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METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

**TECHNICAL PAPERS OF THE TENTH
METALLOGRAPHIC GROUP MEETING HELD
AT KNOLLS ATOMIC POWER LABORATORY,
OCTOBER 24, 1955**

**Compiled by
H. P. Roth**

**December 1956
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**Metallurgy Development Advisory Committee
Washington, D. C.**

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OCTOBER 24, 1955

Compiled by

H. P. Roth

METALLURGY DEVELOPMENT ADVISORY COMMITTEE
Washington, D. C.

Attendance List

Metallographic Group Meeting At
Knolls Atomic Power Laboratory
October 24, 1955

C. Whitney, Atomic Energy Commission, Schenectady Operations Office
D. Peterson, Ames Laboratory
J. E. Baumrucker, Argonne National Laboratory
B. Blumenthal, Argonne National Laboratory
A. E. Dwight, Argonne National Laboratory
K. M. Ferguson, Babcock & Wilcox
D. M. Cheney, Battelle Memorial Institute
M. F. Garufi, Bridgeport Brass Company
H. S. Rubenstein, Bridgeport Brass Company
J. F. Willging, Dow Chemical Company
C. L. Angerman, duPont, Savannah River Laboratory
F. F. Wyman, duPont, Savannah River Laboratory
E. W. Filer, General Electric, Aircraft Nuclear Propulsion Project
S. M. Bishop, General Electric, Knolls Atomic Power Laboratory
C. A. Bruch, General Electric, Knolls Atomic Power Laboratory
W. M. Cashin, General Electric, Knolls Atomic Power Laboratory
J. W. Czarkowski, General Electric, Knolls Atomic Power Laboratory
T. F. Fisher, General Electric, Knolls Atomic Power Laboratory
A. N. Holden, General Electric, Knolls Atomic Power Laboratory
M. C. Houle, General Electric, Knolls Atomic Power Laboratory
W. E. McHugh, General Electric, Knolls Atomic Power Laboratory
M. C. Peek, General Electric, Knolls Atomic Power Laboratory
L. P. Pepkowitz, General Electric, Knolls Atomic Power Laboratory
W. Scholl, General Electric, Knolls Atomic Power Laboratory
D. W. White, General Electric, Knolls Atomic Power Laboratory
T. I. Jones, Los Alamos Scientific Laboratory
C. O. Matthews, Los Alamos Scientific Laboratory
D. J. Murphy, Los Alamos Scientific Laboratory
J. A. Fellows, Mallinckrodt Chemical Works
H. C. Kloepper, Mallinckrodt Chemical Works
W. R. Yankee, Metals & Controls Corporation
K. H. Clark, National Lead Company of Ohio
P. R. Morris, National Lead Company of Ohio
H. P. Roth, Nuclear Metals, Inc.
S. J. Broderick, New Brunswick Laboratory
G. Bentle, North American Aviation, Inc.
M. J. Feldman, Oak Ridge National Laboratory
R. J. Gray, Oak Ridge National Laboratory
E. J. Manthos, Oak Ridge National Laboratory
T. K. Roche, Oak Ridge National Laboratory
R. W. Campbell, Sylvania Electric Products, Inc.
H. Woods, Sylvania Electric Products, Inc.
F. M. Cain, Jr., Westinghouse Atomic Power Division
R. Wolfe, Westinghouse Atomic Products Division

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A MACROETCH FOR URANIUM

R. B. Russell

Aqueous hydrochloric acid has been used as a macroetch for uranium for some time at the Hanford Works and at Mallinckrodt, yet this etchant is apparently not well known. The procedure is based on the fact that uranium dissolves rapidly in concentrated hydrochloric acid and that this acid corrodes uranium grains at very different rates which depend markedly on the kind of crystallographic face of the grain exposed to attack. By using such an acid, grains, and even twin bands within them, may be made clearly visible to the naked eye or with low magnifications. A satisfactory etching procedure is as follows:

- 1) Remove any heavy scale from the sample by dipping it in concentrated nitric acid. It is not necessary to grind a smooth surface on the sample preparatory for etching.
- 2) Dip the sample and agitate it in concentrated hydrochloric acid until the metal is evenly coated with a dull black film. This occurs after a few seconds of violent evolution of hydrogen and the appearance of a hyacinth-red solution of uranium trichloride.
- 3) The black film is then removed by dipping the sample in concentrated nitric acid for a few seconds until the grains have maximum contrast after rinsing and drying the sample.

If nitric acid cleaning is continued too long, the grains will lose their contrast, presumably because the corrosion rate in nitric acid is less orientation dependent and the sharp edges of the etch pits will be rounded off. If the contrast is lost through overetching in nitric acid, repeat procedures 2 and 3. These etching procedures seem to work well at room temperature.

Another etch which uses the chloride attack is the electrolytic method with an electrolyte of trichloroacetic and hydrochloric acids. This has been used successfully by E. S. Fisher at Argonne National Laboratory, * but it seemed difficult to get high enough contrast among the grains.

* E. S. Fisher, ANL-5159 p. 12, (Nov. 18, 1953) SECRET

It would seem that hydrochloric acid could be incorporated in some milder etchant for microexamination. The concentrated acid used for this macroetch pits the surface too much for such high magnifications.

In Figures 1 through 5 examples of various uranium grain sizes may be seen. In figure 5 note the twin bands which are revealed.

THE USE OF CONCENTRATED NITRIC ACID WITH URANIUM-ZIRCONIUM ALLOYS IS ESPECIALLY DANGEROUS, OWING TO THE EXPLOSIONS WHICH SO READILY OCCUR.

Figure 1 Longitudinal 7½X
 Extruded at about 625°C. Extrusion ratio
 25:1. Quenched into water from 725°C for
 5 minutes.

Figure 2 Longitudinal 7½X
 Extruded at about 700°C. Extrusion
 ratio 25:1.

Figure 3 Transverse
Extruded at 900°C. Extrusion
Ratio 13.6:1

4X

Figure 4 2½X
Same as Figure 3 except that it is
longitudinal exterior.

Figure 5 Transverse
Extruded at 907°C.

35X

CASTO-MOLD -- A SELF CURING PLASTIC FOR MOUNTING SPECIMENS

by H.P. Roth

Among the numerous types of plastics tried we have found one which is exceptionally good and which, therefore, we use for mounting all of our metallographic specimens. It is called Casto-Mold* and is packaged and marketed specifically for use in the metallurgical laboratory.

Following are the main advantages to using this plastic: Mounted specimens are prepared at room temperature without applied heat or pressure. Any number of specimens can be prepared simultaneously. Unused mounting material will keep indefinitely.

The unit of material consists of one pound of plastic powder, which, I believe, is of the polymethylmethacrylate type, and a bottle of liquid. Equal volumes of powder and liquid are mixed together in a beaker and poured around each sample to the desired depth in the mold. Mounts are self curing and require no further attention from the technician. Since no special mounting or curing equipment is needed, unlimited numbers of samples can be cast at once.

Figure I shows the material and helps to convey the simplicity of using it. Included in the photograph is the jar of powder and of liquid with a suitable measuring glass. This will serve for measuring both, since it can be wiped clean with tissue in a second or two. Two different sample sizes are shown here, but a great variety of shapes and dimensions are permissible with this method.

Regarding molds, any hollow shape open at two ends is satisfactory. Short lengths cut from pipe or tubing are good and are usually readily available. These can be used repeatedly by lightly coating the insides with powder or grease for ease in ejecting the mounts, or the rings can be retained and polished as part of the mount. There is economy in varying the size of the mold to conform to the size of the specimen. A glass plate or bench top provides the best base for mounting so that the resulting mount has a smooth face to start with. Identities of samples can be marked beside each one directly on the glass plate with wax crayon. Samples are placed in rows with a mold around each one. Enough plastic for about 4 or 5 samples is mixed each time since it thickens within a minute or less and should then be poured. Consecutive batches are readily mixed and poured to any amount.

Very fine wire or thin sheet are conveniently mounted by suspending them erect and gently pouring the plastic around them. Since pressure is not used, they will be kept in place and are always visible for positioning.

* Distributors of Casto-Mold are Macalaster Bicknell Company, Laboratory Supplies and Equipment, of New Haven, Connecticut; Cambridge, Massachusetts; and Syracuse, New York

Cutting the metal specimens to different lengths and allowing the ends to project from the back of the mount permits placing several in a mount. The projecting ends of differing lengths serve for identification and also as contact for electrolytic polishing.

On single crystal samples and those studied for slip and twin habit, this room temperature casting method avoids the deformation effects due to heat and pressure. It is particularly advantageous for thin sheets or very small beryllium samples which are so light that they tend to float and become displaced within the mount. A thin layer can be poured around the sample carefully and as it congeals the sample position can be watched and controlled. Added plastic layers weld themselves together to form solid mounts of any desired height.

There are other applications for Casto-Mold in the laboratory. It has been used for mounting x-ray specimens in a specially shaped mold which tapers and has an extended neck at the end of which the sample is located. Special holders can be molded by using the plastic in much heavier concentrations so that it can be formed with the hands like plasticine or modeling clay. Since it sets fairly rapidly it is not likely to deform.

DISCUSSION

Discussion after paper given by H.P. Roth - Nuclear Metals, Inc.

C. O. Matthews, Los Alamos. I'd like to ask Miss Roth the curing time for this plastic.

H. P. Roth. It takes about an hour to an hour and a half for curing, depending on room temperature. Solidification, of course, takes place much sooner.

C. O. Matthews. Thank you; also, what are the wetting characteristics. How much space do we find around the metal?

H. P. Roth. It wets very well. This is why we use it as fluid as we do, so that it will completely surround the sample. It withstands most acids fairly well, except boiling mixed concentrated acids. It seems to be the temperature which causes most harm in this case.

Francis Cain, Westinghouse Atomic Products Division. Who is the supplier?

H. P. Roth. The supplier of Casto-Mold is Macalaster Bicknell Co. - a laboratory supply house with branches in Syracuse, New York, Cambridge, Massachusetts and New Haven, Connecticut.

R. J. Gray, Oak Ridge National Laboratory. How brittle is this, does it fracture easily?

H. P. Roth. No.

H. J. Gray. Also, how is it against alcohol?

H. P. Roth. Very good. The recommended solvent for it is ether and this is very slow.

E. W. Filer, ANP. How does this compare with Koldmount which cures in about 20 minutes?

H. P. Roth. I don't know, I am not familiar with the product.

E. W. Filer. It seems to work very well.

H. P. Roth. I am being conservative about this. Casto-Mold is set much sooner than the time I gave, but I think that it perhaps has not cured completely, and that it reaches maximum hardness by setting for about an additional hour. I would say that in 20 minutes if one wanted to polish this, one could; we just never do this.

During the hottest summer months we often found a large shrinkage cavity at the top or back of the mount. This was easily rectified by directing a current of air from an ordinary fan toward the samples while solidifying.

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NEW ETCHING METHODS FOR THORIUM

David Peterson and Donald Westlake

A number of etching, electroetching, and electropolishing methods for thorium metal have been reported. The most successful methods have been electrolytic procedures using a bath of perchloric acid dissolved in acetic acid or in ethyl alcohol. These procedures are able to delineate the grain boundaries quite well. However, the inclusions are badly obliterated and a number of small black specks are usually found in the surface of the sample. Whether these specks or peppering represent a feature of the microstructure or an artifact of the procedure has not been established. The development of an etching method for thorium which did not involve potentially explosive solutions and which did not eat away the inclusions appeared desirable. In addition, it might be helpful in determining the nature of the peppering observed with previous electrolytic methods. A review of the literature on electroetching and electropolishing of thorium indicated that there were no aqueous solutions which were satisfactory and that only perchloric acid gave encouraging results in organic solvents. This dearth of information and the lack of a theoretical correlation of the chemical properties of the electrolyte, the solvent and the anode metal with the behavior of an electroetching or polishing cell made a systematic approach to the problem difficult. An attempt was made to formulate a logical approach on the following grounds.

Any successful electropolishing procedure must start with an electrolytic reaction which gives a rapid and clean removal of metal from the anode. This electrolytic reaction consists of three basic processes. A reduction process takes place at the cathode. This usually consists of the reduction of hydrogen ion to free hydrogen but might be the reduction of a metallic ion. The current is carried through the solution by the migration of positive and negative ions. These may be the ions which take part in the anode and cathode reactions or may be ions furnished by a supporting electrolyte. A supporting electrolyte is used primarily to reduce the resistance of the solution by increasing the number of current carrying ions. At the anode, an oxidation reaction takes place. This may be the formation of a positive metallic ion either in solution or in a solid anode product such as an oxide film. Alternately, a negative ion may be discharged such as the discharge of hydroxide ions to produce oxygen or of chloride ions to produce chlorine.

A solvent for an electrolytic solution must ionize the electrolyte so that the solution will be conducting. It should not react with the metal ions produced at the anode to form a film or stain. Water is an excellent solvent as its high dielectric constant and polar nature promote extensive ionization of electrolytes. However, water seems to be unsatisfactory as a solvent for thorium because thorium is such a weak base that the thorium ion reacts with hydroxide ions unless the pH of the solution is very low. This reaction with hydroxide ion produces a film of thorium oxide or hydroxide on the anode surface which leads

to staining and to pitting of the thorium surface. Increasing the hydrogen ion concentration can prevent this precipitation but increases the rate of direct chemical attack on the thorium by hydrogen ions and makes the solutions much too highly conducting to be satisfactory.

Organic solvents usually are much less polar than water, have lower dielectric constants and are not as effective in solvating ions. As a result, many acids ionize only very slightly in organic solvents. To avoid this effect, a number of organic liquids were selected on the basis of their dielectric constants. The dielectric constants of a few organic liquids which have been used as solvents in electrolytic baths are given in Table I.

Table I

Substance	Dielectric Constant
Water	78
Acetic Acid	6
Ethyl Alcohol	24
Ethylene Glycol	37
Acetic Anhydride	21
Formic Acid	58

Solutions of hydrochloric acid in glacial acetic acid, ethyl alcohol, and ethylene glycol were tried as electrolytic baths. All of these solutions were characterized by very high resistances

which indicated that the hydrogen chloride was not significantly ionized. A small amount of current was passed through the bath at voltages of 50 to 100 volts. The result was a very extensive peppering of the thorium surface with no delineation of the grain boundaries. Formic acid was a logical choice as an organic liquid which might promote ionization of hydrogen chloride. Solutions of hydrochloric acid in formic acid when used as electrolytic baths were indeed found to have quite low resistances. The thorium anode was cleanly attacked and an excellent electro-polishing action was evident.

The grain boundaries were not well delineated by this bath even on severely attacked samples. However, a very clean and well polished surface was obtained. Hydrobromic acid gave results quite similar to hydrochloric but the surface was not as smooth. Hydroiodic acid produced a rather rough and dark surface with the grain boundaries very heavily delineated. By combining hydrochloric acid and hydroiodic acid in a bath, the clean reaction and the polishing action characteristic of hydrochloric acid were retained and the grain boundaries were made visible by the hydroiodic acid. This combination gave the best results of the baths tested. Sulfuric acid did not form a conducting solution in formic acid and hydrofluoric acid coated the thorium surface with an insulating layer of thorium fluoride.

Several examples of the results which have been obtained by using formic acid solutions are shown in the photomicrographs. All of these samples were etched using a bath consisting of 100 parts by volume of formic acid, 2 parts by volume concentrated

hydrochloric acid, and 1 part by volume of 50 per cent hydroiodic acid. The formic acid used was 98 per cent formic acid assay. A sample of cold-worked, recrystallized, calcium-reduced thorium is shown in Figure 1. The grain boundaries have been fully developed without obliterating the inclusions. In Figure 2, the same sample is shown at 100 diameters for comparison with Figure 3, which shows the same sample after a more severe electropolish and etch. The delineation of the grain boundaries is approximately the same in both figures. The inclusions have been obscured by the more severe treatment illustrated in Figure 3. The peppering or formation of small black specks in these samples was not increased by the drastic etching which indicates that this may well be a feature of the microstructure rather than an etching artifact. The microstructure of an as-cast thorium sample is shown in Figure 4 at a magnification of 100 diameters.

An etching procedure for thorium metal has not been completely developed. However, formic acid solutions of hydrogen chloride and hydrogen iodide seem to be very promising. The use of potentially explosive mixtures is avoided, obliteration of inclusions seems to be reduced, and extraneous pitting of the samples seems more easily controlled. Investigation of this bath will be continued to determine whether a simple and satisfactory procedure can be developed.

DISCUSSION

Discussion after paper: "Progress on New Etching Methods for Thorium"
David Peterson - Ames Laboratory

G. Bentle, North American. Have you tried cathodic etching?

D. Peterson: I have not tried it personally, no. It has been tried with, I believe, moderate success. My personal opinion is that it works well, but it's an awful lot of trouble, takes a lot of equipment and is not generally suited for all small and occasional laboratory uses.

P. R. Morris, National Lead. We have obtained our best results on the start of the attack by running about 4,000 volts. The pressure is difficult to determine because we have been using a mixture of argon and xenon. A thermocouple gauge was used. The apparent pressure (air calibration) was 2 microns of mercury. You might get a pressure measurement from the fact that the potential was 4,000 volts and the current would run about 20 mils. The start of the removal of metal seems to be relatively slow. In general, our samples require about 45 minutes before the etching process starts, and we have had our best luck with xenon-argon mixtures.

D. J. Murphy, Los Alamos Scientific Laboratory. Please repeat the mixture of acids used.

D. Peterson: We have tried, primarily 4 parts of hydrochloric and 100 parts of formic acid. We have also used hydrobromic and hydroiodic. Our best results have been with hydrochloric acid in about that concentration and with solutions of about 4 parts of hydrochloric to 100 plus 1 to 2 parts of hydroiodic. The hydroiodic seems to give us better delineation of the grain boundaries. The hydrochloric gives smoother polishing but very little contrast.

Fig. 1 - Recrystallized Thorium Metal. Formic Acid-HCl-HI Etch. 1.5 amp. per sq. in. for 8 sec. 250X B.F.

Fig. 2 - Recrystallized Thorium Metal. Formic Acid-HCl-HI Etch. 1.5 amp. per sq. in. 100X B.F.

Fig. 3 - Recrystallized Thorium Metal. Formic Acid-HCl-HI Etch. 5 amp. per sq. in. for 6 sec. 1.5 amp. per sq. in. for 2 sec. 100X B.F.

Fig. 4 - As-cast Thorium Metal. Formic Acid-HCl-HI Etch. 5 amp. per sq. in. for 6 sec. 1.5 amp. per sq. in. 100X B.F.

INCLUSION COUNTING METHODS FOR URANIUM

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R. F. Dickerson, Battelle Memorial Institute
A. E. Guay, National Lead Company
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INTRODUCTION

The Metallography Sub-committee of the Metal Quality Working Committee was asked to formulate a method for rating the inclusion content of cast and wrought uranium shapes⁽¹⁾. This Sub-committee had previously done work on the classification of the stringers and identification of the inclusions occurring in reactor grade uranium⁽²⁾. A method for determining the inclusion content of uranium would be a valuable tool in investigations of the effect of inclusions on the reactor performance of fuel elements, the correlation of ingot quality with slug yields, and determining the significant variations of inclusion content in individual slugs and from slug to slug.

The methods recommended in this report were decided upon after reviewing the methods for determining the inclusion content in steels and other metals as recommended by the SAE⁽³⁾, and the ASTM⁽⁴⁾, and the general subject of lineal analysis⁽⁵⁾. Further insight into the problem was obtained by experimenting with the various recommended methods as applied to uranium.

Any method for rating the inclusion content should provide information as to the identity and the concentration of the individual inclusions. With uranium, this is best accomplished by a micro method which (a) will give the identity, concentration, and length of the stringers of inclusions, and (b) will give the concentration of the other inclusions not aligned in stringers (i.e. background). Due to the large numbers of inclusions that are usually found in reactor grade uranium, this micro method would be laborious and time consuming. Therefore, a macro method would be useful as a relatively fast means of rating the total inclusion content of a sample neglecting the identification of the inclusions.

METHODS FOR DETERMINING THE INCLUSION CONTENT OF URANIUM

I. MACRO

A. Wrought Metal

A general impression of the inclusion content of a sample is to be determined by examination of a longitudinal, as-polished specimen at a magnification of 3X. The minimum size sample shall be such that any variation in inclusion

content of the wrought shape may be detected.* An as polished surface is required to prevent loss of inclusions and exaggeration of defects by etching.

The rating is to be accomplished by comparison to the standard chart "Macro Rating of the Inclusion Content of Uranium". (See Figure 1.) The numbers corresponding to the fields represented in the chart, which most closely resemble the sample being examined, are reported.

B. Cast Metal

A sample 1/2 inch by 1/2 inch is to be prepared as described above for wrought material. The rating is again obtained by comparison to the Standard Chart (Figure 1) using columns "c" and "C" only. The reporting is as above for wrought metal.

II. Micro

A. Wrought Metal

A complete description of the inclusion content of a sample will be a laborious and time consuming procedure in the case of extremely dirty metal, consequently, it is not readily applicable to a routine quality control examination. To alleviate this problem, two methods are recommended. Both micro methods are to be supplemented by the macro method described above. Method A gives only the total length, and total number of inclusions with a visual estimation of the amount of each type of inclusion present. Method B gives the total number and actual size of each type of inclusion. The choice of method would be dependent upon the requirements of each particular application.

For the purpose of this rating system, a stringer shall be defined as a single inclusion or a linear group of inclusions equal to or greater than one unit in length (1 unit is defined under the descriptions of the methods listed below). A continuous stringer is referred to as one containing not more than one break of less than 1/2 unit for each unit of the stringer length. A discontinuous stringer is defined as a) one that contains at least one break or discontinuity that is greater than 1/2 unit but less than 1 unit or b) one that contains more than one break or discontinuity of less than 1/2 unit for each unit of the stringer length. A discontinuity of not less than one unit along the length of a stringer divides it into two stringers.

Method A (Abridged Method)

It is recommended that the same sample used in the macro examination by used for the micro. The surface shall be prepared by a suitable polish followed

* For slugs, the recommended sample size would be r (the radius of the slug) by 5/8 inch. For plate type elements, the size would be t (the thickness of the plate) by 5/8 inch.

by any treatment needed for identification(2). Initial examination will be performed by traversing in the direction of working, at a magnification of 50X. At this magnification the total length and total number of stringers in the entire specimen surface will be determined by projection on to a ground glass screen which is ruled with a series of parallel lines 1/4 inch apart. The distance between any two parallel lines is called a unit, in terms of which the lengths of the stringers shall be measured.*

The estimation of the relative amounts of each type of inclusions shall be done at 250X (or any other magnification required for identification). Enough of the sample is scanned for the observer to form a visual estimation of the percentage of each type of inclusion present in both continuous and discontinuous stringers.

Results of the examination will be reported in tabular form as follows: For a hypothetical sample having 12 stringers whose total length was 136 units and contained 50% slag, 1% UC, 20% UO_2 , 10% UH_3 , 18% UC-UN and 1% globular slag:

Sample No.	No. Stringers	Tot. Length	Per Cent					
			Slag	UO_2	UH_3	UC	UC-UN	Glob. Slag.
X	12	136	50	20	10	1	18	1

Method B

The minimum sample size shall be the same as for the macro. A 1/2 inch grid at a magnification of 100 diameters will be used to measure the length and number of each type of stringer. Positive identification of the specific types of stringers may involve examination at 250 diameters magnification.

The entire surface area of the sample will be examined and traverses will be made in the direction of working. Record will be made of the counted number, the measured length, and the average estimated width of each stringer. The rating of the stringers in successive fields examined will be recorded: the description of each stringer in those fields will be entered in the appropriate columns (distinguished by composition and continuity). The report of each field will include: (a) the total number of each type (composition) of stringer, (b) the total length of each type of stringer, and (c) the average width (in units of sixteenths of an inch at 100X) of each type of stringer. In addition to the above, the length of the longest stringer of each type found on the sample surface will be recorded.

- * Instead of projecting the image on a ground glass ruled with parallel lines 1/4 inch apart, in the form of a grid. It may be more convenient to use an eye piece containing a micrometer disk ruled with parallel lines separated by a distance equivalent to 0.005 inch on the specimen.

An example of the reporting is shown in Table 1. To explain these figures, we show that the examination of a sample involved the reporting of 80 fields. The sample contained continuous and discontinuous stringers composed of only the hydride. For the continuous hydride stringers, 274 separate stringers having a total length of 856 units and an average (estimated width of 2 times $1/16$ inch). Similarly, the discontinuous hydrides numbered 169; their total length was 515 units; the average width was $1/16$ inch.

BACKGROUND

Background will be considered as all inclusions appearing in wrought material that cannot be classified as stringers and must be rated as a part of both Methods A and B. In order that this background may be determined the specimen, as prepared for either Method A or Method B above, will be examined at a magnification of 100 diameters with a $1/2$ inch grid superimposed on the field (distance between parallel lines represents a distance of 0.005 inch on the specimen). The field so observed will be compared with the "Chart of Background Inclusion Sizes and Concentrations" (Figure 3). Using a number (0 through 50) and a letter (a through g) report: (1) A uniform background: use one number and one letter, i.e. 6a, (2) A non-uniform background: report the range by using two number-letter combinations, i.e. 6a-16c.

Sequences of small inclusions, aligned in the direction of working, shall be classed as background if by definition they cannot be considered as a discontinuous stringer.

B. Cast Metal

The sample shall be a minimum of $1/2$ inch x $1/2$ inch in size and shall receive the same type of surface preparation as specified under "Wrought Metal". The sample shall then be scanned under bright field illumination at 100X and the rating made by comparison with sections 1, 2, and 3 in the "Inclusion Chart for Cast Metal", (Figure 4). Sections 1, 2, and 3 in the inclusion chart detect dispersed, clustered, and pseudo grain-boundary type inclusions respectively. The rating shall be reported as a series of letters and numbers as found associated with the various illustrations on the charts which most closely resemble the fields being examined.

All material smaller than the 60 mil units depicted in the top row (15 minutes actual size) will be counted as background. The relative proportion of slug, hydride, etc. will be estimated (Method A - Wrought Metal). The "Inclusion Chart for Cast Metal" will be used to rate porosity in cast metal. Such a rating must be reported as porosity.

REFERENCES

1. "Quarterly Report of the Working Committee on Metal Quality and Fabrication", December 17, 1954, DPST-54-580, (Secret).
2. H. A. Saller, ed., "Classification of Stringers and Identification of Inclusions in Reactor - Grade Uranium", November 29, 1954, BMI-965, (Secret).
3. SAE Handbook, "Determination of Inclusions in Steels", 1952, pp 136-139.
4. ASTM, "Tentative Recommended Practice for Determining the Inclusion Content of Steel", E-45-46T, (1946).
5. Transactions of the AIME, Vol. 172, 1947, pp 413-427.

Field No.	Continuous Stringers								
	Hydride			Slag			Oxide		
	No.	Tot. Len.	Avg. Wid.	No.	Tot. Len.	Avg. Wid.	No.	Tot. Len.	Avg. Wid.
1	4	24	2	---	---	---	---	---	---
2	3	13	2	---	---	---	---	---	---
3	3	12	2	---	---	---	---	---	---
4	4	14	2	---	---	---	---	---	---
5	4	14	2	---	---	---	---	---	---
:									
:									
70	4	10	1	---	---	---	---	---	---
80	4	14	2	---	---	---	---	---	---
Total	274	856	2						

[illegible]

REFERENCES

1. "Quarterly Report of the Working Committee on Metal Quality and Fabrication", December 17, 1954, DPST-54-580, (Secret).
2. H. A. Saller, ed., "Classification of Stringers and Identification of Inclusions in Reactor - Grade Uranium", November 29, 1954, BMI-965, (Secret).
3. SAE Handbook, "Determination of Inclusions in Steels", 1952, pp 136-139.
4. ASTM, "Tentative Recommended Practice for Determining the Inclusion Content of Steel", E-45-46T, (1946).
5. Transactions of the AIME, Vol. 172, 1947, pp 413-427.

CHART FOR MACRO RATING OF INCLUSION CONTENT

FIGURE 1

INSTRUCTIONS

1. PREPARE SPECIMEN TO PREVENT LOSS OF INCLUSIONS OR EXAGGERATION OF DEFECTS.
2. EXAMINE AT 3X.
3. REPORT NUMBER-LETTER COMBINATION CORRESPONDING TO THE FIELD ON THE CHART WHICH MOST CLOSELY RESEMBLES THE SPECIMEN.

FIGURE 2

CHART OF BACKGROUND INCLUSIONS

INCLUSION CHART FOR CAST URANIUM

MICRO EXAMINATION

INSTRUCTIONS

1. SAMPLE SIZE - 1/2" X 1/2" MIN.
2. SURFACE PREPARATION - ANY SUITABLE POLISH WHICH PREVENTS LOSS OF INCLUSIONS OR EXAGGERATION OF DEFECTS FOLLOWED BY ANY TREATMENT NEEDED FOR INCLUSION IDENTIFICATION.
3. COMPARE SPECIMEN AT 100X TO CHART.
4. REPORT NUMBER (SIGNIFYING CONCENTRATION) AND LETTER (INDICATING SIZE) OF THE FIELD ON THE CHART WHICH MOST CLOSELY RESEMBLES THE SPECIMEN, i.e. RANDOM GLOBULAR-2d, CLUSTERED GLOBULAR-16a, PSEUDO GRAIN BOUNDARY-6c.
5. THE NUMERICAL VALUES IN INCHES AT THE SIDE OF EACH SECTION ARE APPROXIMATE, CLASSIFICATION AS TO SIZE (a, b, c, etc.) SHOULD BE BASED ON COMPARISON WITH THE CHART.
6. ESTIMATE THE PER CENT OF SLAG, HYDRIDE, ETC., PRESENT IN THE SAMPLE.
7. ALL INCLUSIONS SMALLER THAN 0.060" (15 MICRONS ACTUAL SIZE) SHALL BE CONSIDERED AS BACKGROUND.

MICROHARDNESS EVALUATION OF ALPHA HOT-ROLLED URANIUM ROD FOR DRAWING

M. T. McGowan, H. S. Rubenstein, R. M. Treco

ABSTRACT*

A detailed microhardness investigation of hot rolled uranium rod before and after beta-treatment and drawing revealed the presence of non-uniform hardening throughout the cross-section. This investigation included compiling data to show radial and angular variations in hardness which might have been introduced during processing. Significantly hard annuli were found on transverse sections of material both drawn and not drawn in the region immediately below the surface to a depth of 0.50". The inhomogeneity in hardness present in the hot-rolled rods remained with area reductions up to 9% and die angles up to 15 degrees.

Beta-treating followed by cold drawing apparently shifted the hardness maximum towards the center of the rods. The greatest effect on hardness seemed to be at a point near 0.050" below the surface. The data were obtained using a Kentron Microhardness Tester with a Vickers Diamond Pyramid Indentor and further check tests were made with a Rockwell Hardness Tester.

DISCUSSION

Discussion after paper: "Microhardness Evaluation of Alpha Hot-Rolled Uranium Rod for Drawing"

M. T. McGowan, H. S. Rubenstein, R. M. Treco,
Bridgeport Brass Co.

P. R. Morris, National Lead Co. This effect that we referred to as the cruciform pattern in the ultrasonic test - and we're not the first to refer to it - we feel is due to a variation in orientation with radial direction, and I would not expect that you could observe this effect on a cross-sectional sample. It could be best observed on longitudinal samples which are taken along different radii - a radial variation in longitudinal samples.

H. S. Rubenstein. Most of the information I had seen on it was on transverse samples which showed this clover-leaf very beautifully.

P. R. Morris. In etching, yes, but it's a refractive dispersion that gives rise to it in ultrasonics and that is due to a variation in orientation with radial direction.

* This complete investigation is published elsewhere as an AEC Research and Development Report, number BRB-7, RMT-50. Consequently, only an abstract of the material is presented here.

H. S. Rubenstein. We believe that the method that we used, although very good for most of the things that we're looking for such as hardness inhomogeneity, is not quite sensitive enough due to the fact that the inclusions are present in such large numbers and we couldn't be very confident about anything like that without a large amount of data.

Dr. B. Blumenthal, Argonne National Laboratory. What was the carbon content of that material?

H. S. Rubenstein. It was standard feed material. We have no analyses on it here.

METALLOGRAPHIC DETERMINATION OF URANIUM-NIOBIUM
PHASE DIAGRAM UP TO 10% NIOBIUM

A. E. Dwight

It is the purpose of this paper to discuss the uranium-niobium phase diagram up to 10% niobium as determined by metallographic examination. Earlier work, summarized in EMI 1000⁽¹⁾, has established the general type of diagram. However, a more accurate binary diagram was needed to serve as a base for the investigation of the ternary uranium-niobium-zirconium system. The attempt was made to establish the binary uranium-niobium system with as high a degree of precision as was consistent with the quality of the available alloys.

In general the method was to bracket the boundary of a phase field within increasingly narrow limits of temperature, until eventually a $\pm 2^\circ$ bracket was obtained. The uranium-niobium system has a continuous series of solid solutions above 770, which greatly simplifies the method of temperature brackets. All specimens were held at 800 or 900°C to obtain the gamma solid solution. Then in most cases the specimen was transferred quickly to another furnace at the desired transformation temperature, held there until transformation was complete, and water quenched. The time required to complete transformation varied with temperature, but the practice was followed of transforming at various times from 24 hours to 1 week. If, for example, the structure of a 24 hour specimen was identical to that of a 48 hour specimen at the same temperature, it was assumed that both were completely transformed, but the 48 hour specimen was photographed. As a check, some specimens were quenched from the gamma range, and quickly reheated to the transformation temperature. Both treatments led to the same temperature brackets for a given alloy.

The number of specimens which were studied is best shown in Figure 1, which shows the phase diagram as determined by this investigation. All compositions listed in this paper are in weight per cent, all temperatures in Centigrade. The major difference between this diagram and the original diagram reported by B. Sawyer⁽²⁾, is that the eutectoid is now established at 634 ± 2 and $8 \pm 1\%$ Nb, a lower temperature and higher Nb content than originally reported.

The metallographic technique for the uranium-niobium alloys is simple. The mounted specimens are wet ground through 600 paper, then polished on cloth wheels through 1 micron diamond paste. Etching is done with an electrolytic bath of phosphoric acid, ethyl alcohol, and ethylene glycol in the ratio of 8:5:5, and a current density of 30 m.a./cm². Etching times vary from 5 seconds for 2 phase alloys to 1 minute or more for retained gamma alloys.

Phase identification is one of the more interesting problems involved in the determination of a phase diagram by metallographic examination. For example, at 680°C, the sequence of phases, with increasing niobium content, is beta uranium, beta + gamma, then gamma. Figure 2 exhibits the microstructure at the 680 level. In the first three photomicrographs, it is apparent that the

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dark phase increases in quantity as the niobium content increases. It is therefore the gamma phase, and the white phase was beta at the transformation temperature, though at room temperature is probably alpha. In the fourth photomicrograph of the series, the structure is all gamma, as shown by the equiaxed grains and the longer etching time required. The dispersed particles are unidentified inclusions which do not respond to heat treatment.

A second method of phase identification is available. The phases which were alpha and beta at transformation temperature will stain rapidly in air, whereas gamma is unaffected. Therefore in cases where a sequence of specimens is not available it is only necessary to compare a freshly etched structure with the structure after several hours exposure to air. The fact that beta is light in the first three micros is peculiar only to a freshly etched specimen, and by itself is not a means of phase identification.

Referring again to Figure 1, the evidence for locating the gamma/alpha + gamma line will be presented in the form of microstructures above and below the line. The upper three photomicrographs in Figure 3 exhibit retained gamma plus the usual inclusions. The three alloys shown have different fabrication histories which accounts for the difference in the gamma grain size. The lower three photomicrographs exhibit alpha particles in a gamma matrix for the same three alloys at temperatures from 3 to 7° below the corresponding gamma structures. Other specimens of the same three alloys, not shown here, permit bracketing the gamma/alpha + gamma line within $\pm 2^\circ$. As the established points could be fitted by a straight line, the line was extrapolated to meet the eutectoid line at 8% Nb. As extrapolation is often uncertain, the eutectoid composition is placed at $8 \pm 1\%$ Nb. This range of uncertainty will be narrowed when alloys close to 8% Nb are available.

Referring again to Figure 1, the line dividing the gamma and beta + gamma fields was determined by the same method. The difference between gamma alloys and beta plus gamma alloys is readily apparent, though with lower niobium contents the gamma cannot be retained by ordinary water quenching. The study of a sequence of several alloys at one temperature readily permits identification of the phases which existed at the transformation temperature.

It is now apparent that the lines forming the lower limit of the gamma field are not continuous; i.e., a change of slope exists at the alpha to beta transformation. The data can best be fitted by locating the change of slope at 668°C. A considerable effort was made to locate the alpha to beta line by metallographic examination. As shown in Figures 4 and 5, identical structures are obtained by transforming at 664 and 667°C, in alloys up to 2% Nb. Other specimens transformed at 653, 660 and 670 showed similar structures, leading to the conclusion that the alpha to beta transformation, in the presence of gamma, cannot be definitely located by metallographic examination. It is considered that high temperature X-ray work is needed to definitely locate the temperature of alpha to beta transformation. The diagram as drawn requires a peritectoid rather than a eutectoid at the uranium end, which has been a controversial point among the other investigators of the system.

Referring again to Figure 1, the eutectoid line is the remaining line subjected to investigation. Three alloys were used, two of which were hypo

and one hyper eutectoid. The higher niobium content and lowered temperatures required longer transformation times, and in most cases, 72 to 96 hours were adequate to complete the transformation. The metallographic evidence for the location of the eutectoid temperature at 634 ± 2 is presented in Figure 6. Here again, three alloys are shown, at temperatures above and below the eutectoid. Above the eutectoid line, the two hypo eutectoid alloys exhibit an alpha plus gamma structure; the third alloy is all retained gamma. Below the eutectoid, a pearlitic structure is exhibited. The pearlite platelets become more perfectly formed with increasing niobium content, but some tendency to form pearlite is noticeable in the 4.9% alloy. Other specimens not shown here permit the eutectoid to be established at 634 ± 2 . As mentioned above, the eutectoid composition cannot yet be located closer than $8 \pm 1\%$ Nb. The phase diagram requires two gamma phases above 634 and beyond 8% Nb. We have not yet obtained metallographic identification of two phases in specimens quenched from above this line, though X-ray diffraction gives lines of 2 body centered cubic phases. However, indirect metallographic proof of the two gamma phases is presented in Figure 7. This figure shows the growth of a nodule of pearlite into the metastable gamma matrix at a temperature below the eutectoid. The interface of the nodule advances into the gamma by the usual lengthwise growth of alpha platelets separated by the niobium-rich gamma solid solution. At high magnification a difference in color can be detected between the metastable gamma and the niobium-rich gamma.

In conclusion, metallographic examination has determined the eutectoid line and the lower boundaries of the gamma field but has not conclusively established the alpha to beta transformation line.

REFERENCES

1. Compilation of US and UK Uranium and Thorium Constitutional Diagrams BMI 1000, H. A. Saller and F. A. Rough.
2. The Uranium-Columbium System, ANL-4027, B. Sawyer.

DISCUSSION

Discussion of paper - "Metallographic Determination of the Uranium-Niobium Phase Diagram Up to 10% Niobium"
A. E. Dwight, Argonne National Laboratory

Question - Describe again your quenching technique, please?

A. W. Dwight. The usual evacuated vicor capsule with the specimen wrapped in tantalum, is plunged into a bucket of water and smashed.

Question - What was the etch?

A. W. Dwight. We call it the Ames etch. We believe it was developed at Ames.* It's 8 parts of phosphoric acid to 5 of ethylene glycol to 5 of ethyl alcohol. I didn't go into any details of chemical analysis or fabrication history but I can supply that to anyone who is interested afterwards.

R. J. Gray, Oak Ridge National Laboratory. Did you try any dilatometric work or is this too sluggish for that?

A. W. Dwight. No, but other people have and some of the work reported by other laboratories is based upon dilatometric work, but ours is entirely metallographic.

S. M. Bishop, Knolls Atomic Power Laboratory. Do you believe that some microhardness determinations on the constituents might pin-point the beta-to-alpha transformation isotherm?

A. W. Dwight. That can best be determined after we settle the point whether beta can be retained. We do not believe it can. We think at room temperature we're dealing with alpha.

S. M. Bishop. I don't mean that it would necessarily be retained beta, but that beta transformed to alpha in quenching might be harder than beta transformed to alpha isothermally.

A. W. Dwight. That's a point we would like to go into.

*Editor's Note: This appears to be a variation of the first Uranium electrolyte which was "standard" for a number of years. It consisted of 5 parts phosphoric acid, 5 of ethylene glycol and 8 of ethyl alcohol. The development of this electrolyte was reported as follows: F. Foote, "Metallographic Group, Section D", Metallurgical Lab Report No. CT-539, March 27, 1943. USAEC.

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Figure 1

Figure 2

Figure 3

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MICROSTRUCTURE OF U-Nb ALLOYS NEAR THE $\alpha+\gamma/\beta+\gamma$ REGION

γ SOAK

667 C

W.Q.

γ SOAK

664 C

W.Q.

.5 w/o Nb

1 w/o Nb

Figure 4

MICROSTRUCTURE OF U-Nb ALLOYS
NEAR THE $\alpha+\gamma/\beta+\gamma$ REGION

Figure 5

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MICROSTRUCTURE OF U-Nb ALLOYS NEAR THE EUTECTOID

638 C

636 C

636 C

γ SOAK

W.Q.

627 C
4.9 w/o Nb

627 C
6 w/o Nb

630 C
10.5 w/o Nb

Figure 6

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PEARLITIC NODULE IN METASTABLE GAMMA

10.5 w/o Nb

2000x

γ SOAK

633-24 Hrs.

W.Q.

47

Figure 7

METALLOGRAPHY OF THE EPSILON PHASE IN THE URANIUM-ZIRCONIUM SYSTEM

A. N. Holden

Knolls Atomic Power Laboratory*

Introduction

Metallurgists frequently attempt to understand an alloy system by using exclusively one or another of the several possible techniques for studying phase equilibria. This procedure is often dangerous, since a complete understanding of the system may require the use of all techniques. This is certainly necessary with the uranium-zirconium system. It is intended to show in this paper how the various techniques were used in studying the uranium-zirconium system, and incidentally to show the important part played by metallography.

Previous Phase Equilibria Studies

In the past several years the U-Zr system has been studied mainly by metallography at MIT, Ames, Battelle, and briefly at other sites. Conflicting diagrams were developed that were in greatest disagreement concerning the extent and very existence of any intermediate phase, epsilon.* This disagreement was so serious as to result in the publication of a diagram⁽¹⁾ with a question mark in the epsilon region. On the other hand, work has also been done using X-ray methods exclusively, and these tend to support the non-existence of an epsilon intermediate phase in the system. Typical of these results is the diagram in Fig. 1 given by Summer-Smith⁽²⁾. Using X-ray methods he found no evidence for epsilon.

Recently, work by Holden and Seymour⁽³⁾ using all of the available methods have suggested the phase diagram shown in Fig. 2. The metallographic portion of Holden and Seymour's work forms the basis for this paper.

Structure of Coarse Grained Castings

The method of preparation of uranium zirconium alloys is by vacuum arc melting and casting. The ingot produced in this way cools at such a rate that the grains are coarse. This is particularly true of castings in the composition range where epsilon is indicated on the phase diagram. If such a casting is etched heavily with mixed 50% HNO₃ and 5% HF acids, the large coarse grains are revealed nicely. However, in order to answer

* The Knolls Atomic Power Laboratory is operated by the General Electric Company for the U.S. Atomic Energy Commission under contract No. W-31-109 Eng. 52.

* Various called either epsilon or delta, but I shall use only epsilon in this paper. Delta will be used to refer to the zirconium solid solution only.

the question as to whether or not they were single crystals, it was necessary to deviate from the metallographic study and use X-ray methods. A back reflection Laue pattern from such a large grain as in Fig. 3 showed it to be a single crystal of apparent cubic structure.

At this point the assumption might be made that alloys of about 50 wt % zirconium consist of a homogeneous single phase, perhaps retained gamma, or perhaps an intermediate phase. Additional examination of the cast structure showed rather startling results, however. If the large grained sample was polished metallographically and then etched in the conventional manner for this system, the microstructure was an unresolvable diffuse mess. If the polished sample was not etched, no structure was visible under bright field, but a structure was visible under polarized light. The nature of this structure was fine network of alternate light and dark patches not unlike a checkerboard. Such a structure is shown at 250 X magnification in Fig. 4. Since the Laue pattern had been taken with a beam that covered several hundred of these patches, it was obvious they were closely related to a single crystal.

The next question which needed to be answered was whether this was an equilibrium structure, and the following was done: coarse grained samples were heated to various temperatures above 700°C and quenched, then repolished and examined with polarized light - there were no resolvable sub grains or patches. Samples were then reheated to 500°C for an hour, and the subgrains or patches were again visible with polarized light after polishing. However, after reheating they were very much finer than in the original casting, as shown in Fig. 5, for a specimen heated to 950°C, quenched, and reheated to 500°C. A view of a similarly treated specimen across a macro boundary is shown in Fig. 6.

This information was used to support a belief that the structure of patches was an equilibrium structure, henceforth called epsilon, and that the structure obtained by quenching was retained gamma.

Other data such as thermal analysis data and resistance-temperature data also supported a transformation near 600°C. Below 600°C epsilon is stable, and above 600°C gamma is stable.

The only transformation that can give an optically active substructure to a single crystal that originally is optically isotropic is an order-disorder transformation. In other words, if the structure after transformation is still cubic, but the preferred location of uranium atoms is such that a lower symmetry results, then the structure will be optically anisotropic. Confirmation of an order-disorder transformation was obtained with X-ray powder patterns, where the only difference in the powder pattern of retained gamma and epsilon was the appearance of super-lattice lines in the latter. This similarity is illustrated in Fig. 7. An important metallographic test was also made as follows: If the transformation is by order-disorder, then the macrocrystals should not change in shape or

orientation on transformation. In Fig 8 is shown the result of heating a specimen of coarse grained epsilon at 600°C, 700°C, 850°C, and 950°C, and quenching from each temperature. The boundaries have not changed except small amounts by grain growth, while the specimen has changed from epsilon, as-cast and after heating at 600°C, to retained gamma at 700°C and above. Furthermore, an X-ray beam was impinged on the same crystal after each treatment, and the orientation of the crystal did not change during the transformation.

DISCUSSION

The optical activity of the small patches in ordered epsilon arises from the following considerations. The structure is body-centered cubic just as is the gamma structure, but the uranium atoms prefer certain sites in the structure to others which sets up a super-lattice and gives rise to the extra lines in the X-ray pattern. While all ordered structures give super-lattice lines, due to the difference in X-ray scattering power of the two elements and their preferential locations, not all ordered structures show optical anisotropy. For example, if there were sufficient uranium to occupy the center of every body-centered cube (50 atomic percent) and it ordered in that way, the material would be optically isotropic. In the epsilon phase the uranium evidently orders by forming in layers, or something similar, that requires three a_0 distances to complete the ordered arrangement. The symmetry of the ordered cubic structure therefore is tetragonal or orthorhombic giving rise to optical anisotropy.

The separate optically active patches are the result of ordered domains. Domains are regions in the crystal in which the long range order is the same. For example, if uranium atoms order parallel to $\{111\}$ planes, as some X-ray work⁽⁴⁾ has indicated, the ordered epsilon phase has a choice of four ways of doing this because there are four distinct $\{111\}$ type planes. These domains nucleate on one or another of the $\{111\}$ planes in the crystal and grow until they touch each other. The resultant structure is what is seen with polarized light in figures 4, 5, and 6.

Domains of order are known to affect the mechanical properties; in particular, they harden the metal. The reasons are, that they prevent slip through domain boundaries, and that each domain has a preferred easy slip direction that produces least disorder. Thus a large grained sample that is soft in the unordered condition becomes effectively a very fine grained hard specimen because of ordered domains. The effect of this resistance can be seen in Fig. 9, where slip through the domain structure appears very similar to polycrystalline slip. Each kind of domain in Fig. 9 has its obvious preferred slip plane.

The hardness of ordered epsilon is about 280-350 Vickers compared to unordered gamma at 150-180 Vickers.

Polishing and Etching

The best metallographic treatment for the study of epsilon is a mechanical metallographic polish used in conjunction with polarized light. Any chemical polishing or etching techniques usually have produced a film on the surface that obliterates the epsilon underneath. This film is probably an oxidation product.

Stability of Epsilon

When oxygen is present even in minute amounts, it will react with epsilon at 250°C and higher to change the surface to zirconium and uranium. This is because the ternary system U-Zr-O is such that the epsilon disappears at a few percent oxygen to form the terminal uranium and zirconium solid solutions.

An annealed massive sample, if only examined by X-rays on the surface, will appear to have transformed to uranium and zirconium. If lightly polished, it will give again a pattern for epsilon. Such a result is illustrated in Fig. 10. This same behavior is found in powders. The reason Summer-Smith found no epsilon was because he heated powders and made no attempt to remove surface reaction products. Epsilon is now known to be a stable equilibrium product.

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2. D. Summer-Smith, "The Constitution of Uranium Zirconium Alloys" Inst. of Metals, 83, 277 (1955).
3. A. N. Holden and W. E. Seymour "The Uranium Zirconium System". Preprint, No. 101, Nuclear Congress, Engineers Joint Council, Cleveland Ohio, December 1955.
4. J. S. Lukesh, unpublished information.

DISCUSSION

Discussion after paper: "Metallography of the Epsilon Phase in the Uranium-Zirconium System", by A. N. Holden, Knolls Atomic Power Laboratory.

David Peterson - Ames Laboratory. I would like to ask the magnification and composition of the first photomicrograph which you showed.

A. N. Holden: The magnification of Figure 4 was 250 X. The domains in that photograph were actually of an 80 wt % Zr, 20 wt % U alloy. At that composition the epsilon domain structure is unstable thermally, but the domains were so photogenic compared to other domains in the 50-50 U-Zr alloys that they are shown instead. All other photographs are of 50-50 alloys, however.

Dr. Blumenthal: Are you familiar with the work that M. M. Mueller and S. T. Zegler did at Argonne on the uranium-zirconium system where they also found the epsilon phase? I think they gave a talk about it at the Society of Metals in Philadelphia.

A. N. Holden: I presented an argument about their work at the Society for Metals in Philadelphia. Yes, I'm familiar with their work. We both agree, I think, on the existence of epsilon, but the question is whether epsilon belongs on an equilibrium diagram. I think Mueller and Zegler feel it exists but it doesn't belong on an equilibrium diagram. I think it belongs on an equilibrium diagram. We both know about each other's work and are keeping in touch.

R. J. Gray: Oak Ridge National Laboratory. Does the transformation temperature have anything to do with the size of these order domains? You may have said this and I didn't get it.

A. N. Holden: Well, I didn't say, and it does. In very slow cooled material the epsilon domains are much larger than they are if we quench and retain gamma and then transform at some lower temperature. We have work going on to establish the sizes that one may get and I don't have any information on this yet.

R. J. Gray - ORNL. If you drop just below the temperature and hold there would this have a tendency to make them quite large?

A. N. Holden: I think that makes them large. I think that is why they are large in the castings because these have transformed at a temperature just below the transformation temperature. The casting is a molten puddle at the top and it cools very slowly.

David Peterson: I think this is a very interesting phase diagram - it's one that's been in controversy since 1945 and I think that there are a few features which make it a very interesting thing to study. I'd like to ask whether you think the simple order-disorder mechanism would satisfactorily account for the relatively large and prompt heat effect which is observed at 600°C. Also we have been working with some single crystals which we

prepared by simply cutting a columnar section from the coarse-grained arc melted casting. We studied these by means of the Weissenberg camera and we've gotten some very nice patterns. It appears to be a perfectly normal single crystal as we get a cubic pattern with full four-fold symmetry.

A. N. Holden: I'll answer the second one first. Our Weissenberg patterns are also of cubic symmetry. That is, we see the full four-fold pattern, if you want to look at it that way. The unit cell is about 3 times the size of the γ unit cell, but there's still the possibility that this is false information about the structure. You see, you may have tetragonal structure in which ordered layers of uranium atoms are parallel to the cube faces in every third body-centered cube. With this tetragonal building block making up each domain the X-ray pattern would be tripled in all three a_0 directions because all the possible domains contribute to the pattern. If it were possible to isolate one domain, then the pattern would show the tetragonal structure, but because all the possible domains are present the pattern is cubic. Until we can grow a large enough single domain to look at, we are not satisfied that we have the structure.

The abnormal heat effect I am not sure is abnormal. It is large; we also get a good "blip" when we do thermal analysis, but I think that there are other ordered systems where there has been a reasonable "kick" observed in the thermal arrest on ordering. However, I don't pretend to understand the effect either.

There is another anomaly in that the ordered system has a higher electrical resistance than the disordered system. We feel that this can be explained, however, because we have these domains of order in the structure after ordering is complete, whereas in many other systems, these domains do not persist after ordering. For example, if you order only at the centers of every cube, this is a perfectly isotropic kind of ordering, and a domain that starts in one place joins on when it gets to the next domain with a minimum of discontinuity. There are no domain walls to influence conductivity. We think that it is the domain walls that override the normal effect of ordering on resistivity.

Fig. 1 The Uranium-Zirconium System.

KS-6227

Fig. 2 Uranium-Zirconium System.

KS-4783

Fig. 3 Back Reflection Laue Pattern of a Grain in Coarse Grained Epsilon Casting.

Fig. 4 Cellular Structure Within a Single Grain of Epsilon, 250X, Polarized Light.

Fig. 5 Cells Formed by Quenching from 950°C.
and Reheating at 500°C. 250X.

Fig. 6 Structure of Epsilon Across a Grain Boundary after Quenching from 750°C. and Annealing at 500°C. 250X.

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Fig. 7 Comparison of Powder X-ray Pattern of Gamma (Top) and Epsilon (Bottom).

Fig. 8 The Effect of Several Annealing Temperatures on the Macrostructure of a 50 weight percent Ingot.

Fig. 9 Deformation of the Ordered Domain Structure of the Epsilon Phase. 500 X.

Fig. 10 The Effect of Annealing and Etching on the X-ray Pattern of the Surface of an Epsilon Sample. Top, 24 hrs. at 500°C. Center, Same After Etching. Bottom, After Re-annealing of Etched Sample for 24 hrs. at 500°C.

A PRELIMINARY REPORT ON THE URANIUM-CARBON SYSTEM

B. Blumenthal

Argonne National Laboratory

The investigation is concerned with the system at low carbon concentrations. The liquidus curve is being determined by liquation and saturation experiments. The liquation experiments resulted in a liquidus curve at lower carbon concentrations than the saturation experiments (Figure 1). The cause of the gap between the two curves is as yet not evident.

The gamma solubility curve is being determined by the metallographic method. A summary of the results obtained to date is shown in Figure 2 which is self-explanatory. For more detailed information, see the Quarterly Reports of the Metallurgy Division, Argonne National Laboratory, 4th quarter, 1954 (ANL-5423), 2nd quarter, 1955 (ANL-5465), and 4th quarter, 1955.

106-2110

Figure 1. Liquidus Temperatures of Uranium-Carbon Alloys from Liquation and Saturation Experiments

18,409

Figure 2. Solubility of Carbon in Gamma-Uranium

METALLOGRAPHY FOR THE GENEVA REACTOR FUEL ELEMENTS

Oak Ridge National Laboratory

R. J. Gray

The fabrication of aluminum plate-type fuel elements for service in the Geneva Conference Display Reactor required the utilization of special metallographic techniques. A complete description of this type of reactor component by J. E. Cunningham and E. J. Boyle was presented in paper No. 953 in the Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, August 8-20, 1955. The metallographic work concerned in the development of these fuel elements is presented in this paper. A major problem which was encountered in the fabrication of the elements is also discussed, and some photographs and photomicrographs are presented which illustrate the difficulties encountered.

DESCRIPTION OF FUEL ELEMENTS

The MTR-type fuel elements are composed of an assembly of plates as shown in Fig. 1. Each plate consists of a core, composed of an enriched-uranium--aluminum alloy which is clad on both sides with aluminum. The plates are spaced so that water, which serves both as coolant and moderator, can flow between them.

Fabrication of a fuel plate is accomplished by means of the picture-frame components shown in Fig. 2. The fuel-bearing plate with the clad and core soundly bonded is obtained by hot-rolling the picture frame at 590°C to 0.070 in., a total reduction of 84%. The plates are coated with a brazing flux and are annealed at 610°C for 1 hr to remove hydrogen. A final cold reduction consisting of several passes is made so that the plates obtained are 0.060 $\pm$ 0.001 in.; they are then annealed at 590°C for 1 hr. Each plate is shaped to the desired curvature and after being inspected is ready for assembly. The component assembly is made by furnace brazing the fuel plates into grooves machined in the side plates. The assembly is held in place by ceramic jigs as shown in Fig. 3. A transverse view of the completed assembly with the fuel core visible in each plate is shown in Fig. 4.

MTR fuel plates (Fig. 5) are composed of a uranium-aluminum-alloy core containing 10 to 20 wt % uranium. When greater amounts of uranium are necessary, on account of the considerable difficulty that is encountered as a consequence of segregation, it is advisable that the alloy core be replaced by a mixture of UO_2 and aluminum powder which requires the application of powder-metallurgy techniques. Because A.E.C. limits the uranium shipped out of the country to only 20% enrichment, an alloy could not be used on account of the higher uranium content that was necessary. Thus, the core in Geneva Reactor plates was composed of 54 wt % UO_2 and 46 wt % aluminum powder compact (Fig. 6), but the same general procedure followed in preparing these fuel plates and assemblies as is used for the MTR fuel plates.

FABRICATION PROBLEM

A hot-rolled plate for the Geneva Reactor is shown in Fig. 7 with the grey UO_2 distributed in the aluminum. It was at this stage in the process that considerable difficulty was encountered with this type of core. During the flux anneal, blistering and warping of the plate occurred, as shown in Fig. 8. Metallographic examination of the plates showed that the UO_2 and the aluminum had reacted. The reaction product was found to contain UAl_2 , UAl_3 , UAl_4 and Al_2O_3 . The physical makeup of the UO_2 powder, that is, the surface-to-volume ratio, had a substantial effect on this reaction. A fuel plate containing considerable fine UO_2 might react completely, as shown in Fig. 9. The fine powder could originate either from an agglomerate of the oxide which breaks up during the rolling operation or from fine powder which might be clinging to the coarser powder in spite of screening. Coarser powder reacted only at the periphery, as shown in Fig. 10, but blistering and warping still developed. Only after the method of producing the UO_2 was changed, so as to obtain a dense non-friable powder, was it possible to prevent this reaction and the subsequent warping and blistering of the plates. A more complete report covering the methods for producing UO_2 will be submitted at a later date by the Metallurgy Division of ORNL.

The cause of this blistering and warping is not yet known. M. L. Picklesimer of this laboratory found hydrogen in the blisters, which may be a reaction product in the reduction of the UO_2 by the aluminum. A longitudinal view of a fuel plate for the Geneva Reactor is shown in Fig. 11.

COLOR PHOTOMICROGRAPHY

Color photomicrographs were made for the display at the Conference. The technique for preparing these photomicrographs was to grind the specimens on a series of abrasive papers ranging through 600 grit. After this operation the specimens were polished with No. 20 to No. 40 μ diamond paste on canvas and then by No. 4 to No. 8 μ diamond paste on canvas. The next step consisted of a short polish with Linde B alumina and a napped cloth (AB Microcloth). Electrolytic polishing followed; the electrolyte consisted of 15 parts ethyl alcohol (99.5%) and 1 part perchloric acid (72%). The electrolytic polishing period was confined as much as possible to reduce the "under cutting" and the subsequent removal of the UO_2 . The condition of the specimen with respect to scratches and over-all cold work determined this period; however, 15 sec at 35 volts was usually sufficient. The specimen was then anodized at 35 volts and 10°C in a solution containing 10% orthophosphoric acid (85%), 2.5% water, 26.5% ethylene glycol, and 1.0% hydrofluoric acid. The anodizing treatment required 5 to 10 min. The advantage of the anodizing treatment is that an anisotropic oxide film is produced which reveals the grain by color differentiation with sensitive tint. Two grains will only show the same simultaneous sequence of color changes upon stage rotation when they have identical orientations.

Y-9250

Fig. 1. MTR-Type Fuel Element.

Y-15937

Fig. 2. Exploded View of Composite Fuel Plate Prior to Rolling

Y-15939

Fig. 3. MTR-Type Fuel Element held in Position by Ceramic Blocks Preparatory to Furnace Brazing.

Y-15938

Fig. 4. Transverse View of Geneva Reactor Fuel Assembly Showing UO₂ in Aluminum-Clad Plates.

Bright Field Illumination Y-17405

Polarized Light

Y-17406

Fig. 5. Typical Appearance of MTR Plate with Uranium-Aluminum-Alloy Core.
Etchant: Anodized to show grain contrast with polarized light.

Bright Field Illumination Y-17403

Polarized Light

Y-17404

Fig. 6. Powder Compact of UO_2 and Aluminum Prior to Rolling.
Etchant: Anodized to show grain contrast with polarized light.

Bright Field Illumination

Y-16829

Fig. 7. Hot-rolled Core of UO_2 (Grey) and Aluminum. Unetched.

Y-15056

Fig. 8. Blistered and Warped Plates after Simulated Brazing Treatment.

Bright Field Illumination

Y-16827

Fig. 9. Fuel Plate After Brazing Showing Reaction Between UO_2 and Aluminum. Note the complete reaction in the fine agglomerated powder. Unetched.

Bright Field Illumination

Y-16828

Fig. 10. Fuel Plate After Brazing Showing Reaction Between UO_2 and Aluminum. Note the peripheral reaction with the UO_2 . Unetched.

Bright Field Illumination Y-17423

Polarized Light

Y-17424

Fig. 11. Geneva Conference Reactor Fuel Plate With UO_2 -Aluminum Core. Note absence of reaction between UO_2 and aluminum after brazing treatment. Etchant: Anodized to show grain contrast with polarized light.

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TECHNIQUES FOR THE PREPARATION OF UO₂ COMPACTS FOR MICROSCOPIC EXAMINATION

F. M. Cain, Jr.

Suitable techniques for the preparation of UO₂ compacts for microscopic examination were found after several possible approaches were investigated.

Sectioning

Sectioning was best accomplished on bare compacts using an abrasive cut-off machine with silicon carbide and/or diamond rimlocked wheels. Clad samples were cut without mounting. The tendency for bare compacts to crack or chip when held in a steel vise-chuck during abrasive wheel cutting was minimized by first mounting samples to be cut in Kelon (a liquid plastic setting at room temperature). This plastic, as received from the manufacturer, is thought to be a mixture of monomer and polymer methacrylates. After adding the catalyst the plastic can be poured into a suitable mould containing the sample, allowed to set up at room temperature for at least six hours and cured at 140°F for one hour. One-inch I.D. glass tubing cut in one-inch lengths served as suitable moulds; the plastic shrinks just enough during curing that it can be removed from the glass mould by finger pressure. Kelon plastic can be purchased from the Kelon Plastic Corp., 7914 Frankstown Ave., Pittsburgh, Pa.

Mounting

Kelon plastic also serves as a satisfactory mounting medium for holding compacts while performing grinding and polishing operations. The small cracks, initially contained in some compacts, were aggravated by the mounting pressures required for thermoplastic and thermosetting powders.

*WAPD-T-275

However, compacts were mounted in Kelon at atmospheric pressure with apparently no effect on existing cracks. It was also observed that Kelon could be injected into the open pores of compacts and was thus used to help preserve the original shape of open pores during grinding and polishing.

The necessity of mounting UO_2 compacts prior to polishing is dependent in part upon the type of microscopic observations desired and also upon the known characteristics of the compacts. For example, it was found necessary to mount green or unsintered compacts and sintered compacts with low densities (below 86% theoretical) before they could be polished with any degree of satisfaction. Sintered compacts with densities 90% of theoretical and higher were polished and etched without mounting; however, if examination of open porosity shape was of importance, compacts were then mounted in Kelon under hydrostatic pressure (500 psi). Samples to be cathodic vacuum etched, unless polished unmounted, required special mounting. This involved using cylindrically shaped copper or zirconium tubes approximately $3/4$ in. OD x $1/2$ in. ID x $3/8$ in. high as moulds. The procedure was similar to that when using glass moulds except that a red phosphorescent dye was added to the plastic. (Apparently the dye changes the structural characteristics of the Kelon sufficiently to make it stable at C.V.E. temperatures--which are somewhere below 232°C). After the plastic had been cured, the top and bottom faces of the entire mount, including the metal mould, were ground so that the two faces were flat and also parallel with one another, and the face containing the surface to be examined was then polished. When the sample was clamped to the continuously cooled cathode of the etching unit, this preparation afforded sufficient thermal conductivity between mount and cathode as to keep the plastic below the decomposition temperature during etching.

Grinding

Rough grinding was performed on a belt grinder using #400 and #600 silicon carbide belts or on #1-0, 2-0, and 3-0 emery paper hand grinders. It was later discovered that better grinding results could be obtained using a new type silicon carbide paper (#400 and #600 grits) available from Buehler Ltd. under the commercial name "Microcut".

Polishing

Polishing was done by hand on silk covered stationary glass laps using diamond compounds 6, 3, 1, and $1/2 \mu$ grit sizes, respectively. The adhering diamond compound was removed between each step by swabbing the sample with clean absorbent cotton saturated with ethyl alcohol.

Etching

Two of the several etching procedures tried, cathodic vacuum etching and chemical etching in a solution consisting of one part of concentrated sulphuric acid in nine parts of 30% hydrogen-peroxide, gave the best results. Other chemical solutions such as concentrated nitric acid in hydrogen-peroxide and nitric acid and ammonium hydroxide gave fair results.

Remarks

The proper application of the previously mentioned procedures permits microscopic examination and photography with vertical illumination of such compact characteristics as porosity size and shape, grain size and shape, and additional phases. Lineal microscopic analysis* of the volume percent of pores or phases can also be made using a Hurlbut Counter.

* R. T. Howard and M. Cohen: Quantitative Metallography by Point Count and Lineal Analysis, AIME Trans., 1947, Vol 172, 413-426

It might be well to point out that sintered UO_2 compacts have a tendency to smear during polishing in a manner similar to that of some metals. It has been observed that as-polished surfaces in most cases appear scratch-free only to have numerous scratches appear after etching has dissolved the smeared material. Scratch-free etched surfaces can be obtained by repeated repolishing and re-etching.

Open porosity determination by microscopic means is a point of particular interest. Attempts to hydrostatically inject Kelon containing phosphorescent and fluorescent dyes into open porosity of compacts and then examine with ultra violet or some suitable illumination have not been too successful.

Remote metallography can be performed on UO_2 compacts by slight modifications of the above mentioned procedures. The techniques are also applicable to UO_2 powders.

Figures 1A, B, and C and 2A and B are illustrations of results obtained by these techniques.

A. 93% of theoretical density
as-polished X 500

B. Same as above after cathodic
vacuum etching X 500

C. 92% of theoretical density -
etched 30 sec. in hydrogen
peroxide - sulphuric acid
solution X 500

Figure 1. Mallinckrodt UO_2 Compacts Cold Pressed and Sintered.

A. 93% of theoretical density, as polished,
showing islands thought to be partially
sintered UO_2 X 1440

B. Different field on above sample, etched 5
seconds in hydrogen peroxide - sulphuric
acid solution - showing bright islands of
second phase X 1440

Figure 2. Mallinckrodt UO_2 Cold Pressed and Sintered.

MICROSTRUCTURE OF SOME IRRADIATED NONFISSIONABLE METALS

C. A. Bruch and W. E. McHugh - Knolls Atomic Power Laboratory

A rather extensive program is in progress at KAPL to determine the effect of neutron irradiation on some mechanical and physical properties of metals¹. To this end a representative group of metals are being studied which include copper, nickel, iron, molybdenum, zirconium and titanium. Part of the program is concerned with possible changes in microstructure of these metals due to irradiation. The results to be presented here are for two of the high-purity metals, nickel and iron.

Specimen Preparation

Specimens of both metals in the annealed condition, approximately 1/4" in diameter and an 1/8" in thickness, were polished and etched to reveal the transverse-section microstructure prior to irradiation. The polished surface was divided into quadrants with scratches to facilitate the location of a particular area at some later time. Several Knoop hardness indentations were then made in one quadrant only. Finally the fields around these indentations were examined and one typical field was selected and photographed.

Irradiation

The specimens were enclosed in water-tight containers together with other specimens not to be described here, and were irradiated in position L-41 of the MTR for about three weeks. The capsules were 22 inches in length and since there is approximately a cosine flux distribution about the reactor center-line, the integrated flux varied for each specimen according to its position. The estimated range in integrated thermal flux for iron was 2.3 to 6.9×10^{20} thermal nvt and for nickel was 2.1 to 6.4×10^{20} thermal nvt. The estimated ratio of fast flux (>1 Mev) to thermal flux in this facility is 0.25.

Also included in the capsules were temperature monitors used to determine the maximum temperature of the specimens when in pile. An examination of the monitors showed that the temperature of the specimens did not exceed 90°C .

This radiation exposure produced very significant changes in the mechanical and physical properties of these metals, as illustrated by the following table:

<u>PROPERTY CHANGE</u>			
<u>Metal</u>	<u>Brinell Hardness Numbers, 500 Kg.</u>	<u>Yield Strength, Percent</u>	<u>Electrical Resistivity, Percent</u>
Iron	+ 34	+ 228	+ 9.0
Nickel	+ 56	+ 435	+ 3.1

Post Irradiation Metallography

It was possible to conduct the metallographic work outside of a cell using a regular metallograph because the radioactivity had dropped to a sufficiently low level. The metallographic examination of the two metals first involved a study of the field in the "as irradiated" condition, followed by a study of the field with progressive additional etching. By this process of examination, it is possible to find metallographic changes such as slip lines, twins, recrystallization, grain growth, and the presence of new phases.

The results for iron are shown in Fig. 1. Figure 1a shows the field prior to irradiation, with a portion of the Knoop hardness indentation at the lower left of the section. Figure 1b shows the same field without additional polishing or etching. As shown, the surface has been contaminated, but this is not unexpected in view of the experimental conditions. Figures 1c and 1d show the same field after etching for a total of 20 and 40 seconds, respectively, in a 3% nital solution. The etching technique not only deepened the grain boundaries, but also removed some of the surface contamination. There is no evidence of new phases, recrystallization, or grain growth; hence, it is concluded that the irradiation did not produce any changes in microstructure.

The results for nickel using the same techniques are shown in Fig. 2. Once again the surface of the irradiated specimen has been contaminated and has become stained during the handling. Additional etching has merely deepened the grain boundaries and developed rather deep etch-pits. It is also concluded that the irradiation did not produce any changes in the microstructure of nickel.

Annealing Studies

It was also desired to learn if enough energy is stored in a metal by the irradiation process to promote recrystallization or grain growth during annealing. Therefore, iron and nickel metallographic specimens were given annealing treatments adequate to remove all of the radiation damage, as measured by hardness. Subsequently they were etched and examined microscopically.

The results for iron are shown in Fig. 3. Figures 3a and 3b show the same field prior to and after irradiation. Once again the surface has become contaminated during irradiation and handling. Figures 3c, 3d, and 3e show the same field after annealing, and after etching in a 3 percent Nital solution, a total of 20 and 55 seconds, respectively. From the results of this study it can be concluded that there is not sufficient energy stored by this irradiation to produce microstructural changes. In particular there is neither recrystallization nor grain growth.

The results of a similar study for nickel are shown in Fig. 4. Figures 4a and 4b show the same field before and after irradiation. Figures 4c, 4d, and 4e show the same field after annealing and after etching a total of 30 and 60 seconds, respectively. The only possible changes in microstructure due to irradiation were the development of sub-structures in several of the grains as shown in Figures 4d and 4e. However, a close inspection of the negatives used for Figures 4a and 4b showed that there were faint traces of these sub-boundaries already present and these were eventually made more prominent by the additional etching. Hence, it is also concluded that the energy stored in nickel by this irradiation was not sufficient to promote any microstructural changes.

Discussion

The findings of the present study show that neutron exposures up to about 6.5×10^{20} thermal nvt at a temperature of 90°C . do not produce microstructural changes in high-purity nickel and iron, even when the radiation hardening is removed by annealing. In a paper presented by Konobeevsky, et al.² at the Geneva Conference, some metallographic studies of iron, nickel, copper, and zirconium were reported. These authors concluded that neutron radiation produced grain growth in copper and nickel, recrystallization in zirconium, and no change in the microstructure of iron.

A comparison of some of the Russian results with the present results is given in the following table:

Irradiation Effects in Nickel and Iron

Metal	Observers	Irradiation Conditions Temp., $^\circ\text{C}$	nvt $\times 10^{-20}$	Property Change, Percent		% Change In Grain Diam.
				Tensile Strength	Percent Elongation	
Iron	Konobeevsky, et al.	250-300	1.1 to 1.4	+ 61	- 67	0
	Bruch, McHugh	90	2.3 to 6.9	+ 41.7	- 42.7	0
Nickel	Konobeevsky, et al.	250-300	1.1 to 1.4	+ 56	- 55	+ 51.5
	Bruch, McHugh	90	2.1 to 6.4	+ 26.5	- 43.0	0

The following observations drawn from these data are considered important:

1. The property changes were greater for each metal in the Russian work.
2. In the Russian work, the exposure temperature was greater. Neutron₃ damage has been observed to be decreased with increasing irradiation temperature³.
3. In the Russian work, the integrated neutron exposure was lower. It has been shown for many metals that the property change increases with increasing nvt until saturation is attained⁴. Since the type of flux has not been specified in the Russian article, it will be assumed here that it is thermal nvt. If the fast nvt is being specified, then the neutron exposures in the two experiments were approximately equal.

Although the property changes in both metals were greater in the Russian work than in the present work, a comparison of the exposure data indicates that they should have been less. Aside from this, it can be assumed that there has been a larger amount of energy stored in both metals in the Russian experiments, accompanied by grain growth in the nickel specimens. Conversely it appears that there has been less irradiation annealing in the metals used in the Russian experiments.

In view of these considerations it is evident that there are certain anomalies in the Russian results, and in particular the microstructural results for nickel are not in agreement with the present work. It is suggested that the Russian work is in error in this respect, and two possible reasons for the error are: (1) The metallographic section studied after irradiation was not the same as that studied before the irradiation and originally had a different grain size; (2) The nickel specimens were heated to a temperature higher than the annealing temperature causing grain growth prior to irradiation. Of the two, the first is considered to be the most reasonable.

Acknowledgments

The authors would like to express their appreciation to J. W. Czarkowski and Miss L. Doig for much assistance in the metallographic work. They are also indebted to R. W. Hockenbury for annealing data.

References

1. KAPL-954
2. S. T. Konobeevsky, N. F. Pravdyuk, and V. I. Kutaitsev, "The Effect of Irradiation on the Structure and Properties of the Structural Materials" A/Conf. 8/P/680, USSR, 5 July 1955.
3. KAPL-11402, p. 57
4. KAPL-11458

DISCUSSION

Discussion of paper - "Microstructure of Some Irradiated Nonfissionable Metals",
C. A. Bruch and W. E. McHugh
Knolls Atomic Power Laboratory

Question - Were these changes in tensile strength in agreement with changes in hardness?

C. A. Bruch - Yes. However, there was a better correlation between changes in yield strength and hardness. The Russians did not report yield strength, just tensile strength. They did measure microhardness, but we did not make the comparison, since so many conversion factors would be involved.

Question - What were the magnitudes of the changes in yield strength for these metals?

C. A. Bruch - For iron it was + 228 percent, and for nickel, 435. These are very significant changes.

Bob Gray, Oak Ridge - What's the purity of this iron?

C. A. Bruch - The Russians used Armco iron; we used National Research, vacuum re-melted, iron.

Bob Gray - What kind of nickel?

C. A. Bruch - I don't know what the purity of their nickel was. The nickel we used was National Research, high purity.

Bob Gray - How pure does the nickel run, 99.99?

C. A. Bruch - Well, it was supposed to be in the range of 99.9 to 99.99. We had some trouble with it. It appeared that there were small amounts of impurities segregated at grain boundaries in some of the ingots and this caused some inter-granular fractures. Complete chemical analyses were not made of the material. However, the microstructural studies included specimens from ingots which did not display abnormal grain-boundary behavior. A fairly complete description of the materials used in this investigation is given in KAPL-1402, p. 59.

Figure 1. Iron. Final Magnification, 150X.

Figure 2. Nickel. Final Magnification, 350X.

a—Iron etched, prior to irradiation

b—Same as a, after irradiation without additional polishing or etching.

c—Same as b, except annealed at 500°C for 1 hr.

d—Same as c, except etched 20 sec.

e—Same as d, except etched an additional 35 sec.

Micrographs of the same field for various conditions.
Etched with 3% Nital Solution. X250.

Figure 3. Iron. Final Magnification, 150X.

Figure 4. Nickel. Final Magnification, 275X.

TECHNIQUES FOR THE METALLOGRAPHY OF HIGH-PURITY ALUMINUM

T. K. Roche

This account is not intended to disclose new methods for the metallography of high-purity aluminum, but rather to show how three existing techniques concerned with aluminum metallography have been combined and adapted for use at ORNL. The work is being done as a part of the effort which is being devoted by the Fundamental Research Group to a study of the preferred orientation developed in extruded bars of the high purity material, (approximately 99.99% Al).

Basically, the three techniques that are being used for the metallographic work are: (1) electropolishing, (2) anodization, and (3) the use of etch pits. Electropolishing and anodizing the specimens followed by examination under bright-field illumination permit the determination of such things as the amount of deformed material, the degree of recrystallization, and the grain size of the recrystallized material in the extruded bars. The use of etch pits affords some idea of the preferred orientation developed in the bars. The mechanics and results of each technique are described in the following paragraphs.

Because of the softness of aluminum and, hence, its tendency to flow when abraded, the preparation of aluminum for metallographic examination by mechanical means is difficult and time consuming. Thus, a simpler approach to the metallographic preparation of aluminum is more desirable. Electropolishing is particularly adaptable to material which is relatively free of impure inclusions. Inclusions, as ordinarily found in commercial-grade aluminum, are either removed or left in relief when this method of preparation is used. As stated previously, the preferred orientation study deals with high-purity aluminum; therefore, electrolytic methods are being used exclusively for the final preparation of these specimens. Intermediate polishing steps with rapid-cutting diamond abrasives precede the final electrolytic preparation.

Several electrolytes have been recommended for electrolytically polishing aluminum, but the most satisfactory one found to date consists of 15 parts ethyl alcohol to 1 part perchloric acid. When a stainless steel cathode is used and 35 v is applied across the cell, polishing is completed in a matter of several minutes and results in a specular surface that is free of any disturbed material that was introduced during intermediate mechanical polishing.

Figure 1 shows a typical specimen of high purity aluminum that was electropolished by the technique described above. A Tukon hardness indentation has been made on the specimen to show in contrast the specular character of the surface.

If ordinary chemical-etching techniques are used after electropolishing, complete structure delineation of the material in question is not well-defined. The high-purity extruded material contains deformed areas, each of which has the same orientation transverse to the extrusion direction but which contains within itself deformation bands or subgrains which are separated from one another

by low-angled orientation boundaries. It is these low-angled boundaries that are virtually impossible to delineate by ordinary chemical etching. Anodization of the specimens followed by examination under polarized light offers a convenient method of revealing this substructure.

Without an anodic film, aluminum is optically isotropic (typical of cubic metals), and its microstructure can not be revealed under polarized light. However, when an anisotropic anodic film is applied to the surface of the specimen, the microstructure becomes evident under polarized light. The deposition of the anisotropic (oxide) film is dependent upon the orientation of the substrate (i.e. the aluminum), and, therefore, the light which is reflected from such an anodized surface varies in intensity by virtue of the variation in oxide-film thickness from grain to grain. The maximum variation in this intensity would presumably be between two reflecting grains with widely different orientations.

The solution used for anodization is an electrolyte made up of 70 parts orthophosphoric acid, 26.5 parts ethylene glycol, 2.5 parts distilled water, and 1 part hydrofluoric acid. This is essentially the same composition as described by Hone and Pearson,¹ with the exception that ethylene glycol has been substituted for diethylene glycol monoethyl ether. With a stainless steel cathode and with 35 v applied across the cell, the anodic film is deposited on the specimen in approximately 2 minutes. One advantage of this electrolyte is that higher-angled orientation boundaries in the specimens are nicely etched concurrent with anodization, and satisfactory examination under bright-field illumination is afforded. However, polarized light must be used for complete details of the substructure. If a sensitive-tint plate is introduced into the optical system, the microstructure can be viewed in color, and the detailed structure will be more or less apparent, depending upon the thickness of the anodized film.

Figure 2 shows a transverse section of an extruded aluminum bar which has been electropolished, anodized, and photographed under bright-field illumination. This photomicrograph shows how the higher-angled orientation boundaries between the recrystallized and deformed portions of the bar are etched concurrent with anodization. Figure 3 shows the same field as in Figure 2, but photographed with polarized light. The substructure in the deformed portion of the bar as well as equiaxed grains of recrystallized material are clearly shown.

The polishing and anodizing techniques described have made it possible to determine whether a particular specimen is deformed, recrystallized, or partly recrystallized; but nothing is learned of the orientation developed. In order to increase the scope of the metallography of these specimens, and as an aid to the Fundamental Research Group in their x-ray determination of the preferred orientation developed in the aluminum bars, etch pits are being used to show the approximate relative orientations of deformed and recrystallized material in the specimens. Before etch pits were used, there was no simple way of determining the individual orientation of recrystallized and deformed portions of the bars even though the gross orientation had been determined. Thus, if an extruded bar was found to have a duplex orientation x and y, it was not evident which of the two orientations was assumed by deformed material and which was assumed by recrystallized material. As stated, etch pits alleviate this problem.

Lacombe and Beaujard², in their paper dealing with etch figures in pure aluminum, state that the distribution and form of etch figures is very sensitive to the existence of the cold-worked layer which results from mechanical polishing because a cold-worked layer disturbs the true crystalline orientation of the metal substrate. For this reason, electropolishing prior to pitting is recommended.

Various mixtures of hydrochloric, nitric, and hydrofluoric acids have been reported in the literature as being suitable for producing etch pits in aluminum. The etchant³ currently being used consists of 80 parts hydrochloric acid, 25 parts nitric acid, 20 parts distilled water, and 5 parts hydrofluoric acid. Solutions of this type develop the (100) planes in aluminum. A square pit is indicative of a (100) orientation, and an equilateral triangle indicates a (111) orientation; no attempt will be made to analyze further the various possible etch-pit shapes in their relation to a specific orientation.

In order to produce the pits, transverse sections of the extruded bars are immersed into the etchant after electropolishing. If the specimen is held with a Chromel A or stainless steel tongs while being dipped into the etchant, pits can be produced in several seconds. On the other hand, by cooling the etchant in an ice bath and by eliminating the tongs, the pitting period can be extended. In view of the behavior of the specimens to the pitting solution, it has been assumed that the galvanic action between the specimen and the tongs facilitates the nucleation and growth of etch pits.

Anodization of the specimens after the etch pitting takes advantage of the fact that the higher-angled orientation boundaries are etched concurrently. Because of this expedient, the deformed and recrystallized areas with their characteristic etch pits can be observed under bright-field illumination. Also, under polarized light or with a sensitive-tint plate, the substructure is revealed. No apparent damage is done to the etch pits in anodizing the specimens.

The last four figures illustrate etch pits produced by the technique described above, and representative results obtained by a combination of the three metallographic techniques are depicted. Figure 4 shows a transverse section of an extruded bar which has been electropolished and pitted. Square pits delineate material with a (100) orientation, and triangular pits indicate material with a (111) orientation. Little or no grain boundary etching has been accomplished by the pitting treatment. Figure 5 shows the same field as in the preceding figure but after anodization of the specimen. The higher-angled boundaries have been etched thereby separating deformed (111) areas from recrystallized (100) areas. Figure 6 shows a different transverse section of the same extruded bar described in Figure 5. This section has likewise been electropolished, pitted, anodized and photographed under bright-field illumination. Deformed and recrystallized areas are seen with their characteristic etch pits. Figure 7 presents the same field seen in Figure 6; however, a sensitive-tint plate was used in photographing so as to show the substructure in the (111) deformed area.

A brief description has been presented of three metallographic techniques for high-purity aluminum. Results obtained by applying them in combination are shown and described. The procedures are relatively simple; but they, nevertheless, have been of value in the correlation of x-ray data obtained on extruded bars of the high-purity material in the course of a preferred-orientation study being carried out at ORNL.

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Fig. 1 Electropolished Specimen of High-Purity Aluminum. Bright-field illumination. 200X

Fig. 2 Transverse Section of an Extruded High-Purity Aluminum Bar, Electropolished and Anodized. Etching of boundaries between deformed and recrystallized areas has taken place concurrent with anodization. Bright-field illumination. 500X

Fig. 3 Same Field as Shown in Fig. 2 but Showing the Substructure in the Deformed Area and the Equiaxed Grains of Recrystallized Material. Polarized light. 500X

Fig. 4 Transverse Section of an Extruded High-Purity Aluminum Bar, Electropolished and Pitted. Square pits delineate material with a (100) orientation, and triangular pits indicate material with a (111) orientation. Bright-field illumination. 500X

Fig. 5 Same Field as in Fig. 4 but after Anodization of the Specimen. Boundaries separating the deformed area and the recrystallized areas have been etched. Bright-field illumination. 500X

Fig. 6 Same Type of Structure as Shown in Fig. 5. A transverse section of the extruded high-purity aluminum bar has been electropolished, pitted, and anodized. Bright-field illumination. 500X

Fig. 7 Same Field as Shown in Fig. 6 with Substructure in the (111) Deformed Area being Evident. Sensitive-tint. 500X

COOPERATIVE PROGRAM ON IDENTIFICATION OF INCLUSIONS IN URANIUM

D. W. White

In 1953 the Metallographic Group decided to undertake a systematic study of non-metallic inclusions in uranium. The basic approach was to make up samples containing synthetic inclusions (representing those chemical elements which could conceivably reside as impurities in commercial uranium), using high-purity, inclusion-free uranium (Argonne electrolytic grade) as the base material. The synthetic inclusions were to be unequivocally identified by such techniques as removal and subsequent x-ray and microchemical analyses, and definitive etchants determined. The samples then were to be circulated among the participating laboratories for comparison and for a recheck on the etching techniques.

The first set of samples for this program involved the addition of a second element to the high-purity uranium in such an amount that it just began to make its appearance as a second phase in the microstructure. The second set of samples was to have been similar to the first, except that the uranium samples would contain two added elements rather than one, thus allowing for the possible formation of second phases by interaction between the two additives as well as between the additives and the uranium. Subsequent sets of samples might have involved several additives to each uranium sample.

The progress on this cooperative program has been disappointingly slow. In fact, some of the participating laboratories had not yet completed their work on the first samples (those with a single additive) by late 1955 and it was not possible to determine when all of them would have completed their work. Because some of the original objectives of the Metallographic Group's cooperative program on uranium inclusions have already been achieved in separate programs at individual laboratories and in a program by the AEC Metal Quality Committee, the Steering Committee has decided to abandon the cooperative program with the recommendation that the participating laboratories issue individual reports on the work they have accomplished in connection with this program. The Steering Committee does not suggest that all of this work be combined into one report. Since the program as a whole is not complete such a report might lack coherency and might be less valuable than separate reports issued by each individual laboratory on its own work.

Although the Metallographic Group was not able to carry through to completion its cooperative program on the identification of inclusions in uranium as originally planned, this effort has had positive benefits. Useful metallographic techniques were developed in the work on the program, which has undoubtedly stimulated interest in the subject of the identification of inclusions in uranium and has given impetus to individual

laboratory investigations on various aspects of this subject.

In considering the future role of the Metallographic Group, it is the decision of the present Steering Committee that the Group should restrict its activities primarily to holding periodic conferences at which papers dealing with the metallography of reactor materials would be presented and information on metallographic techniques would be exchanged. It is felt that the Group will not at present attempt to sponsor any cooperative experimental project because any such effort would have to be worked in as portions of existing programs of the individual participating laboratories and financed by the operating funds of each laboratory. While this method of carrying on cooperative projects through the Metallographic Group worked with considerable success in years gone by, the nature of the programs at various laboratories today generally does not allow the extent of flexibility needed for cooperative group effort without official sponsorship and funding of such effort by the Atomic Energy Commission.