore, surfaces produced by a cut-off wheel are unsatisfactory unless the affected metal is subsequently removed. Lathe cutting with a water-soluble oil coolant generates little localized heating and produces a relatively good starting surface, especially if the final lathe cut is held to depths of about five mils.

Figure 1. Schematic Drawings Showing Sampling Procedure for Macroetching of Two Uranium Alloy Ingots: (a) Arc-Cast or Induction-Cast 145 kg Log Ingot; and, (b) Induction-Cast 500 kg Hollow Cylindrical Ingot.

Efforts to directly macroetch lathe-machined surfaces of uranium alloys were in many cases not totally satisfactory. This does not mean that the true macrostructure could not

be seen, but that the quality of the macrostructure could be improved. This was, in part, caused by smeared or flowed metal over the surface which partially concealed the true macrostructure. As a result, some mechanical or electrolytic polishing is beneficial prior to etching.

Surface Preparation

When a suitable specimen has been selected and removed from the whole by hacksawing or some similar method, the surface generally needs further preparation prior to etching. Often the presence of cutting marks, or heat affected or cold worked metal, so seriously efface details revealed by etching that it is difficult to interpret correctly the macro test results. The degree of required metal removal or surface smoothness depends upon the sample, the etching reagent selected, and the condition that is most likely to be revealed by the etch. Generally, the more drastic the action of the etching reagent, the coarser the surface finish may be. When it is desirable to reveal fine and delicate details of the structure, the surface must, of necessity, be correspondingly smoother but it need not approach the degree of polish required for microscopic examination.

Two methods of metal removal and surface smoothing have proven satisfactory with uranium alloys:

1. **ELECTROLYTIC MACRO-POLISH PROCEDURE.** In this procedure the machined sample is made the anode in an electropolishing cell. The parameters for metal removal and surface smoothing of uranium alloys are listed in Table 1.

Table 1. Electrolytic Macro-Polish Procedure.

Electrolyte	60 vol% Orthophosphoric Acid 35 vol% Water 5 vol% Sulfuric Acid
	or Power-Kleen Solution*
Current density	0.04 amps/cm ²
Voltage	8-9 volts d.c.
Time	30 minutes (starting from rough machined surface)
Temperature	140°C
Electrolyte container	304 stainless steel
Cathode-to-anode distance	15 cm
Cathode	Copper plates

*Proprietary orthophosphoric acid solution marketed by Molecotrics, Inc., Inglewood, California.

The electropolishing procedure for the recommended time does not totally remove rough machining marks. Longer times would undoubtedly improve surface smoothness; however, in high-inclusion content samples (e.g., greater than 1 vol% inclusions) there is undue pitting caused

by inclusion attack. Therefore, there are reasons other than economic ones for not significantly increasing the electropolishing times.

This electropolishing procedure works extremely well for nonflat specimens. This condition is encountered often in slab samples cut to 100-mil thicknesses for X-ray radiographic purposes. It is very difficult to hold flatness on parts this thin. No mechanical grinding is required and the electropolished sample can be directly macroetched by immersion in the HNO₃-HAc solution discussed in a subsequent section.

It is possible to electroetch the electropolished sample in the same solution used for polishing. All that need be done is to lower the current density to 0.10 amps/cm² for several minutes. However, samples etched in this manner lack the contrast that is desirable in macroetched samples.

2. **MECHANICAL GRINDING PROCEDURE.** For samples that have flat sections and for which it is desirable to reveal fine and delicate details of the structure, then the surface must, of necessity be correspondingly smoother than that produced by the electrogrinding procedure. That is, it is desirable to remove all traces of machining marks. The procedure starting with a rough machined surface is 5 to 10 minutes on 120-grit Si-C paper, followed by 1 to 2 minutes each on 320, 400, 600, and 600 soft Si-C paper on a low speed rotary lap. Care must be taken to flood the sample with cool water to prevent an excess of frictional heating of the surface during grinding. The Si-C papers should be frequently changed to maintain sharp cutting particles at the grinding interface

Macroetching

Assuming that the electropolishing or mechanical grinding procedures have removed sufficient machining marks, as well as heat-affected and worked metal then the specimen is ready for macroetching. Because of chemical, mechanical, and physical heterogeneities on a macroscale, certain regions of the sample will be attacked at a faster rate than others by the etching solution and a pattern will be developed that is visible to the unaided eye. This pattern, if interpreted properly, can be related to the physical, mechanical, or chemical heterogeneity is an undesirable one, it can be eliminated; or if it is a beneficial one, it can then be enhanced or reproduced in subsequent castings, forgings forgings, etc.

Two methods of macroetching have proven satisfactory with uranium alloys:

1. IMMERSION MACROETCH PROCEDURE. In this procedure the sample is merely immersed in an acid solution and allowed to set for a certain length of time. The parameters for this procedure are listed in Table 2.

Table 2. Immersion Macroetch Procedure.

Immersion etch solution	50 vol% nitric acid 50 vol% glacial acetic acid
Immersion time	30 minutes
Immersion etch container	304 stainless steel tray or tank

Caution is recommended concerning the use of strong oxidizing acids such as nitric acid and uranium alloys under certain conditions. Massive uranium alloys in certain heat treated conditions can explode during or after immersion in nitric acid. The nitric acid reacts with an alpha precipitated alloy (often with a carbon contaminated surface) to form a highly unstable surface product which decomposes violently when dropped, struck, or sparked. The conditions and mechanisms under which the explosions occur are outlined in a report by Jackson and Johns.¹

After the macro specimen has been etched, it should be rinsed with running water, washed with a detergent soap and again thoroughly rinsed with running water. After washing, the sample can be dried with an air blower. During these and subsequent operations care should be taken not to directly touch the prepared surface. Rubber surgeon gloves can be used to protect the hands from the etching solution and the sample from fingerprints.

Photomacrographs of a vertical section of an as-arc-cast U-6.3 wt% Nb ingot electropolished for 30 minutes and then immersion etched in HNO_3 -HAc for 30 minutes is shown in Figure 2. The sampling procedure is that described in Figure 1a. The ingot was consumably arc-cast and weighed about 145 kg. Freezing started at the bottom of the macro-photograph and proceeded upward. The freezing interface was concave and parallel to the visible lines that trace out a semicircle (macrobands). Inverse segregation occurs and the ingot is niobium rich at the center and edge. However, this is not obvious from the photomacrograph. The macrobands (parallel to concave freezing interface) however, are small regions over which cyclic inverse segregation occurs. The repeating macrobands are due to a cyclic fluctuation in the thickness of the mushy zone during arc casting. Near the top of the ingot there is a general darkening caused by a higher inclusion content which masks out the macrobands in this region (due to overetching). The very dark region near the shrinkage cavity is a region of porosity and high inclusion content.

Figure 2. Macroetched Vertical Sections of a 145 kg As-Arc-Cast U-6.3 wt% Nb Ingot. The sections were electropolished for 30 minutes followed by immersion etching in HNO_3 -HAc for 30 minutes. Reflected illumination.

The immersion-etch procedure works well for induction-cast ingots. Photomicrographs of a vertical section of an as-induction-cast U-6.3 wt% Nb ingot electropolished for 30 minutes and then immersion etched in HNO_3 -HAc for 30 minutes is shown in Figure 3. The sampling procedure is that described in Figure 1a. The ingot was a bottom-poured induction casting and weighed about 145 kg. The ingot was hot topped, and again freezing started at the bottom of the photomicrograph and proceeded upward. The freezing interface is more V-shaped than in the arc-cast ingot and there is a noted absence of a shrinkage cavity. The absence of the shrinkage cavity is owing to the hot-topping operation.

The electrogrinding, immersion-etch procedure works well for as-cast or as-cold-worked uranium alloys, but often does not yield satisfactory results on well-homogenized castings or recrystallized cold-worked material. In these instances, provided there is a relatively flat surface, a more highly polished starting surface is required. This can be achieved by mechanically grinding through 600-grit Si-C soft paper as discussed earlier, and then immersion etching. If a better polish is required, then vibratory polishing with one-micron alumina for 15 to 18 hours prior to immersion etching may be necessary. A horizontal disk sample from a U-7.1 wt% Nb arc-cast ingot that was subsequently homogenized 18 hours at 1100°C is shown in Figure 4. This sample was mechanically polished and immersion etched. A similarly prepared U-6.3 wt% Nb cold-forged sheet is shown in Figure 5.

2. VIBRATORY POLISH-ATTACK MACROETCH PROCEDURE. A procedure that works well, when the macropattern is hard to develop, consists of a vibratory polish-attack. The procedure, outlined in Table 3, requires a flat surface and at present is limited to samples about 8 inches in diameter.

Table 3. Vibratory Polish-Attack Macro-Etch Procedure.

Grinding (starting from rough machined planar surface)	5-10 min. on 120-grit SiC* 1-2 min. on 320-grit SiC* 1-2 min. on 400-grit SiC* 1-2 min. on 600-grit SiC* 1-2 min. on 600-grit SiC soft*
Vibratory polish-etch cloth	Medium-nap synthetic cloth
Vibratory polish-etch solution	100 g of one micron Al_2O_3 20 ml of 10% by weight chromic acid in water 500 ml of distilled water
Vibratory polish-etch time	16-18 hours

*Low speed rotary lap flooded with water.

A horizontal disk from a U-5.2 wt% Nb arc-cast ingot homogenized 18 hours at 1100°C is shown in Figure 6. A cross-section of a recrystallized extruded tube of composition U-4.2 wt% Nb appears in Figure 7. Both of these

Figure 3. Macroetched Vertical Sections of a 145 kg As-Induction-Cast U-6.3 wt% Nb Ingot. The sections were electropolished for 30 minutes followed by immersion etching in HNO_3 -HAc for 30 minutes. Reflected illumination.

Figure 4. Macroetched Horizontal Section of a 145 kg Arc-Cast U-7.1 wt% Nb Ingot that Had Been Homogenized 18-Hours at 1100°C. The section was mechanically polished and immersion etched in HNO_3 -HAc. Reflected illumination.

Figure 5. Macroetched U-6.3 wt% Nb Alloy Forged at 23°C. The section was mechanically polished through one micron alumina and immersion etched in HNO_3 -HAc. 9X.

Figure 6. Macroetched Horizontal Section of a 145 kg Arc-Cast U-5.2 wt% Nb Ingot that Had Been Homogenized 18 Hours at 1100°C. The section was mechanically ground and then vibratory attack-polished for 18 hours in a dilute chromic acid solution. Reflected illumination.

Figure 7. Macroetched Cross-Section of a 15 Foot Long Recrystallized Extruded Tube of Composition U-4.2 wt% Nb. The section was mechanically ground through 600-grit Si-C (soft) and then vibratory attack-polished for 16 hours in a dilute chromic acid solution. Reflected illumination.

specimens were prepared by the vibratory polish-attack procedure outlined in Table 3.

Recording the Macroetching

Conventional photographic methods are probably the best available for recording details of macroetched uranium alloy specimens. A 4 by 5-inch studio camera mounted horizontally on an adjustable track is ideal for photomacrography purposes. Almost any photographic lens of high quality and appropriate focal length is well suited for photomacrography. High quality lenses are well corrected for aberrational errors and are capable of excellent resolving power and the formation of an extremely sharp image. Furthermore, these lenses have an adjustable iris diaphragm — a requisite of the lens that is essential for photomacrography purposes — which may be “stopped down” to improve the depth of focus and image sharpness. A Polaroid MP-3 Industrial View Land Camera with several lenses is near ideal for photomacrography.

The use of studio-type camera for photomacrography usually requires artificial lighting facilities to illuminate properly the specimen of interest. The truest rendition of macroetched surfaces is normally obtained with reflected lighting. A large white poster board, e.g., 22 by 28 inches, with a lens hole is placed in the same plane as the lens. Two high intensity lamps are placed in the plane of the sample and directed toward the white poster board. With such an array of lighting equipment it is possible to secure an image that appears natural and realistic. A photomacrograph taken with direct 45° illumination rather than reflected illumination is shown in Figure 8. This is to be compared with Figure 6 which was taken with reflected illumination. It can be readily seen that the specular areas are dark with the 45° direct illumination whereas with reflected illumination they are natural and realistic.

Sometimes in this arrangement a small reflection from the lens appears on the specimen. This can ordinarily be eliminated by tilting the specimen a few degrees from the horizontal. Sometimes it is necessary to use auxiliary direct

Figure 8. Same as Figure 6 Except Taken with 45° Direct Illumination.

lighting to adequately shadow and highlight irregularly shaped specimens.

No special precautions are necessary to protect the surface after macroetching and macrophotography. The samples darken after extended periods of storage but this usually enhances the etch pattern. As an example, macroetched samples stored at room temperature for several years in nonsealed plastic bags suffered no damage to the patterns developed when they were macroetched.

REFERENCE

1. R. J. Jackson and W. L. Johns, "Explosive Nature of Uranium-Base Niobium alloys After Immersion in Nitric Acid," USAEC Report RFP-1575, 1970.