MASTER

NMI - 4998

TECHNICAL PAPERS OF THE SIXTEENTH
METALLOGRAPHIC GROUP MEETING, HELD
MARCH 28 - 29, 1962 AT HANFORD ATOMIC
PRODUCTS OPERATION, RICHLAND, WASHINGTON

Compiled by
H. Roth Roman

August 31, 1964

Division of Textron
Nuclear Metals, Inc.
West Concord, Massachusetts

This document is
PUBLICLY RELEASABLE
Hugh Kincer H. Kincer
Authorizing Official
Date 11/28/06

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Other issues of this report bear the number CONF - 620301.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This report has been reproduced directly from the best available copy.

Printed in USA. Price \$4.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va.

Technical Papers of the Sixteenth
Metallographic Group Meeting
Held March 28 - 29, 1962
at Hanford Atomic Products Operation
Richland, Washington

Compiled by
H. Roth Roman
Nuclear Metals
Division of Textron, Inc.
West Concord, Massachusetts

Steering Committee

D. T. Peterson	Past Chairman
A. E. Guay	Chairman
C. L. Angerman	Sr. Member
R. J. Van Thyne	Jr. Member
H. Roth Roman	Secretary

Date of Issuance
August 31, 1964

Nuclear Metals
Division of Textron, Inc.
West Concord, Massachusetts

ATTENDANCE LIST

C. G. Rhodes	Atomics-International
A. E. Pickett	Atomic Power Equipment
A. A. Bauer	Battelle Memorial Institute
M. S. Farkas	Battelle Memorial Institute
M. F. Garufi	Bridgeport Brass Company
R. C. Bailie	Dow Chemical Company
G. R. Mallett	Dow Chemical Company
L. L. Nelson	Dow Chemical Company
T. Van Torous	Dow Chemical Company
J. O. Gardner	General Atomic
A. E. Guay	Hanford Atomic Products Operation
L. A. Hartcorn	Hanford Atomic Products Operation
J. R. Dvorak	Illinois Institute of Technology
R. J. Van Thyne	Illinois Institute of Technology
E. N. Hopkins	Iowa State University
D. T. Peterson	Iowa State University
L. S. DeLuca	Knolls Atomic Power Laboratory
C. G. Hoffman	Los Alamos Scientific Laboratory
H. C. Kloepper, Jr.	Mallinckrodt Chemical Works
J. W. Colby	National Lead Company of Ohio
C. F. Hall	National Lead Company of Ohio
W. N. Wise	National Lead Company of Ohio
E. W. Filer	Nuclear Materials and Propulsion Operation
R. C. Rau	Nuclear Materials and Propulsion Operation
H. P. Roth	Nuclear Metals
R. S. Crouse	Oak Ridge National Laboratory
R. J. Gray	Oak Ridge National Laboratory
J. O Stiegler	Oak Ridge National Laboratory
C. L. Angerman	Savannah River Laboratory
E. Meyer	Sylvania Electric Products
H. E. Watts	Sylvania Electric Products
F. B. Litton	United Nuclear Corporation
D. R. Lewis	Vallecitos Atomic Laboratory
F. W. Cotter	Watertown Arsenal

TABLE OF CONTENTS

Page No.

<u>MOUNTING OF METALLOGRAPHIC SAMPLES IN EPOXY RESINS USING MULTIPLE CAVITY MOLDS.</u> D. M. Hewette II and R. S. Crouse, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee	1
<u>THE APPLICATION OF WAX LAPS TO VIBRATORY POLISHERS.</u> E. N. Hopkins and D. T. Peterson, Ames Laboratory, Iowa State University, Ames, Iowa	2
<u>THIRTY-FIVE MILLIMETER COLOR PHOTOMICROGRAPHY.</u> E. N. Hopkins and D. T. Peterson, Ames Laboratory, Iowa State University, Ames, Iowa	14
<u>METALLOGRAPHIC STUDY OF THE ANNEALING BEHAVIOR OF ALUMINUM SILICON EUTECTIC ALLOY.</u> R. H. Todd, Hanford Atomic Products Operation, General Electric Company, Richland, Washington	20
<u>MICROSTRUCTURAL CHANGES DURING THE α-β-α TRANSFORMATION OF URANIUM.</u> C. L. Angerman, Savannah River Laboratory, E. I. duPont de Nemours and Company, Aiken, South Carolina	42
<u>METALLOGRAPHY OF URANIUM AT ELEVATED TEMPERATURES.</u> W. N. Wise, National Lead Company of Ohio, Cincinnati, Ohio	48
<u>IDENTIFICATION OF CARBIDES, NITRIDES, AND OXIDES OF COLUMBIUM BY ANODIC STAINING.</u> R. S. Crouse, Oak Ridge National Laboratory, Oak Ridge, Tennessee	57
<u>MATERIALS RESEARCH WITH THE SCANNING MICROPROBE ANALYZER.</u> J. W. Lenke and R. F. Domagala, Metals and Ceramics Division, Armour Research Foundation of Illinois Institute of Technology, Chicago, Illinois	65
<u>ELECTRON MICROSCOPY OF SINTERED BERYLLIA.</u> R. C. Rau, Nuclear Materials and Propulsion Operation, General Electric Company, Cincinnati, Ohio	77
<u>ELECTRON MICROSCOPE STUDIES OF IRRADIATED A-286 ALLOYS.</u> R. C. Rau, Nuclear Materials and Propulsion Operation, General Electric Company, Cincinnati, Ohio	95
<u>POSSIBLE ARTIFACTS ASSOCIATED WITH THE MICROSTRUCTURE OF URANIUM DEVELOPED BY ION BOMBARDMENT.</u> T. K. Bierlein, B. Mastel and R. D. Leggett, Fuels Development Reactor and Fuels Research and Development Operation, Hanford Atomic Products Operation, Richland, Washington	108

MOUNTING OF METALLOGRAPHIC SAMPLES IN EPOXY RESINS USING MULTIPLE CAVITY MOLDS

D. M. Hewette II and R. S. Crouse
Oak Ridge National Laboratory*
Oak Ridge, Tennessee

Multiple cavity molds have been developed for mounting metallographic samples in epoxy resins. For general laboratory use the molds are fabricated from stainless steel. The use of a metal mold requires application of an appropriate mold release for each mounting operation. In glove box facilities where contamination is a problem and where volatile solvents cannot be tolerated, a Teflon mold, which does not require a mold release, has been used with moderate success. Flexible molds of silicone rubber vulcanized at room temperature have been fabricated and show considerable promise.

INTRODUCTION

The use of epoxy resins as a metallographic specimen mounting material has been increasing since their introduction about fifteen years ago. The pressureless cold-setting characteristics of this material make it ideal for mounting temperature-sensitive friable metals and ceramics. The use of multiple cavity molds makes it possible to mount a large number of specimens at one time in a small space, such as a glove box. The multiple mount feature is also attractive for application in general metallographic operations. This report describes some multiple cavity molds, their construction and use.

MOLD DESCRIPTION

The construction of the mold is quite simple, consisting of a mold block containing a convenient number of cavities bolted or clamped to a base plate. Samples are placed in the various cavities and the cavities are subsequently filled with epoxy resin. Identification of the samples is accomplished either by including an embossed metal tag in the cavity or by reference numbering the cavities of the mold block, and subsequently numbering the samples after the mounts have cured. After the resin has cured, the two mold parts are separated and the samples are ejected from the mold block by gently tapping the back of each sample with a suitable punch.

MATERIALS OF CONSTRUCTION

Molds have been fabricated from metal and Teflon, with the choice of material being dictated by the situation in which the mold is to be used. For general laboratory use where a great number of samples are processed, a hardenable stainless steel is preferable. However, due to the bonding which

* Operated for the U. S. Atomic Energy Commission by the Union Carbide Corporation.

takes place between the epoxy resin and metals, coating of the mold with a suitable release is required prior to each mounting operation. These mold releases are either greases, oils, or organic solids dispersed in a flammable volatile solvent.

A typical metal mold is shown in Figure 1. Notice that the mold cavities are cross referenced by numbering the ranks and lettering the files. A mold of this type costs \$300-\$400, but is practically indestructible.

The use of a mold release is objectionable in glove box metallographic facilities because the presence of greases or oils can present a decontamination problem; however, the use of flammable solvents is also objectionable from a fire hazard standpoint. Teflon is a better material for mold construction in this instance because epoxies will not bond with this material, and therefore, the use of a mold release is obviated.

In fabricating these molds, a solid piece of Teflon is used for the mold block, and Teflon-covered stainless steel sheet is used for the base plate with the mold block being clamped to the base plate with a toggle clamp. A typical mold of this type is shown in Figure 2.

Using Teflon as a mold material has its disadvantages. The material is quite soft and considerable care must be exercised to avoid marring the surface. Machining the material requires considerable care to produce a smooth surface.

CONCLUSIONS

The use of multiple cavity molds has proven to be a practical, convenient, simple technique for the mounting of metallographic samples in epoxy resins. In instances when the molds are to be used by a number of people in processing large numbers of samples, molds fabricated from metal have a longer wear life and are more suitable than molds fabricated from Teflon. In situations when the use of mold releases is impractical or when fewer samples are to be mounted and greater care can be exercised in handling the molds, Teflon has proved to be the preferable mold material.

APPENDIX

(Information obtained after completion of above manuscript)

A third type of mold has been used recently and found to be quite good. It is of the same general configuration as the steel and Teflon molds, but is made of a room-temperature vulcanizing (RTV) silicone rubber. It is flexible and tough and readily releases the cured mounts with little manipulation. Figure 3 is a picture of a two-piece mold with six cavities and a one-piece mold with a single cavity.

A multiple cavity one-piece mold may also be used. The cured specimen mounts are popped out of the mold by flexing it much in the same way one removes ice cubes from a rubber tray.

(a)

Y-43615

(b)

Y-43614

Figure 1 - A sixteen cavity metal mold for general laboratory use. (a) Shows the mold assembly with the cavities filled with epoxy resin. (b) An exploded view with a finished mount.

Figure 2 - (a) Y-39022 (b) Y-39023
 - A typical four-cavity mold of Teflon for use in a glove box.
 (a) Shows a mold assembled for use. (b) An exploded view with a finished mount.

Y-45476

Figure 3 - Two types of silicone rubber molds - a two-piece, six-cavity assembly and a single-cavity unit with a finished mount.

The rubber conforms exactly to the contour of the master mold, and when vulcanized, becomes rigid enough not to sag and cause misshapen mounts. The master mold may be as simple as a cardboard box of appropriate size with mount blanks secured to the bottom in the desired geometry, or one may wish to have a permanent master of some sort.

Silicone rubber, RTV,⁽¹⁾ is available from several suppliers and the method of use differs very little. The rubber is a viscous liquid which is mixed with a catalyst in the prescribed amount, poured into the master mold, and allowed to cure. This may take from 1/2 to 24 hr, depending upon the rubber and the amount of catalyst used. It seems preferable to allow an overnight cure. The mold may be used as soon as it can be removed from the master successfully, but it does continue to harden for a few hours until it becomes quite firm, yet remains flexible. For prolonged life of the mold a release compound should be used.

REFERENCES

1. Dow Corning Corporation, Midland, Michigan; General Electric, Silicone Products Department, Waterford, New York.

17:65/6

THE APPLICATION OF WAX LAPS TO VIBRATORY POLISHERS*

E.N. Hopkins and D. T. Peterson
Ames Laboratory
Iowa State University, Ames, Iowa

In combining the wax lap and the vibratory polisher a very versatile method of sample preparation has been established. In contrast to cloth the wax lap is capable of long periods of polishing before replacement is necessary.

INTRODUCTION

The literature concerning metallographic sample preparation contains descriptions of many and varied methods. Metallographers often find that a preparation technique that is satisfactory to one individual is not satisfactory to another. This is the metallographic art, the human element. The last two decades have produced several polishing procedures which have helped reduce this human element. One of these methods is mechanical polishing by the vibratory polisher.

The use of laps for preserving edges, inclusions and flat surfaces has been known for many years. The lead lap is probably the best known example but is laborious to prepare. The wax lap method for rotating polishing wheels was reported by Schaeffler⁽¹⁾ in 1944. This method has never gained wide acceptance among metallographers.

Wax laps have been used successfully on rotating wheels in our laboratory for some time. In this paper the adaptation of the wax lap surface to the vibratory polisher is described. The wax lap required little maintenance during the life of the lap. It is not necessary to remove any of the holding devices on the bowl to clean and recondition the lap. The bowl is merely washed out, recharged and placed in operation. The wax lap will not wrinkle or tear, nor is it necessary to change it each day such as the silk or nylon cloths.

One of the most promising aspects of a wax lap is the ability to maintain specimen edges during long periods of polishing. Maintaining flatness to the edge of the specimen is difficult by polishing on

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 1139.

¹ Anton L. Schaeffler: "Rapid Hand Polishing of Micro Specimens", Metal Progress, Vol. 46, pp. 285-287.

rotating cloth covered wheels. Wax laps avoid this problem since the specimen may be polished as long as necessary to obtain a fine surface preparation while still preserving the specimen edges and flatness. Often the metallographer wishes to study inclusions as an integral part of the examination. These are often difficult to retain in their true sizes and shapes. The wax lap will retain inclusions with no evidence of pitting or rounding, and again the time of polishing is not critical.

PROCEDURE

Wax lap preparation for the vibratory polisher is quick and simple. The wax is melted, poured into the bowl and allowed to solidify. As soon as the wax surface begins solidifying, cold water may be used to hasten cooling to room temperature. There is no necessity for preparation of the bowl prior to casting of the wax. The wax adheres to the bowl without difficulty. The wax used in this laboratory is A-B Uniwax, a Buehler Ltd. product.

Specimens to be polished on the wax lap were mounted in bakelite or lucite. The specimens were ground using successively finer silicon carbide papers, normally finishing with 600 grit abrasive, and cleaned in an ultrasonic cleaner. Specimen mounts were clamped in the conventional holders used with the vibratory polisher. The vibratory polisher equipped with the wax lap was used with Linde A abrasive. It was found that a small quantity of liquid detergent (Vel) was very beneficial in preventing the pick-up of wax on the specimen. Polishing was continued until only fine scratches were visible at 100 diameters. The samples were then transferred to a micro cloth covered bowl using Linde B abrasive for final polishing. This final polish was kept short to minimize pitting and edge rounding. Specimens were cleaned ultrasonically and examined.

The time required to polish on the wax lap varies from a few minutes to several hours, depending on the hardness of the material. The times seem to be approximately the same as those used with cloth on the vibratory polisher. However, a complete and quantitative comparison has not been made. The time for the final polish on the cloth is usually less than one-half hour.

Our present wax lap has been in operation for over nine months and is not in need of replacement. After every polishing cycle the bowl was washed in warm water providing a clean surface each time the wax was used. After several weeks a shallow groove will have formed at the periphery of the bowl. This can be removed by melting the surface of the wax with hot water and allowing it to solidify again.

RESULTS

Photomicrographs of typical metals and alloys studied in this laboratory are shown in Figures 1 through 20. All specimens have been mechanically polished on a Syntron vibratory polisher equipped with a wax lap and Linde A abrasive. The specimens have also been given a final polish for a short period of time on a Syntron polisher equipped with a micro cloth and Linde B abrasive.

CONCLUSIONS

The metallographic art is becoming a science. The vibratory polisher is one device that is speeding this transformation. By combining new ideas with some of the worthwhile older methods we can create a more scientific atmosphere in the field of metallography. The wax lap adapted to the vibratory polisher is one example. There are many other methods and ideas which need investigation.

Figure 1 - Nickel 150X
Etch: HNO_3 - $\text{C}_2\text{H}_6\text{O}_2$

Figure 2 - Chromium 150X
Etch: Oxalic Acid

Figure 3 - Niobium 150X
Etch: HF - HNO_3 - H_2SO_4

Figure 4 - Molybdenum 150X
Etch: Murakami's

Figure 5 - Manganese 150X
Etch: Nital

Figure 6 - Grey cast iron 750X
As polished

Figure 7 - 1090 Steel 450X
Etch: Nital

Figure 8 - 60-40 Brass 150X
Etch: Alcoholic FeCl_3

Figure 9 - Uranium-chromium in niobium
crucible 250X
Etch: Oxalic acid

Figure 10 - Niobium with 6% O₂ 750X
As Polished

Figure 11 - Niobium with oxide layer
450X
As Polished

Figure 12 - Intermetallic niobium
tin embedded in tin
matrix 100X
As Polished

Figure 13 - 94 ^w/o uranium-manganese
150X
Etch: Oxalic acid

Figure 14 - 89.5 ^w/o uranium-nickel
150X
Etch: Oxalic acid

Figure 15 - 88.3 ^w/o uranium-iron
150X
Etch: Oxalic acid

Figure 16 - 44 ^w/o nickel-zirconium
150X
Etch: HF - HNO₃ - glycerine

Figure 17 - 42.5^{w/o} cobalt-zirconium
950X
Etch: HF - HNO₃ - glycerine

Figure 18 - 86^{w/o} cobalt-zirconium
450X
Etch: HF - HNO₃ - glycerine

Figure 19 - Vanadium carbide 150X
Etch: HF - HNO₃ - glycerine

Figure 20 - Tantalum carbide 950X
Etch: HF - HNO₃ - H₂SO₄

THIRTY-FIVE MILLIMETER COLOR PHOTOMICROGRAPHY

E. N. Hopkins and D. T. Peterson
Ames Laboratory
Iowa State University, Ames, Iowa

A 35 mm camera has been simple adapted to the B and L Research Metallograph. This enables the metallographer to take large quantities of color photographs using all the equipment available on the metallograph and at a reasonable cost.

INTRODUCTION

The principal function of metallography is to obtain information about a solid specimen, usually a metal. The information which is desired may be of many kinds. The size or shape of grains or crystallites, the number and quantity of phases, the change in shape of a solid as a result of service conditions leading to corrosion or fatigue, and many other kinds of information may be obtained by metallography. The function of photography is only to record the information so that it can be transmitted to other people and so that it can be recorded permanently. An ideal record would be one which has three features: fidelity - no qualitative or quantitative change in the information; cost - the ideal cost of the record would be zero; and time - the time for recording should be a minimum and the time for retrieval in a usable form should be zero or as close to that as practical.

Progress in reducing the money and time required for photographic recording has been made somewhat slowly in metallography. The use of glass plates, often of large size, persisted until quite recently in spite of their inherent disadvantages. The development of more convenient photographic methods and equipment has been hindered by the small market which is available and by the long suffering patience of metallographers. However, the pressure to reduce time and expense will mount as a result of the trend toward greater use of quantitative techniques in metallography. These quantitative techniques require that a larger number of fields of view be examined to provide statistically reliable results and consequently a larger number of photographic records. In addition, it appears that the function of performing the quantitative measurements will fall on the metallographer and will be a further drain on the available time. To avoid being buried by the work load, it will be necessary to use all the available techniques for saving time in specimen polishing and in photographic recording.

Color is one of the important properties of a surface which provide contrast in an image and allow one feature of a microstructure to be distinguished from another. The other properties of a surface which

provide contrast are inclination to the optical path, reflectivity and effect on polarized light. The lack of convenient methods for recording color differences has stultified their use in metallography in the past. However, numerous examples of the utilization of color in phase identification show the potential value of this property. Unfortunately, black and white photography does a very poor job of recording this type of contrast.

The principal barriers to more extensive use of color in metallography are the cost in time and money and the inertia of human behavior. The use of 35 mm color film reduces the cost of film and permits the use of existing photographic equipment, some of which is very well designed for convenient use, reduces the cost of the equipment and the time spent in photography. The disadvantages of the small image size do not seem to be significant and the small image size could be a real advantage in storing the pictures. The natural eye appeal of color will probably be a great aid in overcoming the natural reluctance to accept anything new.

PROCEDURE

A standard Leica M1 35 mm camera body without lens, a Leica reflex housing and extension bellows was found to work very well with the Bausch and Lomb Research Metallograph. The camera was supported on the optical bench bar of the metallograph by a simple stand made by the machine shop. Figure 1 shows the camera in place on the metallograph. Figure 2 reveals the front and side views of the stand. The 35 mm camera could easily be removed to allow the conventional camera to be used. The reflex arrangement made focusing of the image and selection of the field of view very convenient. The exposure time was determined by measuring the light intensity on the ground glass screen with a Photovolt light meter. When the magnification must be known, it can be determined with a stage micrometer.

This arrangement is superior to trinocular bench microscopes equipped with a 35 mm camera in several ways. The curvature of the image plane is much less with the Bausch and Lomb Research Metallograph and photographs which are in focus over the entire film can be obtained. This generally cannot be done with the standard desk microscope. In addition, the full range of accessories of the Research Metallograph, such as polarized light, oblique lighting and dark field illumination, are available.

Figure 3 is a photomicrograph of a stage micrometer photographed on a desk microscope equipped with a 35 mm camera. For comparison, Figure 4 is the same area photographed on the Bausch and Lomb Research Metallograph with the Leica M1 35 mm camera. This comparison shows the increased resolution and flatness of field obtained on the metallograph.

Figure 1 - Leica M1 35 mm camera mounted on the Bausch and Lomb research metallograph.

Figure 2 - (a) Side view and (b) Front view of the stand used to mount the camera on the metallograph.

Figure 3 - Photomicrograph of a stage micrometer photographed on a desk microscope equipped with a 35 mm camera.

Figure 4 - Photomicrograph of the same area photographed on the Bausch and Lomb research metallograph with the Leica M1 35 mm camera.

CONCLUSIONS

The use of thirty-five millimeter film will allow differences in color to be used in identification of constituents in metallography. With the advent of quantitative metallography the smaller size film will enable the metallographer to conveniently photograph many areas of a specimen for analysis. Film storage problems will lessen with the use of smaller film.

16.9.15
METALLOGRAPHIC STUDY OF THE ANNEALING
BEHAVIOR OF ALUMINUM-SILICON EUTECTIC ALLOY*

R. H. Todd
Hanford Atomic Products Operation
Richland, Washington

The silicon phase of aluminum-silicon (Al-Si) eutectic alloy has shown a definite tendency to spheroidize after prolonged exposure at moderate temperatures. Silicon crystals within the eutectic regions of the alloy change their shape from highly acicular or needle-like crystals to rough spheroids resembling cubes which have been well-rounded. Information developed in this investigation has made it possible to estimate the mean effective temperature to which a specimen of the alloy has been exposed, by a detailed examination of its microstructure after the exposure. A chart is presented depicting the microstructure of the alloy at successive annealing stages from 250°C to 550°C (482°F to 1022°F) at time periods up to 100 days.

PURPOSE

The purpose of this investigation was to establish a means of determining the mean effective temperature at which any specimen of Al-Si had been annealed. After the specimen had been annealed, metallographic examination of the microstructure was to determine the annealing temperature, provided the duration of anneal was known. This procedure could be used to determine the effective temperature of Al-Si objects in locations normally without temperature indicating or recording devices. This is especially applicable to nuclear reactors where each Al-Si brazed fuel element becomes a temperature recorder.

The difference between the normal braze material and the commercially pure Al-Si material used as standard process addition alloy was also sought. This would answer the question: Do the impurities picked up during the brazing process affect the annealing behavior of Al-Si?

REVIEW

A review of the aluminum-silicon phase diagram (Figure 1) shows a simple eutectic at 12.7 weight percent (^{w/o}) silicon which melts at 577.2°C (1071°F). (1,2,3) Casting alloys of aluminum and silicon frequently contain additions of other elements, such as sodium or boron, to control or modify the solidification characteristics.⁽⁴⁾ These are called "modified" alloys. Unmodified alloys of this system are usually called

* Also Report No. HW-69401. Work performed under Contract No. AT(45-1)-1350 between the Atomic Energy Commission and General Electric Company.

Figure 1 - Aluminum-silicon phase diagram according to Hansen (15)

normal even though they contain an abnormal eutectic structure. This eutectic structure is considered abnormal because it lacks any apparent order between the two constituent phases. When solidification occurs from an undercooled or supersaturated melt, solidification of the eutectic regions is dominated by the growth of silicon platelets in dendritic form in advance of the solidifying matrix of α aluminum.⁽⁵⁾

The aluminum-rich α phase may contain as much as 1.5 w/o silicon in solution at 577°C (1071°F). Rapid quenching of a sample of this composition from 577°C (1071°F) to room temperature will retain all of the silicon in solid solution. The silicon-rich phase will retain some aluminum in solid solution⁽⁵⁾ but the amount is so small it is considered essentially pure silicon.

When the alloy is used as a braze for aluminum components, Al-Si always dissolves some excess aluminum while molten. When the assembled part is quenched, the excess aluminum solidifies first as primary dendrites saturated with silicon. The remaining eutectic regions then solidify with the Si forming dendrites of interconnected platelets just ahead of the solidifying α matrix.⁽⁵⁾ This results in the Si platelets retaining a definite orientation with one another. However the matrix α grains in this same region do not bear any orientation relationship to the Si or to each other although they are bounded and limited by the dendritic Si platelets.

EXPERIMENTAL PROCEDURE

One group of test material for this investigation was cut from aluminum caps taken from scrapped fuel elements. A second group of samples was cut from a one-half inch diameter casting of Al-Si. This was virgin braze material which had been chill-cast into a graphite mold.

At least one section from each cap and two sections from the Al-Si casting were polished for microscopic examination in the nonheat-treated condition. In all cases, the primary aluminum dendrites were found to contain no precipitated Si which could be resolved with the optical microscope. The primary Si grains took any of several forms as shown in the nonheat-treated portion of the chart used to establish annealing values.

Heat Treatment Schedule

The schedule for the heat treatment of the specimens was evolved from data provided by Peekema.⁽⁶⁾ His preliminary work provided data (Figure 2) on 28 separate samples which had been exposed to temperatures between 260°C and 400°C (500°F to 752°F) for periods up to 80 days. A portion of these samples had not been annealed sufficiently to cause a recognizable change in microstructure. Extrapolation of Peekema's results established

Figure 2 - An Arrhenius type plot of the time-temperature conditions for Al-Si samples annealed prior to this study.

a region of probable results and of major interest. A variation of the Arrhenius plot was used to analyze Peekema's results and the same method of plotting was used for planning and analyzing purposes for this study.

The zone chosen for detailed study is outlined in Figure 2. It extends from $1/100$ of one day to 100 days and from 250 C to 550 C (482 F to 1022 F). Those points to the right and below the zone chosen would not show sufficient annealing effect to be of any value. The sloped line at the top left of the zone in Figure 2 was above the time-temperature exposures expected to be encountered. These two areas were left out of the study for these reasons.

The region of intended investigation was divided into nine temperature and nine time steps to give equally spaced points on the Arrhenius plot. (See Table I). Three groups of samples were used. Their assigned heat treatments and the results obtained can be seen plotted in Figures 3, 4, and 5. One group of samples, Series A, was divided so that all of the samples for one temperature were cut from one cap. A cross-check was made by heat-treating all samples cut from another cap according to conditions indicated by lines of equal annealing effect as predicted from the preliminary data. This second group of samples became Series B.

TABLE I
DIVISIONS MADE IN TEMPERATURE AND TIME TO GIVE
VALUES EVENLY SEPARATED ON ARRHENIUS PLOT

Temperature Divisions		Time Divisions		Extra Time Divisions for Standards	
$\frac{1000}{T}$ K	$^{\circ}$ C	$\text{Log}_{10} t$	t in days	$\text{Log}_{10} t$	t in days
1.2151	550	-2.00	0.010		
1.3022	495	-1.50	0.0316	-1.75	0.0178
1.3893	447	-1.00	0.100	-1.25	0.056
1.4764	404	-0.50	0.316	-0.75	0.178
1.5635	367	0.00	1.00	-0.25	0.562
1.6506	333	+0.50	3.16	+0.25	1.78
1.7377	303	+1.00	10.0	+0.75	5.62
1.8248	275	+1.50	31.6	+1.25	17.8
1.9119	250	+2.00	100.0	+1.75	56.2

Days Exposure

Annealing Temperature °C

Figure 3 - Simplified Arrhenius plot. Annealing values were achieved by the various heat treatments given samples in Series A.

Figure 4 - Simplified Arrhenius plot. Annealing values were achieved by the various heat treatments given samples in Series B.

Figure 5 - Simplified Arrhenius plot. Annealing values were achieved by the various heat treatments given samples in Series C.

A third group of samples, Series C, consisted of sections of the chill-cast virgin Al-Si. This group was assigned positions across the middle of the region of interest in a broad band parallel to the predicted slope of lines of equal annealing effect. The plotted positions of these three groups can be easily seen in Figures 3, 4, and 5, where the results of the anneals are reported in simplified chart form.

Standards were needed for comparison of results. To obtain standards at intervals close enough to eliminate ambiguity, extra samples were added to Series A at two temperatures. The extra samples were annealed at 275°C and 404°C (527°F and 759°F) at times midway between the times for the balance of the samples. The groups of samples at these two temperatures then had a time spacing on the Arrhenius plot of exactly one-half that of the balance of the specimens.

The extended anneals were carried out in a bank of six Marshall tube furnaces. A Weston Electric Celec-Ray six-point controller was used to control the furnaces at six different temperatures. Furnace temperatures were monitored with a six-channel Brown recorder.

Temperature tests with a ballasted test thermocouple revealed no detectable fluctuation as the furnace current cycled on and off. A variation of about 1°C existed along the six-inch length of the central zone. Less than 2°C variation existed between the readings of the recording thermocouple and the ballasted test thermocouple.

Metallographic Preparation of Samples

The annealed samples were prepared for examination in one of two ways. Each sample was mounted in transparent cold setting plastic. The plastic used bears the trade name of Thalco Resin. Mounted samples were ground on a wet belt sander, then hand processed through successively finer grades of abrasive papers ending with the 3/0 grade. The first samples were polished by hand through six micron diamond paste on Microcloth, using filtered kerosene as lubricant on an eight-inch, high-speed wheel, followed with magnesium oxide powder on Gamal cloth with distilled water on an eight-inch low-speed wheel. Samples of low degrees of annealing value were polished easily by the hand method but the samples of higher annealing value were more difficult to polish. Finally it was decided to polish all of the remaining samples in the vibratory polishing bowls.

For vibratory polishing, the procedure was the same through the step producing a good 3/0 finish on the sample. At this point the sample was weighted and placed in a 12-inch bowl of the vibratory polishing unit. This bowl contained Gamal cloth cemented firmly to the bottom, magnesium oxide polishing powder, and distilled water. It was essential to start with the entire assembly cold, to prevent deterioration of the magnesium oxide abrasive. As the bowl was warmed by the operation of the

machine, the abrasive became slimy to the touch and very ineffective as a polishing agent. This deterioration of the abrasive is probably due to hydrolysis of the magnesium oxide, and low temperatures retard the reaction.

Each sample was etched by swabbing with one-half percent hydrofluoric acid for about ten seconds. This etch cleaned the sample of smeared metal and accentuated the normal difference in appearance between the aluminum matrix and the Si phase. The grain boundaries of neither the aluminum nor the Si were delineated. Representative photomicrographs at 750 diameters were taken of each sample.

Application of Conventional Grain Size Measuring Techniques to Heat-Treated Al-Si

Heyn's and Graff-Snyder's intercept methods of measuring grain size appeared promising until actually tried. The following questions arose concerning the acicular Si grains of low temperature annealed Al-Si:

When using a grid of lines superimposed on a magnified field, a single acicular crystal or grain is crossed by several grid lines. Should this be counted as one grain or should the number of times it is crossed by grid lines be considered the proper value?

Is it better to measure crystals per unit area, or crystals per unit length of line, or phase boundary crossings per unit length of line?

Is it necessary to measure the length to width ratio of the crystals?

These questions became meaningless when it was discovered that by each method of grain size measurement some samples which had received no heat treatment contained larger grains than some which obviously had undergone considerable heat treatment. Figure 6 illustrates this paradox.

The sample represented by photomicrograph A in Figure 6 was not heat treated, while those of photomicrographs B and C were heat treated at 275°C (527°F) for 0.56 days and 3.15 days, respectively. The sample shown in Figure 6 (photomicrograph C) had a duplex structure, the cause of which was not known. In this particular case it is quite easy to demonstrate the failure of grain size measurement to the analysis of annealing effect. Any test of annealing effect will obviously have to provide the same answer for both structures shown in Figure 6 (photomicrograph C).

Ambiguous results were obtained on grain size estimates made on samples of high annealing value, where the spheroidized shapes were more uniform. This can be seen in Table II. For this data, photomicrographs were enlarged to 2000 diameters on 8-1/2 x 11 prints. A transparent grid with 5 mm line separations was laid over the prints. A count was then made of all the Si crystals and all of the squares in the eutectic regions excluding the areas within the primary α grains. This provided data for crystals per square centimeter at 2000 diameters. All crystals intercepted by the grid lines were counted and this number was divided by the length of line in centimeters, again only within the eutectic regions.

(a)

(b)

(c)

Figure 6 - These selected photomicrographs demonstrate the complexity of the problem of measuring annealing effect. Photograph (a) has received no heat treatment, photograph (b) has received 0.56 days at 275°C, and photograph (c) has received 3.15 days at 275°C, and etched with 0.5 % HF.

Magnification 750X

TABLE II

GRAIN SIZE SUMMARY DETERMINED
FROM PHOTOMICROGRAPHS AT 2000 DIAMETERS

Sample	Temperature		Time Days	Crystals cm ⁻²	Crystals cm ⁻¹	Annealing Number
	°C	°F				
A3G	404	759	10.0	1.22	0.504	24
A4G	404	759	17.8	1.21	0.632	25
A4H	404	759	56.2	1.58	0.660	27
A3I	404	759	100.0	0.86	0.409	28

When it became apparent no meaningful answers would come from use of these methods, an attempt was made to determine the size distribution and length to width ratio distribution of the grains in each sample. This information when plotted on distribution curves would show the overall pattern of grain sizes and shapes. Results from the first three photomicrographs treated in this way indicated good to fair agreement with actual annealing history. Time required for analyzing each photomicrograph was approximately 16 hours. The heat-treated samples numbered 195, and in addition there were 25 control samples, not heat-treated. Because of the forecast time required and the time available, this method of grain size determination was dropped.

DISCUSSION OF EFFECTS OF ANNEALING ON THE Si PHASE

Originally the Si platelets are joined in dendrites; they are uniform in cross-section and all of those of a particular dendrite have a definite orientation toward each other. On initial exposure to annealing temperatures, several things begin to happen. These changes can be followed on the excerpts from the original Annealing Number Charts shown as Figure 7. In the eutectic regions the excess silicon held in solid solution in the matrix α aluminum precipitates out on the existing Si platelets. This produces a myriad of uneven lumps on the otherwise smooth platelets. These Si platelets begin to coalesce and round off their edges; to become thicker in some places and to become thinner in others. Each platelet separates into pieces which are nearly equi-axed in dimensions. The thinner platelets accomplish this change first and the thicker platelets last. The thickest platelet that has just broken into smaller segments is an indicator of what annealing stage the sample is in.

While the platelets are breaking up as described above, the primary α grains are also changing. Even after the shortest anneal, the nucleating grains of Si within the α grains can be seen under the optical microscope as small dots. These have the appearance of very fine pepper on the Annealing Charts (Figure 7). Further annealing initially causes a greater number of nucleation sites to appear; those appearing first grow rapidly and soon begin to swallow up their smaller neighbors. As growth continues,

Annealing number 0. Fine structure

Annealing number 0. Coarse structure

Annealing Number 0. Acicular structure

Annealing number 1.

Figure 7 - Progressive stages of spheroidization of the Si phase in Al-Si samples. The degree of spheroidization is represented by the annealing number. Magnification 750X.

Annealing number 4.

Annealing number 7.

Annealing number 10.

Annealing number 13.

Figure 7 (continued).

Annealing number 16.

Annealing number 19.

Annealing number 22.

Annealing number 25.

Figure 7 (continued).

Annealing number 28.

Figure 7 (continued).

a band appears next to the edge of the α primary grains which does not contain any of these secondary crystals of Si. Careful study will show the nearby eutectic zone Si crystals are larger than similar crystals farther from the primary α grain. These crystals have become larger by absorbing the secondary silicon in the band at the edge of the α grain. As annealing proceeds this band, free of secondary Si, grows wider until at an Annealing Number near 22, the primary α grains are once again free of all Si crystallites within their boundaries. Secondary precipitation of Si within the primary α aluminum grains thus becomes another important indicator of the degree of the anneal. The secondary Si does have this drawback as an indicator: at higher temperatures of anneal, more silicon can remain in solid solution, and less will be available for precipitation as secondary crystals. Thus a sample annealed at high temperature may have the same annealing value as a sample annealed for a much longer time at lower temperature; but the appearance of the secondary Si crystals within the primary α grains will be distinctly different. The secondary Si crystals will disappear first from the sample of higher temperature anneal.

MEASUREMENT OF RESULTS

Measurement of the degree of annealing posed a serious problem for the Al-Si system. Nearly all of the grain size measuring methods in use are designed to be used on equi-axed grains in single phase material. (7-13) What was needed here was a method of determining the degree of change of the Si crystals regardless of changes of melt composition, impurity content, and initial size of these crystals.

All of the conventional methods for establishing absolute grain size were tried but without success. A workable arbitrary system of standards was set up as follows: Two sets of samples had been heat-treated for various time intervals at the temperatures of 275°C and 404°C (527° and 759°F). Photomicrographs of these 32 samples were assembled in the order of increasing heat treatment. The series for the two temperatures were compared visually and were found to overlap. A good overlap fit was made and the photomicrographs were numbered consecutively from 1 through 30, representing the least heat treatment as number 1 and the most extensive heat treatment as number 30. These numbers were given the name Annealing Value. All photomicrographs had been taken at the same magnification - 750 diameters. The photomicrographs for the balance of the samples were now compared with the arbitrary standards and each in turn was assigned an annealing value number.

After about one-third of the photomicrographs had been processed it became apparent that something was wrong with the sequence of the arbitrary standards. Also, one picture was being used to compare with many, and the basic structures of the many differed sharply from the first. For a better understanding of what this difficulty was, the author laid out

all of the graded photomicrographs on a large table according to their assigned Annealing Values. With a large number of photomicrographs displayed, it became apparent that there were a variety of basic structures in the initial lot of samples. These basic structures in the initial lot of samples varied from extremely fine, barely resolvable masses of Si crystals, through an open structure, to very acicular, strongly dendritic Si crystals with wide spaces of α aluminum between them. All of these structures were found in the eutectic regions where excess aluminum had already diffused to the primary α grains, leaving these eutectic regions essentially stoichiometric. The graded photomicrographs, already arranged according to Annealing Values, were then further sorted according to basic structure.

At this point it was decided to double check the Annealing Value so arbitrarily assigned to the "standard" photomicrographs. These pictures were removed, shuffled as one would shuffle a deck of cards. Then, without reference to the identifying marks on the back of the pictures, the "standard" pictures were reassigned to their original Annealing Values. A close study of those that did not fit resulted in removal of two standard numbers and recognition of anomalies existing in the standard sample series at three different places. This action reduced the number of standard Annealing Values to 28.

The rest of the photomicrographs were also rechecked. Everything except the standard pictures was removed from the display table and shuffled thoroughly. All of the pictures not yet graded were also shuffled into the stack. Each picture was assigned to a place on the display table according to basic structure and Annealing Value. As the number of pictures displayed increased, it became progressively easier to determine the proper location of each new picture. At this time it became apparent that any standard chart of Annealing Values must contain examples of the various basic Al-Si structures at each Annealing Value.

The Annealing Value Chart, from which the pictures for Figure 7 were taken, is composed of the "standard" photomicrographs and an example of each type of structure under each Annealing Value. Some particular structural combinations were not available for this chart because none were found during this study. A set of three photomicrographs is shown in Figure 7 to illustrate the many variations of structure obtained in the nonheat-treated samples.

A very fine separation exists between the structures of each of the Annealing Values. If the sample identification were known, it would be quite easy to allow the visually determined estimate of Annealing Value to slide two or even three units to one extreme or the other in order to place it into a preconceived relationship with other samples. For this reason no re-evaluations were made. Although there were some obvious errors

in the lower range of Annealing Values, these errors were felt to be unbiased and as such should cancel out in a statistical analysis. In the upper range of Annealing Values evaluations were much simpler and fewer errors occurred. Also these errors serve to indicate the probable error in the use of this chart.

There is more chance for error in the selecting and taking of photomicrographs than in evaluating them. This is due to initial microstructural differences which introduce a consistent bias in evaluation. This is shown by comparing the final Annealing Values of the samples of Series C with those of Series A and B. (See Figures 3, 4, and 5) The casting of Al-Si, from which the samples of Series C were cut, contained a coarse grain pattern as contrasted to the structure of Series A and B. In plotting the results of these series the average positions of lines of equal Annealing Value shift to the left for the Series C samples as compared to both Series A and B. This shift amounts to approximately one position difference on the Arrhenius plot. Similar shifts were noted for individual samples of Series A and B possessing large acicular grains of Si. Because of this variation an evaluation of a single sample should be based on photomicrographs sufficient in number to cover all variations of basic structure within the sample. By evaluating each photomicrograph and averaging the results, a more accurate estimate of the Annealing Value of that sample can be made.

GENERAL DISCUSSION

The fit obtained by the regression analysis is shown in Figure 8 for three values of N. The intercept point for each of these lines (at one day where $\log_{10} t = 0$) was calculated from the formula given by regressive analysis. Each dot on the chart, Figure 8, represents one condition of heat treatment. Each sample with an Annealing Value equal to that of the plotted line is indicated by appropriate encirclement. A broken or dashed encirclement indicates an interpolated value. Interpolated values were used on this figure, where the raw data indicated they were reliable, to increase the amount of data available for direct comparison with the plotted lines. Interpolated values were not used for any other part of this analysis.

From this comparison of raw data versus plotted formulae, the degree of probable error in establishing the proper annealing value of a sample becomes apparent. The cumulative errors in Annealing Values correspond to a maximum temperature error of approximately $\pm 30^{\circ}\text{C}$ regardless of Annealing Value.

CONCLUSIONS

Estimation of the mean effective temperature to which a sample of Al-Si has been exposed for a definite period of time can be made by careful examination of its microstructure. Accuracy of this estimation is within the range of plus or minus 30°C in the range tested ($250\text{-}550^{\circ}\text{C}$) ($482\text{-}1022^{\circ}\text{F}$).

Figure 8 - Comparison of raw data with calculated lines of equal annealing value. The fit of these lines with actual data points is shown by appropriate encirclement of points representing annealing conditions. Points with an annealing value of 25 are designated by triangles; annealing value of 14 by circles; and annealing value of 8 by squares. Broken symbols indicate interpolated data points.

An appreciable error can be introduced due to variations in original microstructure. A coarse, acicular structure will generally result in determinations on the high side but still within the range given above.

Standard methods of measuring grain sizes do not apply to the Si crystals in Al-Si. Comparative grain size measurements at low magnification are not of any value for this type of study. At the magnification required for study of annealing effects (500 to 750 diameters) the only successful method found for measurement of the annealing effects was a comparison chart set up on an arbitrary scale.

Grain size of the Si crystals in Al-Si is not a criterion of the annealing effect incurred. Manifestations of annealing are displayed in the microstructure of Al-Si by secondary precipitation of Si in the primary α dendrites, subdividing of thin Si platelets, coalescence of Si crystals, and general spheroidization of Si crystals.

The impurities picked up during the brazing process of fuel elements do not affect the annealing behavior of Al-Si beyond that induced by the reduction of the size of the crystals of Si in the eutectic regions. The actual change of annealing effect is negligible; but the change in Si crystal size introduces a bias whereby the apparent effect is lowered.

REFERENCES

1. Hansen, M. Constitution of Binary Alloys, 2nd ed., 132-134. New York: McGraw-Hill, 1958.
2. Meussner, R.A. The Aluminum-Silicon Eutectic, Nrl-5331. June, 1959.
3. Craighead, C. M., E. W. Cawthorne, and R. I. Jaffee. "Solution Rate of Solid Aluminum in Molten Al-Si Alloy," J. of Metals 7, AIME. Trans. 203: 81-87. 1955.
4. DePierre, V. and H. Berstein. "Grain Refinement of Aluminum-Silicon (5 percent Si) and Aluminum-Silicon-Magnesium (7 percent Si, 0.39 Mg) Casting Alloys," Trans. Am. Soc. Metals, 43:635-643. 1951.
5. Meussner, R. A. The Structure of Aluminum-Silicon Alloys, NRL-5341. July, 1959.
6. Peekema, R. M. "Spheroidization of Acicular Silicon in Aluminum-Silicon Eutectic Alloy," Unpublished, June 1956.
7. Smith, C. S. "Grain Shapes and Other Metallurgical Applications of Topology," Metal Interfaces. Cleveland: American Society for Metals, 1952.

8. Fullman, R. L. "Boundary Migration During Grain Growth," Metal Interfaces. Cleveland: American Society for Metals, 1952.
9. Beck, P. A. "Interface Migration in Recrystallization," Metal Interfaces. Cleveland: American Society for Metals, 1952.
10. Burke, F. E. and D. Turnbull. "Recrystallization and Grain Growth," Progress in Metal Physics, 3: 220. New York: Interscience Publishers, Inc., 1952.
11. Chalmers, B. "Structure of Crystal Boundaries," Progress in Metal Physics, 3: 293. New York: Interscience Publishers, Inc., 1952.
12. Smith, C. S. and L. Guttman. "Measurement of Internal Boundaries in Three-Dimensional Structures by Random Sectioning," J. of Metals, 5: 81-87. January, 1953.
13. Kehl, G. L. The Principles of Metallographic Laboratory Practice, 3rd ed. New York: McGraw-Hill, 1949.
14. Betcherman, I. I. "Rate Processes in Physical Metallurgy," Progress in Metal Physics, 2: 53-89. New York: Interscience Publishers, Inc., 1950.
15. Darken, L. S. and R. W. Gurry. Physical Chemistry of Metals. New York: McGraw-Hill, 1953.
16. Rosenbaum, H. S. and D. Turnbull. Metallographic Investigation of Precipitation of Silicon from Aluminum, 58-RL-2153. December, 1958.
17. Rosenbaum, H. S. and D. Turnbull. On the Precipitation of Silicon Out of a Supersaturated Aluminum-Silicon Solid Solution, 58-RL-1920. March, 1958.
18. Rosenbaum, H. S. "Precipitation of Silicon From a Supersaturated Aluminum-Silicon Solid Solution," Doctorate Thesis. Troy, New York: Rensselaer Polytechnic Institute. May, 1959.
19. Meussner, R. A. "Isothermal Growth of Silicon Particles in an Aluminum Matrix." Doctorate Thesis. Carnegie Institute of Technology. 1953.
20. Glazov, V. M. and U. N. Vigdorovich. "On Diffusion-Free Crystallization of Metal Alloys," Doklady Akademii Nauk, S.S.S.R. 118: 924-927. February, 1958.
21. Jetter, L. K. and R. F. Mehl. "Rate of Precipitation of Silicon From the Solid Solution of Silicon in Aluminum," AIME Trans., Institute of Metals Division, 152: 166-181. New York: 1943.

17:6680

MICROSTRUCTURAL CHANGES
DURING THE α - β - α TRANSFORMATION OF URANIUM*

C. L. Angerman
Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, South Carolina

The changes in the grain structure of uranium during an α - β - α transformation cycle were examined with a hot-stage optical microscope and photographed on movie film. An apparent "super-heating" effect was observed while heating through the α - β transformation. A finite time at a beta-phase temperature was required before the transformation front passed through the field of view. Cooling to the alpha phase before the α - β front passes resulted in grain growth without the passage of a front. A similar front was observed during the β - α transformation. In both transformations the main front was composed of "sub-fronts" that defined the resulting grain size.

INTRODUCTION

The use of a hot-stage optical microscope in the study of phase transformations offers the obvious advantage that the changes in the microstructure can be observed as they happen. Since the application of this technique to uranium is difficult because of the high reactivity of uranium with gases at elevated temperatures, the majority of the studies of the transformations in uranium have been done by conventional techniques.⁽¹⁻⁵⁾ Some observations employing high-temperature metallography have been made, but no detailed study has been reported.⁽⁶⁻⁸⁾

At the last meeting of the Metallography Group, the equipment and techniques that were developed for the metallography of uranium at elevated temperatures were described.⁽⁹⁾ These techniques allowed only a minimum of oxidation of the uranium sample at the desired temperatures, which minimized any confusion between the oxide film and the structural changes in the uranium. Using these established techniques, a study of the uranium structure during an α - β - α temperature cycle was undertaken because a heat treatment of this nature is employed in the creation of a structure that is relatively stable during irradiation. This paper presents the results obtained to date. Since this is a progress report, the interpretations should be considered as tentative.

* The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U.S. Atomic Energy Commission.

SUMMARY

During both the α - β and the β - α transformations, a main front that was composed of sub-fronts passed through the specimen. The volume of metal traversed by these sub-fronts constituted the grains of the resulting phase. The sub-fronts moved with a jerky motion that suggested a "chain-reaction" type of propagation; the passage of a sub-front through one area generated a new sub-front in an adjacent area. The observed speeds of the main fronts were 10 to 100 μ /sec. for the α - β transformation and 100 to 200 μ /sec. for the β - α transformation. The large grains that are typical of beta-transformed uranium formed during the β - α transformation; no grain growth was observed in the beta phase, even at temperatures as high as 750°C, and during times as long as 30 minutes.

DISCUSSION

Experimental Techniques

As described in detail previously⁽⁹⁾, the hot-stage was a cylinder of Vycor, as shown in Figure 1, that was evacuated to at least 3×10^{-6} mm Hg at room temperature. In most cases the specimens were cylinders with an axial hole for a thermocouple. The surface being examined was 20 to 30 mils below the thermocouple. Some examinations were made with foils 3 mils thick to minimize any temperature gradient between the position of the thermocouple and the surface being examined. Both the cylindrical and the foil specimens were initially in the as-rolled condition.

The specimens were electropolished, inserted into the stage, and heated at a rate of 10°C/min. After the desired time at temperature the heater was turned off, producing an average cooling rate of 85°C/min. over the temperature range of 700 to 450°C. The changes in microstructure were recorded with a movie camera that was operated at a speed of 8 frames/sec.

α - β Transformation

The α - β transformation was found to proceed as a front across the field of view. The main front was not a smooth line, but was composed of short sections, or "sub-fronts." These sub-fronts moved at slightly different speeds and defined the resulting grain size of the beta phase. The impression that one received was that a sub-front moved until it became pinned, for some reason, and then generated a new sub-front that moved at a slightly different rate in a slightly different direction.

McDonell⁽¹⁾, Donze and Faivre⁽²⁾, and Butcher and Baverstock⁽³⁾ observed that, at the lower beta-phase temperatures, the rate of loss of the preferred orientation of the original alpha phase was less than the rate of change in grain size. In order to explain these observations, the changes in grain structure during transformations at temperatures between 670 and 685°C

Figure 1. Cross-Sectional View of the Hot Stage

were examined. Transforming the cylindrical specimens at these temperatures resulted in an apparent "super-heating" effect. A finite time at the temperature elapsed before the transformation front passed through the field. This delay time decreased as the temperature increased; typical delays were 15 minutes at 670°C and 2 minutes at 685°C.

When the specimens were cooled before the α - β front passed, new, large grains appeared that were identical to those formed by a normal α - β - α cycle. There was no front associated with this "grain growth", but the grains grew throughout the field over a short period of time.

No differences in preferred orientation were found between samples cooled before the α - β front passed and those cooled after the front passed. The orientations of the samples were characterized before and after the heat treatments by the X-ray technique of measuring the "texture coefficient" (10). Both types of heat treatments erased the original preferred orientation and randomized the orientation to approximately the same degree. The inability to obtain a statistically significant difference in orientation may have been influenced by the small sample size and the large grain size after heat treatment.

Similar experiments with the foil specimens did not show the super-heating effect. At the heating rate of 10°C/min., the α - β fronts were always observed at temperatures between 670 and 675°C. The specimens could not be heated to 680 and 685°C before the front passed.

The observations of these two experiments did not offer any clear-cut explanation for the results of McDonnell and the others (1,2,3). There are a number of possible interpretations. One explanation for all of the results was suggested by the nature of the transformation front. The transformation may proceed by a "chain reaction"; the transformation nucleates in one area of an isothermal field and, as this area is transformed, its front initiates the transformation in an adjacent area, and so on. Transformation by this means should require a finite time to traverse a relatively large specimen. An alternate explanation is that either the observations on cylindrical specimens in this study, or the results of the others, or both may have been caused by a temperature gradient in the relatively large specimens.

The speeds of the general fronts as they passed through the field of view were measured. A trend toward lower rates at the higher temperatures of transformation was observed, as shown in Table I. However, these rates are only apparent and not the true speeds of the fronts. If the volume of the beta phase is pictured as a sphere of constantly increasing size and the observed front as the surface of the sphere, the apparent speed of the front on a given plane will depend upon the distance of that plane from the center of the sphere.

TABLE I
SPEEDS OF THE α TO β TRANSFORMATION FRONTS

Temp. of transformation (°C)	Speed of observed front (μ /sec.)
635	19
	20
680	94
	31
	21
675	51
670	83
	100

β - α Transformation

The nature of the β - α transformation was the same as the α - β . A general front that was composed of sub-fronts passed through the field of view in a manner that suggested a "chain reaction". The speed of the β - α front was 100 to 200 μ /sec., as compared to 10 to 100 μ /sec. for the α - β front. With the cooling rate of 85°C/min., the temperature of the β - α transformation was depressed, sometimes as much as 115°C (550°C). No relation between the speed and the temperature of transformation was detected.

One purpose of these examinations was to ascertain the origin of the large grains that are typical of β -transformed uranium. The observations showed that they formed during the β - α transformation. Other investigators had suggested that the large grains were the result of a combination of rapid growth of beta grains and the coherency of the transformation^(3,5). No grain growth in the beta phase was observed at temperatures as high as 750°C and during times as long as 30 minutes.

The above observations were illustrated in the accompanying movie.

REFERENCES

1. McDonell, W. R., "Kinetics of the Beta Transformation of Uranium". Nuclear Science and Engineering Conference, Preprint 172, 1958.
2. Donze, G. and R. Faivre, Compte Rendus, 246, 3619, 1958.
3. Butcher, B. R. and D. Baverstock, "The Effect of the Alpha/Beta Phase Transformation on the Preferred Orientation of Alpha Uranium," Atomic Energy Research Establishment, Harwell, Berkshire, AERE-R 3217, 1960.

4. Butcher, B. R., "The α - β Phase Change in Pure Uranium". J. Nuclear Energy, 4, 273, 1957.
5. Klepfer, H. H. and D. Chiotti, "Characteristics of the Solid State Transformations in Uranium", Iowa State College, ISC-893, 1957.
6. Saller, H. A., R. F. Dickerson, and R. J. Carlson, "Equipment for Metallographic Studies at Elevated Temperatures", Battelle Memorial Institute, BMI-X-114, 1954.
7. Bierlein, T.K. and B. Mastel, Private Communication.
8. Mott, B. W. and S. D. Ford, "The Metallographic Examination of Hot Metal Surfaces", Atomic Energy Research Establishment, Harwell, Berkshire, AERE-M/R-1184, 1953.
9. Angerman, C. L., "High-Temperature Metallography of Uranium", To be published as part of the Papers of the 15th Meeting of the AEC Metallography Group.
10. The author gratefully acknowledges the work of Dr. E. F. Sturcken in the measurements of the preferred orientations. The technique employed was that described by E. F. Sturcken, "An X-ray Method for Predicting the Stability of Natural Uranium at Low Burnup", E. I. du Pont de Nemours and Co., DP-251 (Del.), 1957.

17-538

METALLOGRAPHY OF URANIUM AT ELEVATED TEMPERATURES

W. N. Wise
National Lead Company of Ohio

Electropolished samples of uranium having various thermal, chemical, and fabrication histories were studied in a vacuum heating stage. Changes in the microstructure resulting from the allotropic transformations were recorded. Dilute uranium-base alloys were prepared, and their inclusions were examined in situ with an electron-probe X-ray microanalyzer. The effect of alpha annealing on the precipitation of U_6Fe from a dilute solution of iron in uranium is shown.

INTRODUCTION

Examination of the microstructures of uranium at elevated temperatures is desirable because it permits the observation of solid-state reactions as they occur. The use of the heating stage metallograph to study these reactions is made extremely difficult by the high reactivity of uranium with gases at elevated temperatures. Even though working in a vacuum in the range of 10^{-5} mm Hg, the gases evolved from the sample and/or the furnace walls during heating are sufficient to cause a thin oxide film to form on the sample surface. The film is revealed by the presence of interference colors.⁽¹⁾ To minimize the formation of this oxide, a titanium specimen plate was incorporated in the heating stage to act as a "getter" during the heating cycle. The original alpha grain structure became visible at 1000°F (537°C) due to thermal etching. This structure was then compared to the structure resulting from the α - β and the β - α transformations.

Dilute uranium-base alloys were prepared, and the inclusions were examined in situ with an electron-probe X-ray microanalyzer. The effect of alpha annealing on the precipitation of U_6Fe from a dilute solution of iron in uranium is shown.

EQUIPMENT AND PROCEDURES

This series of tests was conducted in the Unitron Model HHS-3 vacuum heating stage. In an attempt to maintain a sample surface free from oxidation, a titanium specimen plate was incorporated in the heating stage to act as a "getter" during the heating cycle. The vacuum system consists of a Welch mechanical fore-pump and a 3-inch, three-stage, oil diffusion pump.

The heating stage is mounted on a Unitron metallograph. A 20X objective with a sufficient working distance to prevent damage from heat is used,

thus allowing magnifications at the film plate up to 400X. The metallograph is equipped for both still photography and time-lapse movies. The light source is a high-intensity xenon arc lamp having a color temperature suitable for the use of daylight type color film without the use of filters.

The samples used were 3/4-inch long by 5/16-inch diameter. They were ground on successively finer grades of silicon carbide papers from 60 to 400 grit. The samples were then alternately mechanically polished, using 1/4 micron diamond paste, and were electropolished in a standard, chromic-acetic acid solution until a suitable surface was obtained.

The thermocouple was spot welded to the OD of the sample approximately 1/8-inch up from the surface to be observed. The sample was placed in the heating stage, which was previously outgassed. A vacuum of 10^{-5} mm Hg was obtained before the heating cycle was started. A heating rate of 20°F (11°C) per minute was maintained with the aid of a motor-driven variable autotransformer. The temperature of the sample was continuously recorded on a recording potentiometer.

TEST RESULTS

Sample 1

This sample was a transverse section of an alpha-rolled rod of normal ingot uranium. Figure 1 shows the typical alpha-rolled grain structure at 1100°F (593°C), just after the α -to- β transformation. The boundaries of the beta-phase grains are now visible. The temperature was increased to 1360°F (737°C) (beta range) and held at this temperature for 15 minutes. Figure 3 shows the resulting structure. Note that there is no significant difference in the grain size or shape on the surface shown in Figure 3 as compared with that in Figure 2.

The power to the furnace was then cut back and the sample was cooled through the β -to- α transformation. Figure 4 shows the structure of the sample at 1000°F (537°C), after the α -to- β and β -to- α transformations. Note that there is no significant difference in the structure shown in Figure 4 when compared with those in Figures 2 and 3. It is possible that, at a magnification of 400X, the entire field shown is within the boundaries of a large beta heat-treated grain cluster.

Sample 2

This sample was a longitudinal section of an alpha-rolled rod of normal ingot uranium. Figure 5 shows the typical alpha-rolled grain structure at 1100°F (593°C) resulting from thermal etching. Figure 6 shows the same field at a temperature of 1350°F (732°C) (beta phase) showing the structure resulting from the α -to- β transformation. Note the boundaries of the beta-phase structure as shown by the light boundaries.

400X

559/292

Figure 1 - α -rolled, normal ingot metal photographed at 1100°F (593°C) (α range) showing the α -rolled grain structure revealed by thermal etching.

400X

559/294

Figure 2 - α -rolled, normal ingot metal photographed at 1250°F (676°C) (β range) showing the grain structure resulting from the α -to- β transformation.

400X

559/296

Figure 3 - α -rolled, normal ingot metal photographed at 3160°F (737°C) (β range) showing the structure resulting from the α -to- β transformation and from being held at 1360°F (737°C) for 15 minutes.

400X

559/298

Figure 4 - α -rolled, normal ingot metal photographed at 1000°F (537°C) (α range) showing the structure resulting from the α -to- β and β -to- α transformation.

200X

559/230

Figure 5 - α -rolled, normal ingot metal photographed at 1100° F (593°C) showing the α -rolled grain structure revealed by thermal etching.

200X

559/234

Figure 6 - α -rolled, normal ingot metal photographed at 1350° F (732°C) (β range) showing the grain structure resulting from the α -to- β transformation.

200X

559/236

Figure 7 - α -rolled, normal ingot metal photographed at 1000° F (537°C) (α range) showing the grain structure resulting from the α -to- β and β -to- α transformations.

Figure 7 is the same field after the sample had been cooled to 1000°F (537°C) (alpha range). The structure shown is the result of the alpha-to-beta and beta-to-alpha transformation. Note the dark boundaries of the large beta heat-treated grain clusters. Some of the light beta-phase boundaries are still visible because these boundaries were etched into the sample surface.

Sample 3

This sample was a longitudinal section of an unrecrystallized alpha-rolled ingot containing 150 ppm Fe and 100 ppm Si. Figure 8 shows the typical unrecrystallized structure of the sample at 700°F (371°C). Argon gas was bled across the face of the sample at 700°F (371°C). The heat tinting that resulted reveals the structure.

The temperature of the sample was then raised to 1150°F (621°C) and held for 90 minutes. No change in the structure resulting from recrystallization was detected. The temperature was again raised, and the sample was taken through the alpha-to-beta transformation. Figure 9 shows the structure at 1240°F (671°C (beta range), just after the alpha-to-beta transformation was observed on the temperature recorder.

The sample temperature was raised to 1360°F (737°C) (beta range). Figure 10 shows the structure at this temperature. Note there is no significant difference in the structure shown in Figure 10 when compared with Figure 9.

Inclusion Study

In an effort to learn more about the effects of inclusions in uranium, the following dilute uranium-base alloys were prepared:

1. A 50-pound ingot containing 2000 ppm iron.
2. A 50-pound ingot containing 1500 ppm iron and 500 ppm silicon.
3. A 50-pound ingot containing 500 ppm iron.

Figure 11 shows an electropolished sample from the ingot containing 2000 ppm iron. The white phase in the center was identified as U_6Fe , when a specimen was examined with an electron-probe X-ray microanalyzer. Almost the entire surface of the specimen was scanned. The only silicon that could be found was in inclusions of the type shown in Figure 13, which analyzed 10 w/o silicon. The electron-probe was then focused on one of these inclusions, and the spectrum was scanned for all elements above sodium in the periodic table. The only element detected, other than silicon, was zirconium. (This does not, however, exclude the possible presence of elements below magnesium.) If the inclusion is assumed to be composed of 10 w/o silicon and 90 w/o zirconium, this would correspond approximately to the composition of Zr_3Si . No compound corresponding to this composition is shown in the zirconium-silicon phase diagram. However, the inclusion could be composed of a mixture of two intermetallics,

300X

559/244

Figure 8 - Unrecrystallized, α -rolled
dingot metal photographed at
700°F (371°C) (α range) show-
ing the grain structure
revealed by heat tinting.

300X

559/248

Figure 9 - Same material as Figure 8,
photographed at 1240°F (671°C)
(β range) showing the grain
structure resulting from the
 α -to- β transformation.

300X

559/249

Figure 10 - Same sample as Figures 8 and 9,
photographed at 1360°F (737°C)
(β range) showing the grain
structure resulting from the
 α -to- β transformation.

400X

732/52

Figure 11 - As-cast structure of uranium containing 2000 ppm Fe, 700 ppm C, and 50 ppm Si. The structure in the center of the photomicrograph was identified as U_6Fe .

400X

732/36

Figure 12 - As-cast structure containing 1500 ppm Fe, 500 ppm Si, and 500 ppm C showing uranium carbonitrides and U_6Fe . The specimen was cathodically etched.

400X

732/28

Figure 13 - Same specimen as in Figure 12 showing inclusion of Zr - 10 w/o Si.

800X

732/45

Figure 14 - As-cast structure of uranium containing 500 ppm Fe, 600 ppm C, and 30 ppm Si. The inclusions shown are uranium carbonitride. The specimen was cathodically etched.

inclusions such as Zr_4Si and Zr_2Si , or the microanalyzer could perhaps be in error by ± 3 percent. If this were the case, the inclusion could be either Zr_4Si (7.14 w/o silicon) or Zr_2Si (13.33 w/o silicon). For the purpose of discussion, the inclusion will be referred to as " Zr_3Si ".

Chemical analyses of the casting showed a difference in zirconium content of samples taken from the edge and center (center, 1.5 ppm; edge, 2.3 ppm). This finding confirmed the belief that the zirconium derived from the magnesium-zirconate mold coating. Assuming all the zirconium was present as " Zr_3Si ", less than 1 ppm of silicon would be accounted for. Hence, it is believed the silicon remained in solid solution.

Figure 14 is a photomicrograph of a cathodically etched sample taken from the center of the ingot containing 500 ppm iron, showing uranium carbonitrides. No U_6Fe was observed in the specimen. Since the ingot had been cast in a cold mold, it is believed that the iron was retained in solid solution. Figure 15 shows a field of the sample in the hot stage at room temperature. The temperature was raised to $1160^{\circ}F$ ($626^{\circ}C$) (Figure 16), the sample was annealed for 17 hours, and was furnace cooled. The sample was removed, repolished, and placed back in the hot stage. Figure 17 shows the finely dispersed precipitate of U_6Fe . The sample was annealed at $1160^{\circ}F$ ($626^{\circ}C$) for an additional 15 hours, furnace cooled, repolished, and placed back in the hot stage. Figure 18 shows the result of the additional 15-hour anneal. No additional precipitate is observed, but it appears that some clustering of inclusions has occurred.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to D. K. Conley of General Electric Company, Nuclear Materials Propulsion Operation, who performed the electron-probe X-ray microanalysis, and to J. W. Colby for his assistance in the inclusion studies.

REFERENCES

1. C. L. Angerman. "High-Temperature Metallography of Uranium," Paper presented at 15th AEC Metallography Group Meeting. May 17 to 19, 1961.

200X

732/19

Figure 15 - As-cast uranium containing 500 ppm Fe, 600 ppm C, and 30 ppm Si. The sample was electro-polished and photographed in the hot stage metallograph at room temperature.

200X

732/21

Figure 16 - Same sample as Figure 15 photographed at 1160°F (626°C).

200X

732/23

Figure 17 - Same sample as Figure 15 after annealing for 17 hours at 1160°F (626°C), furnace cooling, and repolishing. The finely dispersed precipitate which occurred as a result of annealing is U_6Fe .

200X

732/25

Figure 18 - Same sample as Figure 17, after an additional 15-hour anneal, furnace cool. No additional precipitation has occurred.

IDENTIFICATION OF CARBIDES, NITRIDES, AND OXIDES OF
COLUMBIUM BY ANODIC STAINING

Robert S. Crouse
Oak Ridge National Laboratory*
Oak Ridge, Tennessee

Carbides, nitrides and oxides in columbium may be identified in metallographic specimens by anodization. Specimens that have been in carefully controlled atmospheres at high temperatures were polished and anodized and identification of the phases correlated with chemical and X-ray diffraction data. It was found that two carbides, two nitrides and three oxides could be differentiated by their characteristic colors. This technique is used to qualitatively identify carbides, nitrides, and oxides in metallographic specimens. More accurate determinations require more conventional chemical analyses.

INTRODUCTION

In recent years the interest in refractory metals has increased greatly, necessitating a rather complete investigation into their chemical, mechanical, and metallurgical properties. Columbium has been one of the more promising of the refractories and has received much attention.

The investigations of columbium at Oak Ridge National Laboratory (ORNL) have included the interrelation of mechanical properties with heat treatment, alloy additions, and environments. These investigations have required much metallography in an effort to understand better the test results. This report describes the development of a good reproducible technique for the identification of the carbides, nitrides, and oxides which appear to be the major contaminants found in columbium. The metallographic specimens were taken from tests that were run to determine the effect on certain physical properties of columbium of individual elements of atmosphere. Specimens from carefully controlled oxidation tests, run to investigate the mechanism of formation of the oxides, were also used as standards.

PROCEDURE

Ence and Margolin⁽¹⁾ reported a method of identifying the phases in titanium alloys by a technique they called cumulative etching. This technique involved the deposition of an anodic film on the surface of a metallographic specimen

- - - - -

* Operated for the U. S. Atomic Energy Commission by the Union Carbide Corporation.

in an electrolytic cell. The film formation took place at different rates across the surface of the specimen, depending upon the composition of the substrate material. The various phases exhibited characteristic colors, depending upon the phase composition, voltage across the electrolytic cell, and the time of application of the voltage. The technique of Ence and Margolin was applied to columbium by F. J. Huegel of CANEL, Hartford, Connecticut. Following Huegel's initial work, the author established criteria for the identification of the carbides, nitrides and oxides of columbium at ORNL.

The conditions of the staining procedure are as follows:

Electrolyte Composition:	Cathode:
5 g oxalic acid	Stainless steel
5 g citric acid	Voltage:
5 ml orthophosphoric acid	17-20 v
10 ml lactic acid	Temperature:
35 ml distilled water	Room
60 ml ethyl alcohol	Time:
	0.3 - 0.4 sec.

Figure 1 is a photograph of the electrolytic cell setup used. The specimen is mechanically polished to the best finish before anodizing. The results are more satisfactory if electrical contact is made through the back of a mounted specimen, but contact can be made directly at one corner on the polished surface. The best results are obtained at the point farthest from contact in the latter case. The anodizing time of 0.3 - 0.4 sec. is accomplished by rapidly switching the apparatus on and off three or four times. Anode to cathode distance does not appear to be as critical as in the case of titanium.

If the conditions are proper, the anodized specimen will have an overall deep blue appearance. A purple cast indicates too much time at proper voltage, and a brown film indicates too low voltage. It is difficult to anodize for too short a time unless contact is accidentally broken or the switch is only thrown once. If too high a voltage is used, a light blue film is produced with the phase-matrix color relationship somewhat reversed. Slightly extended time will not cause reversal of the phase-matrix relationship but may cause some difficulty in identification due to deepening of the color of the carbides. This will be discussed later.

Carbides and Nitrides

Standards for the identification of carbides and nitrides were established with specimens that had been exposed to atmospheres of methane and nitrogen, respectively, at high temperatures. These specimens were from tests conducted by H. E. McCoy⁽²⁾ of the Metals and Ceramics Division.

Y-5308

Figure 1 - A typical electrolyte cell setup.

Y-45461

Figure 2 - Columbium exposed to 10% CH₄ in argon for 96 hr. at 1300°C. Not the two different shades in the bright layer, indicating two carbide compounds.

Figure 2 is a specimen which had been in a 10% CH₄-Ar atmosphere for 96 hr. at 1300°C. The thin bright layer is lemon yellow and the darker inner layer is orange yellow. These layers were identified by X-ray diffraction as being CbC and Cb₂C. The outer layer was assumed to be CbC since it formed in contact with excess carbon.

Figure 3 shows electron beam melted columbium which contained 500 ppm C and very little nitrogen or oxygen. The correspondence of color between the phase there and inner layer in Figure 2 was quite good.

Figure 4 is a photomicrograph of a columbium specimen which had been exposed to an atmosphere of nitrogen for 1365 hr. at 1200°C. The two layers there were identified as CbN and Cb₂N. By the same reasoning as for carbides, the outer layer was assumed to be Cb₂N. Columbium nitride appears to have about the same yellow color as Cb₂C, whereas Cb₂N appears as a rose pink.

If both carbon and nitrogen occur together in columbium, it is suspected that they will form a carbonitride. X-ray diffraction cannot distinguish between them due to their almost identical lattice parameters. No specimens were available for examination with both elements known to be present in sufficient amount to form both phases.

Figure 5 shows a columbium corrosion coupon that had become contaminated by air near the end of the test. The layers were identified as nitrides.

Overanodization of a specimen containing carbides will cause the Cb₂C color to approach that of the Cb₂N under normal conditions. Apparently, the heavier the layer the darker the color. It would be advisable for anyone planning to use this technique to establish his own standards, using the information in this report as a guide.

Oxides

Standards for the determination of oxides were taken from tests concerning the oxidation of columbium at low oxygen pressures by H. Inouye⁽³⁾ of the Metals and Ceramics Division.

Figure 6 is a photomicrograph of columbium oxidized in air at 5×10^{-4} mm Hg pressure and 1000°C and shows three layers have formed. The inner layer is CbO and appears a lighter blue than the matrix. The middle layer is CbO₂ and has undergone no color change from the as-polished condition where it appears gray green. It is anisotropic and its grain structure normally can be faintly seen, although it is not obvious in this figure. The outer layer is Cb₂O₅ and is a mottled brown. The compositions of these layers were determined by X-ray diffraction examination of successive samples scraped from the surface of duplicate test coupons. The first sample contained primarily Cb₂O₅ and some CbO₂. The second sample was primarily CbO₂ and some CbO, and the third sample was CbO and Cb.

Y-45459

Figure 3 - Carbide needles in Cb - 1% Zr alloy containing 500 ppm C.

Y-45458

Figure 4 - Columbium exposed to nitrogen for 1365 hr. at 1200°C. The bright layer is CbN and is yellow. The dark layer and needles are Cb₂N and are rose pink.

Y-45460

Figure 5 - Columbium from lithium corrosion test after accidental exposure to air leak. Layers and phases are nitrides.

Y-49056

Figure 6 - Columbium oxidized in air at 5×10^{-4} mm Hg at 1000°C. Note three distinct oxide layers.

Figure 7 is a photomicrograph of a single crystal of Cb with CbO and CbO₂ on the surface. (Note the anisotropy of the CbO₂.) This sample had been in oxygen at 1×10^{-4} mm Hg pressure at 1000°C for 50 hr.

CONCLUSIONS

The following table lists the contaminants of columbium, the compounds they form, and their characteristic colors upon anodization.

<u>Contaminant</u>	<u>Compound</u>	<u>Color</u>
Carbon	Cb ₂ C	Yellow
	CbC	Bright yellow
Nitrogen	Cb ₂ N	Rose pink
	CbN	Yellow
Oxygen	CbO	Sky blue
	CbO ₂	Gray green
	Cb ₂ O ₅	Reddish brown (mottled)

This procedure is recommended for the metallographic identification of carbon, nitrogen, and oxygen contaminants in columbium without having to resort to X-ray diffraction or qualitative chemical analysis. It is further recommended that individuals intending to use this procedure first establish their own color standards. Written descriptions of colors are usually inadequate as they reflect the writer's own visual experience.

REFERENCES

1. Ence, E., and H. Margolin, "Phases in Titanium Alloys Identified by Cumulative Etching," J. Metals, 346-348, March, 1954.
2. McCoy, H. E., and D. A. Douglas, "Effect of Various Gaseous Contaminants on Strength and Formability of Columbium," in Columbium Metallurgy, Vol. 10, p. 85, Interscience Publishers, Inc., New York, 1961.
3. Inouye, H., "Oxidation of Columbium at Low Oxygen Pressures," in Columbium Metallurgy, Vol. 10, pp. 649-665, Interscience Publishers, Inc., New York, 1961.

Y-45456

Figure 7 - Single crystal of columbium oxidized in oxygen at 1×10^{-4} mm Hg for 50 hr. at 1000°C . The two layers were identified as CbO (inner) and CbO_2 (outer).

MATERIALS RESEARCH
WITH THE SCANNING MICROPROBE ANALYZER

J. W. Lenke and R. F. Domagala
IIT Research Institute
Chicago 16, Illinois

Electron-beam microprobe analyzers have become an accepted and often vital tool for conducting many research tasks in the materials field. The "scanning" microprobe permits linear traces or two-dimensional X-ray pictures to be presented showing the distribution, depletion, or enrichment of a given element of atomic number 12 or greater in a selected zone. This paper briefly describes some of the studies that have been conducted at the IIT Research Institute using a Cambridge Instruments Ltd. microprobe.

INTRODUCTION

The use of X-rays for chemical analysis dates back to the nineteen-thirties although the principles involved were known in the early nineteen-hundreds. It was not until 1951 that Castaing⁽¹⁾ assembled and demonstrated the first practical electron probe X-ray microanalyzer (microprobe). About the same time a Russian named Borovsky⁽²⁾ also designed and built a probe. Most of the credit for the development of the microprobe, however, is generally given to Castaing. The earliest probes were 'static' and depended on mechanical and/or optical means to locate the specimen under the electron beam. The addition of a 'scanning' and display system by Melford and Duncomb⁽³⁾ greatly increased the versatility and ease of use of the microprobe.

EQUIPMENT

The instrument in use at the Institute is a Cambridge Instruments Ltd. microprobe. A photograph illustrating the unit is shown in Figure 1, while the circuit diagram of the microprobe is schematically represented in Figure 2. From left to right in Figure 1, the first rack contains the power supplies for the electron gun. The desk at the center contains the electron gun, condenser and objectives lenses, scanning coils, counters, optical microscope (180° from the electron beam), and the sample stage. The desk also holds the vacuum system and the controls for the lenses. In the rack to the right of the desk are the display cathode ray tubes with their power supplies and positioning controls, the power supplies for the counters, and the power supplies for the lenses. The next rack contains the pulse monitor, pulse analyzer, ratemeter, and the X-ray channel amplifier. The last rack is the recording rack and contains the scaler and pen recorder. The function of each of these components will become more apparent as the various operations possible with this instrument are discussed.

Figure 1 - View of Cambridge Instruments, Ltd. microprobe analyzer at Illinois Institute of Technology.

Figure 2 - Schematic illustration of the microprobe analyzer.

The actual operation of the probe is quite simple. The specimen surface is bombarded with a beam of electrons which causes X-rays to be generated. In the scanning microprobe, the finely focused (0.5 μ diameter) beam is scanned over the specimen surface in a raster 0.5 mm on a side (the values are for the Institute's microprobe at minimum magnification.) As the probe or electron beam is being scanned, the spots on the faces of the display cathode ray tubes are moving in precisely the same raster only in a 3-inch square thus providing the magnification. The intelligence is provided by the two counters in the column. The scintillation counter consists of a plastic rod with phosphor on one end and a photomultiplier tube at the other. This provides the brightness or "Z" axis modulation for the electron image. The proportional counter in conjunction with the crystal spectrometer provides similar information for the X-ray image.

The electron image is formed by electrons reflected from the surface of the sample striking the phosphor on the end of the plastic rod generating light. The light is conducted up the rod to the photomultiplier tube and then to the display tube. The differences in contrast are produced by the topography of the sample or by the differences in mean atomic number of its constituents. The image obtained in this way is very much like an optical image obtained with oblique lighting. Since the faces of the display tubes are coated with a long-persistence phosphor, it is possible to position the probe in the area of interest in the 'afterglow'. In this way the exact location of the analysis is known. Examples of this type of display are included in this paper and they are labeled "electron image."

The X-ray image is formed in much the same way except that the output of the spectrometer is used. The image is actually an integration of a series of dots on the face of the tube. The contrast is provided by differences in concentrations of the element that the spectrometer is tuned to measure. In all photographs included in this paper, the brighter the area the higher the concentration of the element.

Quantitative spot analyses are obtained by switching off the frame and line time bases and positioning the probe into the area of interest in the afterglow as described above. The intensities of the elements (above atomic number 12) are recorded and compared with the intensities obtained from standards of known composition. The standards are most often pure metals, but alloys are preferred if it is possible to produce them with the necessary accuracy and homogeneity.

SAMPLE AND SAMPLE PREPARATION

The ideal sample for use in the Institute's microprobe is a right cylinder 1/4-inch in diameter and 1/8-inch thick. Smaller specimens are "potted" in Woods metal to give a sample of the proper size. The samples must be metallographically polished but should not be etched. Etching can selectively remove and deposit some of the elements, causing false distribution data to be obtained. Care must be taken to avoid relief-polishing as the hills and valleys caused will give spurious quantitative data. A specimen holder is illustrated in Figure 3.

Figure 3 - Photo of specimen holder, unassembled and assembled.

APPLICATIONS

The identification of inclusions in a variety of metals is one of the many uses for the Institute's microprobe. An illustration of this type of analysis is shown in Figures 4 to 6. Figure 4 is the electron image showing an inclusion in steel. Figures 5 and 6 are X-ray images for manganese and sulfur. In this type of study a presentation of a series of photographs such as this is often all that is required. Comparisons of the brightness of different areas of a given photo are valid and permit qualitative evaluations of the concentration of an element. It is not possible, however, to compare X-ray images of two elements and judge that because the photo for one element is brighter its concentration is greater.

An application that is similar to inclusion identification is that of phase identification in multiple-phase alloys. Figures 7 and 8 represent an example of this type of study. The sample is a Zr-30 w/o Fe alloy heat-treated 313 hr. at 750°C. Figure 7 is the Zr X-ray image, and Figure 8 is the Fe X-ray image. As can be seen, there are three phases present. Spot analyses of the three phases indicated the following compositions:

- (1) 53.4w/o Fe-37.6w/o Zr, corresponding approximately to ZrFe_2
- (2) 23.1w/o Fe-72.9w/o Zr, corresponding to Zr_2Fe
- (3) 16.8w/o Fe-83.4w/o Zr, corresponding to Zr_3Fe .

The microprobe is admirably suited for phase diagram work. A good example of this type of study conducted for the plutonium-iron system has recently been described⁽⁴⁾ by Scott and Ranzetta. In the same journal, an article by Swindells⁽⁵⁾ covers the more-or-less theoretical aspects of phase equilibria studies with the microprobe.

The study of diffusion rates is another area where the microprobe can save a great deal of work. Instead of having to carefully machine layers for wet-chemical analyses it is possible to move the sample along under the probe and perform as many analyses as required to give the desired concentration vs. distance curve. Equally important, very thin diffusion layers can easily be studied. Figure 9 is an example of the type of curve that can be obtained if the diffusion zone is small enough to fit in the 0.5 mm scan of the microprobe. If the diffusion zone is larger, the only additional work that is necessary is to place some sort of guide marks (e.g. microhardness indentations) on the sample along a line perpendicular to the interface at about 0.5 mm intervals. The display shown in Figure 9 was obtained by applying the output of the rate meter to the vertical deflection plates of one of the display tubes and moving the probe across the sample at the same time.

1000X

Figure 4 - Electron image of two globular inclusions in a steel specimen. This view is comparable to a light microscope image as seen with oblique light.

1000X

Figure 5 - Manganese K_{α} X-ray image of the same area shown in Figure 4. A manganese concentration at the inclusion sites is clearly evident.

1000X

Figure 6 - Sulfur K_{α} X-ray image of the same area as shown in Figs. 4 and 5. A comparatively high level of sulfur is indicated at the inclusion sites.

500X

500X

Figure 7 - Zirconium K X-ray image of a Zr-30% α w/o Fe alloy annealed at 750°C.

Figure 8 - Iron K X-ray image of the same area as shown in Figure 7.

1280X

Figure 9 - Line scan of diffusion zone in a couple composed of Ti/Ti + 10% w/o V. This sample was annealed at 700°C for 720 hours. The diffusion zone is 0.0002 inch wide. The vanadium content is represented by the ordinate. The abscissa is distance.

The samples discussed above have all been metallic. Nonmetallics can also be analyzed if they are first coated with some conductor to prevent the buildup of a surface charge that would defocus the electron beam. A vapor-deposited layer of aluminum about 200 Å thick does a fine job in this respect and does not interfere with the analysis. An example of an application of this technique is shown in Figures 10 to 13. These figures do not represent a complete analysis of the meteorite but are included to demonstrate the use of an aluminum coating on a nonmetallic sample.

The microprobe has proved very fruitful in the study of the chemistry of coatings on the surface of samples. The major problem encountered in such work is that of rounding of the edge of the sample and the cracking and spalling of the coating during polishing. By applying careful methods and, in some cases, plating a layer of nickel or some other material over the coating, satisfactory results have been obtained. Figures 14, 15, and 16 illustrate the type of work that has been carried out at the Institute on coated specimens. The coating here is 0.005 inch thick and the iron concentration curve is shown to demonstrate the amount of information which can be obtained from a layer of this thickness.

CONCLUSIONS

The examples of applications for the scanning microprobe analyzer cited above are but a few of the many possible uses to which this remarkable instrument can be applied. It is hoped that this paper will stimulate further interest in the utilization of such units. A few other areas where work can be done include, for example, a study of the chemistry of corrosion products formed on Zircaloy, determination of the extent of diffusion encountered in cladding operation, studies of homogeneity of alloys and composites, and investigations of brazed or welded joints.

REFERENCES

1. Castaing, R., Thesis, Univ. Paris, 1951 O. N. E. R. A. Pub. No. 55.
2. Borovsky, I. B., "Problemy Metallurgii," Moscow, Acad. Science, USSR, 1953, p. 135.
3. Duncumb, P., and Melford, D., "Proceedings of the 2nd Symposium on X-ray Microscopy and Microradiography," Stockholm, 1959 (Published 1960), p. 358.
4. Scott, V. D., and Ranzetta, G. V. T., Journal of the Institute of Metals, 90, 1961-62, p. 160.
5. Swindells, N., Journal of the Institute of Metals, 90, 1961-62, p. 167.

300X
Figure 10 - Electron image of meteorite sample.

300X
Figure 11 - Iron K_α X-ray image of meteorite sample shown in Figure 10.

300X
Figure 12 - Nickel K_α X-ray image of same area as shown in Figure 10.

300X
Figure 13 - Sulfur K_α X-ray image of same area as shown in Figure 10.

350X

Figure 14 - Electron image of coated specimen. The base metal is at the bottom of this photo. Two layers and the intermediate diffusion zones are evident.

350X

Figure 15 - Iron K_α X-ray image of same area as shown in Figure 14. The iron was present in the outer layer. The diffusion of iron into the first layer and base metal and the slight but positive concentration at the diffusion zone adjacent to the base metal are clearly evident.

Figure 16 - Iron concentration curve for the area shown in Figures 14 and 15. This plot is constructed from data taken on a straight line perpendicular to the base metal.

171-20459

ELECTRON MICROSCOPY OF SINTERED BERYLLIA

Robert C. Rau
General Electric Company
Nuclear Materials and Propulsion Operation
Cincinnati 15, Ohio

Porosity, etching characteristics, and general microstructural features of extruded and sintered beryllium oxide have been studied by means of electron microscopy. Replicas were prepared from as-polished, polished and ultrasonically cleaned, polished and etched, and fractured surfaces. The techniques used in preparing and replicating these surfaces are presented, together with typical electron micrographs of the structures observed. Both pore structures and etching characteristics were shown to have a relationship to the hemimorphic hexagonal crystal structure of BeO. A form of twinning possible only in hemimorphic systems was also observed.

INTRODUCTION

With the increasing use of ceramic components in high-temperature nuclear environments, a knowledge of the effect of nuclear irradiation on the physical properties of beryllium oxide has become of vital importance. As part of a program to study these effects, electron microscopy is being used to examine porosity in sintered BeO. This paper deals with the observation of pore configuration in unirradiated beryllia, as well as some of the etching and general microstructural characteristics of the sintered material. It is felt that an understanding of these properties will aid greatly in the later interpretation of the microstructures of irradiated specimens.

BeO CRYSTALLOGRAPHY

Before proceeding with the observations of this study, it is well to review some of the aspects of the crystal structure of BeO, since this structure exerts a marked influence over observed pore structures and etching properties. The crystal symmetry of BeO is hexagonal hemimorphic; that is, the lattice lacks a center of symmetry. In such hemimorphic crystal systems, the unique, or c - axis, possesses anisotropic properties dependent upon the direction along which the c-axis is traversed. In the wurtzite-type crystal structure of BeO, the atoms occupy the following positions in the unit cell:

Be	000;	$1/3, 2/3, 1/2$
O	00u;	$1/3, 2/3, u + 1/2$

where u is near 0.365. This very nearly amounts to two interpenetrating hexagonal close-packed lattices, one containing only beryllium atoms and one containing only oxygen atoms. A model of this structure is seen in Figure 1, where large spheres represent oxygen and small spheres represent beryllium.

Close examination of the model shows that the spacing between layers of atoms along the c -axis (vertical) is not uniform, but consists of alternate short and long spacings between beryllium and oxygen planes. This stacking of the layers is represented diagrammatically in Figure 2, and is used to help explain some of the etching characteristics of BeO. Further examination of Figure 1 shows that the structure might also be thought of as being composed of BeO_4 and Be_4O tetrahedra⁽¹⁾, the apexes of which point in opposite directions along the c -axis respectively. This directionality of the tetrahedral units imparts hemimorphism to the structure, and is the cause of the anisotropy of properties along the c -axis. The direction in which the apexes of the BeO_4 tetrahedra point has arbitrarily been chosen to be positive, as designated in Figure 2.

SAMPLE PREPARATION

Specimens whose structures were studied by electron microscopy were high density (2.90 to 2.95 gm/cm³), sintered cylindrical rods which were fabricated from several BeO materials. These compositions included two commercially available grades (AOX and UOX)* of BeO whose total impurity levels are between 800 and 2000 ppm⁽²⁾, and one specially prepared high purity grade of BeO^+ whose total impurity content was found to be between 100 and 150 ppm⁽²⁾. The specimens of the UOX material which were examined contained 0.5 weight percent of MgO which had been added prior to fabrication. No difference in pore microstructures and/or etching characteristics were noted in the various BeO materials examined.

The BeO rods were formed by extrusion, and, after prefiring in air, were sintered in hydrogen. The sintering times were varied from 2 to 120 hours at temperatures from 1500 to 1700°C to produce bodies of the desired density and grain size. In general grain size control was exercised by heating for short times at the lower temperatures to obtain uniformly fine grain-sized material, and heating for long times at higher temperatures to produce uniformly large grains. In this manner, grain sizes from less than 20 microns to greater than 100 microns were obtained. Observations showed that although general pore configuration was unaffected by grain size, large grained material contained larger pores than did small grained specimens.

- - - - -
- * AOX and UOX grades of BeO supplied by the Brush Beryllium Company.
 - + High purity BeO, designated HPA, prepared by calcination of basic acetate-derived beryllium hydroxide obtained from the Mineral Concentrates and Chemical Company.

Figure 1 - Model of BeO structure.

Figure 2 - Diagram showing mode of stacking along c-axis of BeO.

PREPARATION FOR ELECTRON MICROSCOPY

Surface Preparation

In order to fully characterize the structure of sintered beryllium oxide by means of electron microscopy, sections have been examined in several conditions, each requiring specific preparation and replication techniques. Surface conditions studied include as-polished, polished and ultrasonically cleaned, polished and etched, and fractured. Electron micrographs showing these surface conditions are included in this report.

Proper polishing of BeO surfaces is a very important, and often difficult, step in the preparation for microstructural investigation. In particular, the hardness and brittleness of BeO requires that special care be taken during processing to avoid chipping, grain pull-out, and relief polishing. In order to produce very smooth, damage-free surfaces, the following procedure was used with Buehler Automet automatic polishers. Rough grinding was performed on wet 240 grit Si C paper followed by 400 grit SiC paper. After the 400 grit paper, samples were examined under a light microscope to see if the polishing had begun. It is felt that the 400 grit abrasive actually begins to polish BeO at the end of this cycle due to the breakdown of SiC particles. When such action occurred, the samples were transferred to 3 micron diamond compound on nylon cloth, using kerosene as a lubricant. If subsequent examination then showed an improved surface, the samples were felt to be ready for final polishing. This final polishing was performed using a water slurry of 0.3 micron α -alumina on nylon cloth. Throughout these grinding and polishing operations, fairly light pressures and short operating times were utilized to minimize the chance of mechanical damage to the BeO surfaces.

Subsequent etching of polished BeO was then accomplished by immersing or swabbing in a 50 percent solution of concentrated hydrofluoric acid in water. Etching times varied from a few minutes for a light etch suitable for electron microscopy, to nearly an hour for a heavy etch to delineate grain boundaries at optical magnification. Etching served not only to outline grain boundaries in the BeO, but was also found to be quite helpful in cleaning residual polishing debris out of the pores.

In order to clean polishing debris from pores without resorting to etching, ultrasonic cleaning of as-polished surfaces was attempted. This cleaning, lasting for periods of a few minutes up to an hour, was performed with the sample suspended upside down in the cleaning tank so that debris would fall out as it became loosened. Generally, large or shallow pores were quite effectively cleaned in this manner, but deeper pores of small diameter were only partially cleaned, if at all.

Replication

Two basic techniques have been used to obtain electron microscope replicas of the various types of BeO surfaces. These methods, which do not damage

the original sample surface, have been found to be quite reproducible and accurate in detail over the range of electron microscope magnifications employed.

To replicate fairly smooth surfaces, such as the as-polished BeO specimens, a single-stage direct-stripping technique yielding a negative nitrocellulose replica was used. This method involved forming a thin layer of the plastic on the specimen surface by flowing a 1% solution of nitrocellulose in amyl acetate over the sample. After the solvent evaporated, the plastic replicas were recovered on stainless steel support grids fastened to cellophane tape. Causing moisture from the breath to condense on the plastic-film covered surface immediately prior to stripping allowed the plastic film to separate from the BeO surface without tearing. After stripping, the replica-covered grids were carefully removed from the cellophane tape with tweezers and placed in an evaporator for shadow-casting. Shadowing was performed by depositing chromium metal at an angle of about 30 degrees to the replica surface.

For replicating rougher surfaces containing open pores or etched structures, a more complicated, two-stage method was used. One mil cellulose acetate sheet, softened with methyl acetate, was first placed on the specimen surface to form a "thick" primary replica. After stripping, this primary replica was placed in an evaporator and shadowed with chromium, usually from two different directions about 150 degrees apart. This double shadowing was found to be quite effective in outlining details of these rough surfaces which would have been hidden by a single shadow. After shadowing, carbon was deposited at normal incidence over the shadow layer, and the replicas were removed from the evaporator and coated with the nitrocellulose solution used in direct replication. Small squares were then cut from the replica "sandwich" and placed in a series of dissolution baths which finally yielded electron microscope replicas composed only of the carbon and chromium layers. This dissolution was carried through a total of five baths; two containing ethylene dichloride, one containing three parts ethylene dichloride to one part acetone, one containing equal parts of these solvents, and one containing pure acetone. Dissolution times in each bath were necessarily long (often overnight) in order to prevent disintegration of the carbon film as the plastic layers dissolved. After the final rinse in acetone, replicas could then be picked up on support grids for electron microscopy. Carbon films which had curled during the dissolution process could usually be straightened by placing them on a water surface after the acetone rinse.

Although the above two-stage method was used for most rough-surface replications, a slightly different method was used to replicate the extremely rough surfaces of fractures. The procedure was the same as the above, with the exception that ten mil cellulose acetate was substituted for the one mil sheet used for the primary replica. The thicker sheet better resisted tearing during stripping from the rough specimen. Usually, dissolution

of the plastic layers from the resulting thick-sheet replicas could be performed directly in acetone, since the irregular contours in the replica imparted enough structural strength to the carbon layer to resist tearing by the rapid action of the acetone.

RESULTS

Electron microscopy was performed with an RCA EMU-2B electron microscope operating at a potential of 50 kilovolts. In general, observations on sintered BeO can be divided into three categories: Microstructure of pores, etching characteristics, and observation of twinning.

Microstructure of Pores

Pores having shapes mirroring the crystal symmetry of the surrounding grains have been reported in the past in sintered UO_2 (3) and, more recently, in BeO(4). This fact should not be surprising, since the same energy forces acting on the free surfaces of growing crystals can also act on free void surfaces within those crystals. The present study has shown that pores in BeO occur as negative crystals having hemimorphic hexagonal shape displaying the symmetry of the BeO lattice. Evidence of this pore structure can be seen in micrographs obtained from all the different types of BeO material and surfaces studied.

Figure 3 shows typical electron micrographs of as-polished BeO. Pores are seen to appear as roughened areas on the otherwise smooth surfaces, this roughening being due to the polishing debris with which they are filled. That this debris is tightly packed is attested to by the fact that replication did not pull it out, but rather simply replicated the irregular particles. The micrograph of Figure 3-A shows both inter- and intragranular pores. It can be seen that intergranular pores tend to be elongated along the boundary, and this characteristic is often the only means of identifying the otherwise invisible grain boundaries in as-polished sections. Intragranular pores sometimes exhibit shape characteristics in as-polished sections. Figure 3-B shows a pore with a quite definite hexagonal outline.

In order to see the internal structures of pores in polished BeO, some specimens were studied after ultrasonic cleaning. Distinct pore structures were then observed, as shown in Figure 4. These micrographs, obtained from large grain-sized material, show clearly the hexagonal hemimorphic symmetry of the pores. As explained previously, this hemimorphism is due to the atomic arrangement of BeO. Figure 4-A shows two pores in a grain whose c-axis is tilted with respect to the plane of polishing. Figure 4-B also shows two pores, the smaller of which is still filled with polishing debris. These pores indicate that the c-axis of their surrounding grain is in the plane of the photograph.

5000X

Neg. 566E

(a) Inter- and intragranular pores.

13,500X

Neg. 432C

(b) Intragranular pores.

Figure 3 - Electron micrographs of as-polished BeO.

7500X

Neg. 494E

(a) Intragranular pores, c-axis tilted.

10,000X

Neg. 495D

(b) Intragranular pores, c-axis horizontal.

Figure 4 - Electron micrographs of polished and ultrasonically cleaned BeO surface.

By comparing the pore faces with the crystallographic forms known to occur on crystals of the natural BeO mineral bromellite(5), tentative identification of the faces can be made. On this basis, the hexagonal (or twelve-sided) end faces of the pores in Figure 4-A are assumed to be positive basal planes (0001), and the large flat base of the pore in Figure 4-B is assumed to be the negative basal plane, (000 $\bar{1}$). These positive and negative notations merely indicate arbitrarily the two directions of the c-axis. Also based on the comparison with bromellite, various prism and pyramid faces can also be tentatively identified. For instance, the pronounced faces parallel to the c-axes of these micrographs are believed to be the first order prism faces, (10 $\bar{1}$ 0). Accordingly, the grain containing the pores in Figure 4-B is thought to have an orientation with (10 $\bar{1}$ 0) very nearly parallel to the polished surface. Examples of other such deduced orientations will be seen in succeeding illustrations.

One further illustration of porosity in as-polished BeO is seen in Figure 5. This photograph shows an area where a grain has been pulled out during polishing, exposing a number of grain boundary pores exhibiting various shapes related to their surrounding grains. It must be remembered that this pulled out grain and pores are not protruding from the surface, but are actually depressions. Their appearance as protrusions is due to the replication and shadowing procedure.

As an additional method of observing unetched pores, fractured BeO surfaces were studied. An electron micrograph showing several pores in such a surface is seen in Figure 6. The large pore is seen to exhibit definite hemimorphic hexagonal shape.

Etching Characteristics

As mentioned earlier, specimens were studied after various degrees of etching. This etching outlined grain boundaries, produced etch structures on various grain surfaces, and cleaned polishing debris from the pores. A general view of a BeO surface after a medium etch is shown in Figure 7. This figure shows the extreme differences in etching characteristics dependent upon grain orientation, and also shows grain boundaries quite clearly delineated. Pore structures again exhibit the symmetry of the BeO lattice.

Figure 8 shows a grain boundary pore in an etched surface. The difference in etching of the two grains in the micrograph is apparent. The pore is seen to have some structure, visible as "growth" steps or rings on its sides. These probably represent pyramid faces which intersect the c-axis at an angle, and the flat face is believed to be either the (0001) or (000 $\bar{1}$) face.

Figure 9 shows introgranular pores in an etched BeO surface. The pore in Figure 9-A shows some dark debris surrounding it in the replica, but nevertheless displays quite well its hemimorphic symmetry. By analogy with

7500X

Neg. 529C

Figure 5 - Pulled-out grain in as-polished BeO surface.

17,000X

Neg. 542A

Figure 6 - Pores in fractured BeO surface.

5000X

Neg. 570A

Figure 7 - Electron micrograph of polished and etched surface of BeO.

15,000X

Neg. 427B

Figure 8 - Grain boundary pore in etched BeO.

27,000X

Neg. 424B

(a) Pore showing hemimorphic symmetry.

20,000X

Neg. 430B

(b) Flat-bottomed pore showing hexagonal symmetry.

Figure 9 - Intragranular pores in etched BeO surface.

the bromellite structure, the small striated face that is essentially parallel to the etched surface is believed to represent the second order prism face, $(11\bar{2}0)$, and the sloping pyramid faces are believed to be $(10\bar{1}1)$ planes. Figure 9-B shows a very flat-bottomed pore in a grain whose c-axis is evidently normal to the photograph. This pore displays "growth" rings similar to those of Figure 8 arranged hexagonally around its periphery. These rings probably represent growth stages of the lower pyramid faces, $(10\bar{1}1)$. The large bottom face of this pore is believed to represent the negative basal plane, $(000\bar{1})$.

The etch structure of the grain surface surrounding the pore in Figure 9-B is composed of little hillocks with craters in their centers, much resembling volcanic cones. This rather unusual structure has been found to be characteristic of etched grains whose pores exhibit $(000\bar{1})$ faces nearly parallel to the grain surface. However, this structure is not characteristic of grains whose pores have (0001) faces parallel to the grain surface. This indicates that the etching characteristics of the basal planes of BeO are dependent upon the direction along the c-axis from which those planes are approached. An example of this preferential etching is seen in Figure 10, which shows two pores in large-grained BeO after a 40 minute etch. Figure 10-A, at a lower magnification than Figure 9-B, shows a well-developed "volcano" structure in a grain with near $(000\bar{1})$ orientation, with extraordinarily large cones present in the pore itself. Figure 10-B shows a pore having a well-formed (0001) face which shows little if any attack by the etchant. The surrounding grain surface, though not oriented with its c-axis so nearly normal to the plane of the photograph as was true in Figure 9-B and 10-A, shows the general lack of attack associated with grains having (0001) orientations.

The explanation of this hemimorphic etching behavior of BeO is believed to lie in the atomic stacking within the crystal lattice. As pointed out previously, and shown in Figures 1 and 2, beryllium atoms are tetrahedrally coordinated with oxygen atoms, these tetrahedra all pointing in one direction along the c-axis. Thus, beryllium planes viewed along the negative direction of the c-axis show the beryllium atoms each nestled tightly between three oxygen atoms, while planes viewed along the positive direction of the c-axis show the beryllium atoms quite exposed and each singly bonded to an oxygen atom directly beneath. This arrangement affords the beryllium atoms protection from chemical attack when approached from one direction along the c-axis, but leaves them quite vulnerable when attacked from the opposite direction.

A further example of electron microscopy of heavily etched BeO surfaces is shown in Figure 11. Figure 11-A shows a general view of heavily etched grains, again showing difference in etching behavior with grain orientation. Figure 11-B shows a pore in BeO after 40 minutes of etching. This pore is still of the average size seen in this sample before etching, thus supporting the observation that pores are not greatly enlarged by etching. Figure 11-B shows that the natural pore faces are probably fairly stable against etching

7500X

Neg. 506D

(a) Pore showing $(000\bar{1})$ face.

15,000X

Neg. 509D

(b) Pore showing (0001) face.

Figure 10 - Intragranular pores in heavily etched BeO surface.

4000X

Neg. 515E

(a) General view of surface

13,500X

Neg. 506B

(b) Intragranular pore.

Figure 11 - Electron micrographs of heavily etched BeO surface.

attack, since it can be seen that the surrounding grain surface has been etched into grooves parallel to the pore prism faces. The etched structure is probably approaching the most stable configuration during chemical attack.

Observation of Twinning

From the observations of etched grain structures as previously described, a rather unusual type of twinning was observed in some of the BeO grains. These twins occur with both sections of the twin having their c-axes parallel but pointing in opposite directions. Such twins, possible only in a hemimorphic crystal system, are shown in the electron micrographs of Figure 12. The two portions of the twins are delineated quite clearly by the different etching characteristics of the positive and negative basal planes, as discussed in the preceding section.

The twin boundaries are seen to follow predominantly straight lines, quite unlike random grain boundaries, and angular deflections of roughly 120° are common. The electron micrographs show hexagonal-shaped pores in parallel alignment in both halves of the twins, and occasionally an undistorted hexagonal pore is seen located on a twin boundary. These pores have their hexagonal sides aligned parallel to the twin boundaries. From the assumption that the sides of the hexagonal pores are first order prism planes, it can therefore be deduced that the composition plane observed in twinned BeO is $(10\bar{1}0)$.

CONCLUSIONS

Several microstructural characteristics of sintered beryllia have been studied by means of electron microscopy of surface replicas. These replicas, obtained from several types of BeO material and surfaces, have revealed that pores in the sintered bodies take the shapes of hexagonal hemimorphic negative crystals directly related to the surrounding lattice. Plane faces of these pores have been tentatively identified by comparison with the known crystallographic habit of the natural beryllia mineral, bromellite.

The differential etching characteristics of various BeO planes have also been observed and related to crystallographic orientation by means of the pores occurring in the grains. An interesting observation resulting from this analysis is that the basal plane of BeO etches differently depending upon the direction of approach to that plane. This differential attack is attributed to the atomic stacking which imparts hemimorphism to the lattice.

Twinning, with $(10\bar{1}0)$ as the composition plane, has been observed on etched BeO surfaces. This type of twinning, with the c-axes of the two portions of the twin parallel but pointing in opposite directions, is possible only in a hemimorphic crystal system.

10,000X

Neg. 542C

10,000X

Neg. 543C

Figure 12 - Twinned grains in BeO.

REFERENCES

1. R. W. G. Wyckoff, "Crystal Structures," Vol I, Chap. III, Interscience Publishers, Inc., New York.
2. GEMP-106A, "First Annual Report - High Temperature Materials Program," General Electric Company, Nuclear Materials and Propulsion Operation, Feb. 28, 1962.
3. S. Takahashi, H. Uchikoshi, R. Sato, B. Ishii, and T. Kubota, 3rd Symposium on Atomic Energy, Japan, February, 1959.
4. A. Bisson and H. Frisby, "Observation au Microscope Electronique des Porosites, des Inclusions de Carbone et des Dislocations dans l'Oxyde de Beryllium Fritte sous Charge," J. Nucl. Mat'ls., Vol. 4, No. 2, July, 1961, pp. 133-142.
5. C. Palache, H. Berman, and C. Frondel, "Dana's System of Mineralogy", Vol. I, 1944, pp. 506-507, John Wiley and Sons, Inc., New York

ELECTRON MICROSCOPE STUDIES OF IRRADIATED A-286 ALLOYS

Robert C. Rau
General Electric Company
Nuclear Materials and Propulsion Operation
Cincinnati 15, Ohio

Results of electron microscopy presently being performed on irradiated A-286 alloy specimens are presented. The metallographic polishing and etching techniques used for irradiated and unirradiated control specimens are discussed, together with the replication technique employed for electron microscopy of the specimens. A method of remotely obtaining single-stage direct-stripped replicas from irradiated specimens has been developed, and is also described in this report.

INTRODUCTION

As a part of the High Temperature Materials Program to study the effects of nuclear radiation on high-temperature alloys, structural investigations are being performed on irradiated and unirradiated A-286 alloy specimens. The aim of these structural studies is to determine, if possible, the mechanism of radiation damage in the alloy by delineating the microstructural changes occurring because of irradiation.

Structural studies are presently concentrated most heavily on electron microscopy of the metallographically prepared specimen surfaces, since it is felt that radiation-induced changes in structure will be of such small magnitude as to be observable only at extremely high magnifications. A-286 specimens from two irradiation experiments have thus far been examined.

SPECIMEN PREPARATION

The high-temperature alloy A-286 is a precipitation-hardenable austenitic iron-base alloy having the rather dubious distinction of being extremely complex in its precipitation and phase reactions. Due to this complexity in chemical behavior, the interpretation of microstructures produced by various heat treatments on different lots of A-286 can also become quite complicated. Nevertheless, because of the commercial importance of this alloy, more or less standard heat treating procedures have been devised which produce characteristic and reproducible microstructures. Most of the phases appearing in these microstructures can now be readily identified, due mainly to the extensive work of Beattie and his co-workers.(1-4) Table 1 shows the nominal composition of A-286.

TABLE 1

NOMINAL COMPOSITION OF A-286

<u>Element</u>	<u>Weight Percent</u>
Ni	24.0 - 27.0
Cr	13.5 - 16.0
C	0.08 max
Mn	1.0 - 2.0
P	0.04 max
S	0.04 max
Si	0.4 - 1.0
Mo	1.0 - 1.5
Ti	1.9 - 2.3
Al	0.35 max
V	0.1 - 0.5
B	0.003 - 0.01
Fe	balance

The two irradiation experiments from which samples have been examined by electron microscopy have been designated the shielded-unshielded experiment and the overaged-underaged experiment. The shielded-unshielded experiment was designed to study the relative effects of low energy neutrons on normally aged A-286, while the overaged-underaged experiment was designed to study the effects of reactor neutrons on specially aged A-286. Samples for study were taken from broken stress-rupture bars from which mechanical property measurements had previously been obtained.

Four specimens from the shielded-unshielded experiment were examined by microscopy. Table 2 lists these specimens together with their irradiation histories. The areas examined were the relatively unstressed button heads of the broken tensile bars. By avoiding the highly stressed areas of the reduced sections it was felt that any microstructural changes which might be observed could be ascribed only to the neutron irradiation.

TABLE 2

SHIELDED-UNSHIELDED EXPERIMENT:
SAMPLES SUBMITTED FOR STRUCTURAL STUDIES

<u>Specimen No.</u>	<u>Specimen Type</u>	<u>nvt En > 1 Mev</u>	<u>nvt Thermal</u>	<u>Irradiation Temperature</u>
75L	Unshielded	3.0×10^{16}	1.2×10^{17}	36°C
76L	Shielded	3.5×10^{16}	2.4×10^{16}	36°C
2AS	Control	None	None	-
28J	Control	None	None	-

A-286 specimens for the shielded-unshielded experiment received the standard heat treatment of solutioning and double aging as follows:

900°C	-	2 hours	-	Oil quench
720°C	-	16 hours	-	Air cool
650°C	-	16 hours	-	Air cool

The shielded and unshielded specimens were then irradiated at pile ambient temperature, and both irradiated and unirradiated control specimens were subsequently rupture tested at 650°C.

Specimens from the overaged-underaged experiment are listed in Table 3, together with their irradiation histories. Similar to the samples studied from the shielded-unshielded experiment, microstructural investigations were concentrated in the relatively unstressed button heads in an effort to discover changes due only to irradiation.

TABLE 3
OVERAGED-UNDERAGED EXPERIMENT:
SAMPLES SUBMITTED FOR STRUCTURAL STUDIES

Specimen No.	Specimen Type	nvt En > 1 Mev	Irradiation Temperature
18AA	Overaged	None	-
12AA	Overaged	6.5×10^{19}	540°C
8AA	Underaged	None	-
2AA	Underaged	7×10^{19}	540°C

In order to produce an overaged structure in specimens 12AA and 18AA, they were subjected to the following solution and double aging heat treatments:

925°C	-	2 hours	-	Water quench
815°C	-	200 hours	-	Air cool
650°C	-	100 hours	-	Air cool

Following this, specimen 12AA was irradiated at 540°C for 100 hours while control specimen 18AA was heated at 540°C for 500 hours to simulate a reactor cycle. Both specimens were then rupture tested at 540°C. It is felt that 540°C heating does not influence the structure of A-286 sufficiently enough to be visible by electron microscopy.

Due to a shortage of A-286 specimens for the overaged-underaged experiment, specimens for the underaged portion of that experiment had to be obtained from a supply of machined tensile bars which previously been overaged. Thus,

underaged specimens 2AA and 8AA were first subjected to the overage heat treatment listed previously, followed by a re-solution heat treatment of two hours at 900°C and water quenching. Irradiated specimen 2AA was then irradiated at 540°C for 100 hours and unirradiated specimen 8AA was heated at 540°C for 500 hours to simulate a reactor cycle. Both specimens were subsequently rupture tested at 540°C. This low temperature heating at 540°C is not believed to produce significant aging in A-286.

PREPARATION FOR ELECTRON MICROSCOPY

Structural investigations included both optical and electron microscopy of the metallographically polished and etched surfaces, but since electron microscopy was of prime interest, replica techniques were emphasized. In order to prepare the surfaces for replication, both mechanical and electropolishing methods were tried. However, since the NMPO remote metallographic facility is not presently equipped for electropolishing of irradiated specimens, it was decided to polish all specimens mechanically.

Grinding and polishing was performed on Buehler Automet automatic polishers, using SiC abrasive papers and 0.3 micron α -alumina polishing abrasive. The Automet polishing of irradiated specimens was followed by vibratory polishing on a remotely operated Syntron unit, using 0.1 micron γ -alumina abrasive on pellow cloth, while Automet polishing of non-radioactive specimens was followed by hand polishing with γ -alumina on Gamal cloth. After this γ -alumina polishing, the specimens were given a 30 second immersion etch in a 92HCL-5H₂SO₄-3HNO₃ (volume percent) solution. Since previous experience with A-286 had shown that this first etching serves chiefly to remove the flowed and disturbed surface produced by mechanical processing, the samples were repolished with γ -alumina. Swab etching these repolished surfaces for 10 to 15 seconds in the 92-5-3 solution usually produced surfaces rivaling those prepared by electropolishing. In occasional instances where such treatment still did not produce surfaces showing properly delineated microstructure, a third polish and etch cycle was employed.

The prepared surfaces were then examined optically prior to replicating for electron microscopy. Unirradiated control specimens and the irradiated specimens for the shielded-unshielded experiment, which showed a low induced activity level, were replicated out-of-cell using a single stage direct stripping technique. This technique involved flowing a solution of 1 percent nitrocellulose in amyl acetate over the surfaces and allowing the solvent to evaporate. The resulting thin plastic film replicas were then recovered by lifting them from the specimen with cellophane tape to which stainless steel support grids had been fastened. Allowing moisture from the breath to condense on the plastic film-covered surface before stripping caused the film to separate without tearing. After stripping, the replica-covered grids were then carefully removed from the cellophane tape and placed in an evaporator for shadow-casting. Shadowing was done by depositing a thin layer of chromium metal at an angle of about 30° to the replica surface.

Irradiated samples 12AA and 2AA from the overaged-underaged experiment proved too radioactive to allow replication out-of-cell. Therefore, the

normal procedure was modified to allow remote replication within the cell, using Model 7 Master Slave manipulators. Nitrocellulose replicating solution was flowed over the specimen surfaces by means of an eyedropper. In order to provide the moisture necessary for successful replica stripping, a small electrically heated vaporizer supplying steam was substituted for the breathing operation. Thus, after the plastic films on the specimen surfaces were dry, the specimens were held in the flow of steam from the vaporizer for a few seconds. Immediately after steaming, a strip of cellophane tape, with stainless steel grid attached, was pressed over the specimen. Stripping the tape off the surface retrieved the replica. Replicas prepared in this manner were found to be non-radioactive, and could then be handled directly for shadowing and electron microscope examination.

RESULTS

Optical and electron micrographs were obtained from the prepared specimens and replicas, and are shown in the following illustrations. Due to the limited penetrating power of the 50 kilovolt electron beam of the RCA EMU - 2B electron microscope, no transmission studies on thin foils of the A-286 specimens were attempted.

Shielded - Unshielded Experiment

Figure 1 is an optical micrograph, obtained from the unshielded specimen (75L) showing structure typical of normally heat-treated A-286. Although some of the grain boundaries seem to be enlarged, the higher magnification and better resolution available with the electron microscope is necessary to resolve the complete microstructure. Optical micrographs of the shielded and unirradiated specimens appeared similar to that of the unshielded specimen.

Figure 2 shows representative electron micrographs of three of the specimens listed in Table 2. The microstructures of the unshielded and shielded irradiated bars are seen in Figures 2A and 2B respectively, while Figure 2C shows the microstructure of unirradiated control bar 2AS. Control sample 28J exhibited a microstructure very similar to that of 2AS. As illustrated by these photographs, the microstructures of the irradiated and unirradiated specimens are very similar, with no structural changes due to irradiation being observable. The microstructures shown in the photographs of Figure 2 are quite typical of A-286 after normal heat treatment.⁽²⁾ The phases appearing in the micrographs are identified in the figure.

Relatively large inclusions of the rather inert phases (Ti, Mo) C and/or Ti (C, N) can be seen both within grains and at grain boundaries. Prominent colonies consisting of platelets of eta (η) hexagonal Ni_3Ti phase and fibers of gamma prime (γ') cubic $\text{Ni}_3(\text{Al}, \text{Ti})$ phase are located in the grain boundaries, and a very fine dispersion of γ' is seen evenly distributed throughout the matrix. In addition, evidence is seen of a fine

250X

Neg. R21

Figure 1 - Optical micrograph of unshielded A-286;
Specimen 75L.

(Ti,Mo)C or Ti(C,N)

(a) Specimen 75L,
irradiated, unshielded

7500X

Neg. 503E

γ' Ni₃ (Al,Ti) fibers

η Ni₃Ti platelets

"G" phase, Ti₆Si₇Ni₁₆

(b) Specimen 76L,
irradiated, shielded.

7500X

Neg. 505D

γ' Ni₃(Al,Ti) dispersion

(c) Specimen 2AS,
unirradiated control.

7500X

Neg. MM528-1A

Figure 2 - Electron micrographs of A-286 from the shielded-unshielded experiment.

grain boundary precipitate presumed to be "G" phase, a complex cubic phase whose chemical formula is given as $\text{Ti}_6\text{Si}_7\text{Ni}_{16}^{(5)}$. This "G" phase is quite often a constituent of the microstructure of normally heat-treated A-286.

Overaged-Underaged Experiment:

Overaged A-286 exhibited a microstructure such as that shown in Figure 3. This optical micrograph, obtained from the irradiated specimen (12AA), is typical of both irradiated and unirradiated conditions. Close examination reveals a profusion of fine needles appearing throughout the matrix and many small inclusions at the grain boundaries. The electron microscope clearly resolves this microstructure, as shown in Figure 4. This electron micrograph shows a globular phase in the grain boundaries, probably enlarged "G" phase ($\text{Ti}_6\text{Si}_7\text{Ni}_{16}$). Enlarged globules of γ' [$\text{Ni}_3(\text{Al}, \text{Ti})$] and platelets of η (Ni_3Ti) are quite evident in the matrix.

Figure 4 offers a good example of the mode of precipitation of η phase. Two flat platelets of this phase can be seen nearly parallel to the exposed surface of the surrounding grain. These platelets are seen to exhibit roughly hexagonal outlines, a consequence of their hexagonal crystal structure. In order for such plates to precipitate in the face-centered cubic matrix with the greatest amount of conformity to the surrounding lattice, the basal (0001) plane of the η phase aligns itself parallel to the hexagonal-close-packed (111) planes of the matrix. This allows precipitation to occur with four different orientations, parallel to the sides of a tetrahedron, within each matrix grain. The large grain in Figure 4 exhibits η precipitation with the four possible orientations. In that grain, inclined platelets of η intersect the grain surface in three different directions, giving the appearance of needles roughly 60 degrees apart. These three platelet orientations are parallel to the sides of a tetrahedron, while the two plates parallel to the grain surface are parallel to the tetrahedron base.

A comparison between irradiated and unirradiated overaged structures is shown in Figure 5. From this illustration it can be seen that no definite changes in microstructure can be attributed to the irradiation, since both specimens exhibit the same type of phase distribution. The slightly rougher surface of the irradiated specimen is not due to irradiation, but rather is produced during etching of the polished surface. Such surface preparation is very difficult to reproduce exactly from one specimen to another.

As stated previously due to a shortage of tensile bars, underaged specimens were obtained by re-solutioning bars which had previously undergone the overaging heat treatment. The re-solution treatment given samples 2AA and 8AA was not sufficient to remove most of the microstructural constituents produced by prior overaging, as can be seen by comparing the optical micrographs of Figures 6 and 3. Figure 6, obtained from the irradiated underaged specimen

250X

Neg. R28

Figure 3 - Optical micrograph of overaged A-286;
Specimen 12AA.

5000X

Neg. 561D

Figure 4 - Electron micrograph showing typical structures
in overaged A-286; Specimen 18AA.

5000X

Neg. 560E

(a) Specimen 18AA, unirradiated.

5000X

Neg. 557E

(b) Specimen 12AA, irradiated.

Figure 5 - Electron micrographs of overaged A-286 specimens.

250X

Neg. R30a

Figure 6 - Optical micrograph of underaged A-286;
Specimen 2AA.

10,000X

Neg. 563A

(a) Specimen 8AA, unirradiated.

(b) Specimen 2AA, irradiated.

Figure 7 - Electron micrographs of underaged A-286 specimens.

POSSIBLE ARTIFACTS ASSOCIATED WITH THE MICROSTRUCTURE
OF URANIUM DEVELOPED BY ION BOMBARDMENT*

T. K. Bierlein, B. Mastel, and R. D. Leggett
Hanford Atomic Products Operation
Richland, Washington

16. 20953

Polished metallographic surfaces bombarded by rare gas ions can be etched due to ejection of surface atoms. Of several possible artifacts which may arise as a result of improper etching conditions, two have been studied by statistical metallography. Firstly, atoms which have been ejected from a uranium surface can collide with gas atoms and redeposit at preferential sites on the specimen, rather than deposit on the walls of the etching chamber. Redeposition is shown to increase with increased gas pressure. Secondly, small pores with a diameter of 0.08 to 1 μ intersected by the specimen surface may become artificially enlarged as a result of selective etching of the pore interior. In the case investigated, fission gas pores in irradiated uranium, enlargement of pores does not appear to occur to an appreciable extent. The techniques used and the results obtained are described.

INTRODUCTION

Cathodic vacuum etching or etching by ion bombardment is used in many laboratories to develop the microstructure of various metallic and non-metallic metallographic specimens. It is most popular in laboratories conducting certain AEC-sponsored work which involves characterizing and evaluating material associated with present and future reactor designs.

Etching by ion bombardment offers many advantages over the more conventional chemical or electrolytic etchants; in fact, it can be considered a "universal" etchant.⁽¹⁾ However, the metallographer must always exercise good judgment in interpreting the microstructural detail developed.

Etching by ion bombardment in its simplest form is a purely physical process. If a simultaneous chemical reaction occurs (for example, oxidation of a particular phase due to oxygen contamination of the inert gas), then the resulting microstructure may be adversely affected and erroneously interpreted.

During the past several years, many nonirradiated and irradiated uranium specimens were etched at Hanford by ion bombardment and the resultant

* HW-73476. Work performed under Contract No. AT(45-1)-1350 between the Atomic Energy Commission and General Electric Company.

(2AA), is representative of both irradiated and unirradiated conditions, and shows the needles and grain boundary phases seen in overaged specimens. However, examination of electron micrographs shows that specimens 2AA and 8AA truly are underaged, since no γ' is present. This lack of γ' , the primary hardening agent in A-286, is in agreement with the decrease in hardness observed when these specimens were re-solutioned.

Figure 7 shows electron micrographs of the two underaged alloys. The structures of the irradiated and unirradiated samples are again notable for their similarity. Profuse grain boundary "G" phase and intra-granular η phase platelets, produced during prior overaging, are evident in the microstructure. No general dispersion of γ' is seen, as is present in aged structures. The presence of the large carbide or carbonitride particle in Figure 7A is not a function of heat treatment or irradiation history, since a certain number of these relatively inert phases are always randomly dispersed in A-286.

CONCLUSIONS

Although physical testing of A-286 tensile bars showed property changes apparently caused by irradiation, no visible evidence of structural changes to account for the radiation damage has been observed in the optical and electron micrographs. This apparent lack of change may indicate that radiation-induced structural changes occur only at size levels beyond the capabilities of the present methods of replication and electron microscopy, or that only internal changes, such as dislocation formation, are produced by nuclear irradiation. It is felt that further electron microscopy of additional irradiated specimens may reveal structural changes which are too subtle to be observed in the limited number of specimens thus far examined.

ACKNOWLEDGEMENTS

The author is indebted to our consultant, Dr. J. F. Radavich, for helpful discussions and for furnishing the electron micrograph shown in Figure 2C.

REFERENCES

1. H. J. Beattie, Jr., and W. C. Hagel, "Intermetallic Compounds in Titanium-Hardened Alloys," Trans. AIME, 211, 1957, p. 911.
2. H. J. Beattie, Jr., "Structural Study of Relations Between Solution Treatment and Aging Response in Alloy A-286," General Electric Company, Large Steam Turbine-Generator Department, DF61SL322, May 11, 1961.
3. F. L. VerSnyder and H. J. Beattie, Jr., "The Laves Phase in A-286 Alloy," General Electric Company, Large Steam Turbine-Generator Department, R55TL028, March 1, 1955.
4. H. J. Beattie, Jr., "Occurrence of Phases in Austenitic Superalloys of Sixty Experimental Compositions," General Electric Company, Large Steam Turbine-Generator Department, DF61SL348, September 19, 1961.
5. H. J. Beattie, Jr., "Notes on the Crystal Structure of G Phase," General Electric Company, Large Steam Turbine-Generator Department, Memo Report MAR-1, September 18, 1958.

microstructures have been critically examined. Occasionally, the microstructure of a specimen after etching differed considerably from what was expected, or the validity of a particular microstructural detail was questioned. This prompted the study of two possible artifacts: (a) the deposition of sputtered metal on the uranium surface; and (b) the enlargement of pores which intersect a uranium surface.

SUMMARY AND CONCLUSIONS

Uranium specimens etched by ion bombardment may reveal artificial or spurious microstructural detail. Two possible artifacts have been investigated: (1) deposition of sputtered atoms on the surface of the sample being etched, and (2) enlargement or distortion of pores intersecting the surface of the sample being etched. The number and size of hillocks formed on a uranium surface during etching at four conditions which differ only with respect to the value of krypton gas pressure and etching period has been determined. For conditions of high gas pressure and long etching period, many more hillocks are produced than for low gas pressure and short etching period. It is concluded that the hillocks are artifacts. The number and size of pores intersecting the etched surface of an irradiated uranium specimen have been estimated after a short etching period of 20 minutes and after an additional etching period of 70 minutes. The reproducibility in the estimates of pore volume distribution curves, total pore volumes, and total pore densities is strong support for the conclusion that pores in irradiated uranium etched by ion bombardment are not enlarged or distorted.

EXPERIMENTAL CONDITIONS AND CONSIDERATIONS

A specimen of recrystallized, reactor grade uranium was mechanically polished, electropolished for 30 seconds in an ethylene glycol- H_3PO_4 electrolyte, and then etched with krypton ions in a small chamber previously described.⁽²⁾ Two dynamic equilibrium gas pressures were used: (1) a low pressure in the etching chamber of approximately 3μ of mercury; and (2) a high pressure of approximately 50μ of mercury. The polished specimen was etched for 30 minutes at low pressure and replicated; then it was polished, electropolished, and etched for 30 minutes at high pressure and replicated. The specimen was repolished and etched for 30 minutes at low pressure and an additional 30 minutes at high pressure and replicated. After a final repolishing the specimen was etched 30 minutes at high pressure and an additional 30 minutes at low pressure prior to replication. During etching at low or high gas pressures, the potential difference between cathode (specimen) and anode was 3500 volts d-c. An ultrahigh frequency field of 160 Mc was used during etching at low pressures to provide a current density value identical to the current density value achieved during the high pressure etching. Except for gas pressure, etching conditions (such as specimen temperature, outgassing, and gas purity) were identical during low and high pressure etching. The primary replica,

cellulose acetate, was replicated with polyvinyl alcohol. The positive polyvinyl alcohol replica was shadowed with UO_2 at 30° , backed with carbon, and dissolved in water to free the thin replica.

A wafer of irradiated uranium, 0.29 at. % burnup, which had been annealed at 880°C to develop fission gas pores, was polished and then etched for 20 minutes with argon ions. After replicas of the specimen surface had been prepared, the specimen was etched an additional 70 minutes and replicas of the surface were again obtained. The potential difference between specimen and cathode was 3500 volts d-c; the gas pressure was $\sim 30\mu$ of mercury. The negative, primary replicas (cellulose acetate) were shadowed with UO_2 at 15° and backed with carbon. Identical areas in the two sets of replicas were selected according to a method previously described.⁽³⁾ Hillock diameters and fission gas pore diameters were measured with a Zeiss Particle Size Analyzer.

DISCUSSION

Redeposition of Sputtered Atoms During Ion Bombardment

Hillocks which form on metallic germanium surfaces during etching by ion bombardment have been observed and interpreted in several ways. Meckel and Swalin⁽⁴⁾ studied hillock formation on germanium etched under specific conditions and concluded that hillocks decorate screw dislocations which emanate from the specimen surface. An alternate explanation was advanced by Wehner⁽⁵⁾ that the hillocks bear no relationship to the defect structure initially present in the specimen. Whether a portion of the material forming these hillocks arises from deposition of sputtered metal to preferential sites on the specimen surface is not clear from these accounts. If redeposition actually occurs, then the number and size of hillocks should be a function of gas pressure during etching.

Accordingly, the hillocks which form on a uranium specimen etched under the conditions specified were characterized by count and basal area measurements. Each of the four micrographs (Figure 1) pertain to different gas pressure values during the etching period and are typical examples of the 16 micrographs used for measurements. Diameters of hillocks were classified into cells having successive midpoint values which were related exponentially rather than linearly. This exponential relationship is preferable because the relative error in measurement of a given diameter is constant regardless of cell number, and because resolution or discrimination between small diameters is enhanced (discrimination between large diameters, however, is decreased).

The shapes of the distribution curves (Figure 2) and the estimates of total fraction of the specimen surface covered (Table I) definitely depend on gas pressure. Etching at low gas pressures must be considered superior to etching at high pressures. Although recognition and exclusion of many of the normal precipitates present in uranium was possible by virtue of their characteristic flat topography, those not excluded should only contribute a minor constant error to all determinations.

Figure 1a - Microstructure of uranium etched with krypton ions for 30 minutes at 3μ pressure.

Figure 1b - Microstructure of uranium etched with krypton ions for thirty minutes at 50 μ pressure

Figure 1c - Microstructure of uranium etched with krypton ions for thirty minutes at 3μ pressure and an additional thirty minutes at 50μ pressure

Figure 1d - Microstructure of uranium etched with krypton ions for thirty minutes at 50 μ pressure and an additional thirty minutes at 3 μ pressure

TABLE I

TOTAL FRACTION OF SPECIMEN SURFACE COVERED BY HILLOCKS
AS A FUNCTION OF GAS PRESSURE AND ETCHING TIME

	Number of Mounds Measured	Percent of Area Covered ($100 \sum r_i^2 / \text{Area of Micrographs}$)
Low Pressure -- 30 Minutes	665	3.5
High Pressure - 30 Minutes	931	4.9
High Plus Low Pressure -- 60 Minutes	726	8.5
Low Plus High Pressure -- 60 Minutes	932	11.0

Since etching depends on the physical state of a specimen (namely geometry, surface, degree and nature of contaminants), the conclusions of this study may be specific rather than general. Nevertheless, the data obtained indicates that random hillock formation under adverse etching conditions can mask a considerable fraction of the specimen surface, and that subsequent etching of hillocks under more favorable etching conditions can reduce their number and size.

Since the hillocks (Figure 1) have a topography quite different from that of the matrix, and since their presence can be associated with a considerable number of sputtered atoms which have a mean free path shorter than the distance from specimen to chamber walls, it is concluded that these hillocks arise from concentration of sputtered atoms on the specimen surface. In most cases, the hillocks bear little if any relationship to the true micro-structure, and should therefore be considered artifacts.

Enlargement of Pores in Irradiated Uranium Due to Etching by Ion Bombardment

There is considerable interest in the role of inert gas atoms formed in uranium fuel during fission of U-235. An excellent review (6) covers various aspects of this phenomenon. All swelling studies rely on metallographic evidence for the number and size of pores observed in uranium. This evidence is derived primarily from electron micrographs of replicas of etched uranium specimens. As indicated in a recent report, (7) pore size distributions derived from electron micrographs of uranium etched by ion bombardment may be erroneous if distortion or enlargement of pores occurs during etching. This section presents data on the reliability of pore diameter estimates.

An evaluation of the extent that pores enlarge during etching would be straightforward if a variety of standard specimens, each containing uniformly distributed pores of a known size, could be processed. Such standard specimens do not exist. The enlargement of pores during etching should be a function of etching severity, and the reproducibility of repeated pore diameter estimates in a specimen should be a valuable index.

A free surface is characterized by an abrupt change in the normal lattice array; if polished, the surface contains a considerable thickness of plastically deformed "flow metal". Any small pores in this flow metal layer certainly will be partially filled and hence distorted. For instance, an electron micrograph (Figure 3) of irradiated uranium in the as-polished state, known to contain pores, shows no evidence of them. Before the true pore configuration can be examined, all flow metal must be removed nonselectively. If residual flow metal persists, it is reasonable to expect pores close to the specimen surface to be distorted. The smaller the pore, the greater should be the relative distortion of a given pore. Moreover, the distortion of any given pore should be a function of the orientation of the grain containing the pore and a function of the flow characteristics of the porous matrix in the immediate vicinity of the pore. These complications can be avoided only if the flow metal layer is completely removed. On the basis of X-ray diffraction line width studies of the presence or absence of flow metal layers on uranium surfaces, it has been established that etching by ion bombardment can yield an undisturbed and pit-free surface. Pores intersecting this surface should, therefore, be undistorted unless the etching action of the ion bombardment enlarges pores.

White⁽⁸⁾ studied changes in the geometry of a cavity and aperture in a hollow cathode source. He found that, with cavities of approximately 0.5 inch diameter and apertures of approximately 0.3 mm diameter, very little change occurred in the cavity during etching; but the aperture tended toward a limiting value, $0.25 \times$ cavity diameter. In the case studied, the aperture opening decreased. The unusual stability of a cavity during etching is attributed to the sputtered atoms, most of which are trapped within the cavity and redistributed uniformly over the cavity surface. This argument, however, does not apply to pores or cavities with centers above the specimen surface. In this case, some distortion or enlargement due to etching very likely occurs. Etching will occur at a much lower rate than from a plane surface due to a higher redeposition rate in the crater. Since experiments similar to White's have not been performed on very small cavities, no direct evidence concerning changes in the sizes and shapes of small pores is available.

Indirect evidence that the shapes and sizes of fission gas pores in uranium are not altered appreciably is provided by statistical estimates of total pore volumes and pore size distributions derived from replicas of the specimen surface (Figure 4). Four areas on the surface of the specimen etched for only 20 minutes were compared with equivalent areas in a replica of the specimen etched an additional 70 minutes. The negative replicas were shadowed simultaneously after orientation and photographed. Since no pore present after the briefer etch could be recognized after the longer etch, the thickness of metal removed during the second etch was at least several microns. The areas compared were not identical, but they were equivalent. A worm-shaped crack (Figure 3) served as a convenient reference for mapping out equivalent areas in the micrographs at high magnification, 15,000 X.

Figure 2 - Plot of relative area of specimen covered per unit cell width versus cell number.

As-Polished

Etched 20 Minutes

Etched an Additional 70 Minutes

Figure 3 - Electron micrographs illustrating influence of etching severity on microstructure of uranium containing fission gas pores

2000X

The relationships used to calculate total pore volume fraction and pore density estimates from micrographs of negative replicas shadowed at an angle of 15° are given in the Appendix (Table II). The factors used to convert numbers of pores of a given cell (i) to the i^{th} pore volume fraction and i^{th} pore density contribution are also included. These apply to an exponentially increasing cell classification with particular cell widths (w_i) and cell midpoint values (r_i). The factors include a correction for extrusion of the replicating medium, cellulose acetate, and a correction for the minimum limit of diameter measurements.

Estimates of the total pore volume fraction and the pore density after the 20-minute etch are 0.062 and 6.7×10^{12} pores/cc, respectively; the corresponding estimates after an additional 70 minute etch are 0.074 and 7.2×10^{12} pores /cc. Variance analyses and chi-square tests have been applied. Although the additional etching period results in a slight but consistent increase in pore volume fraction, no conclusive evidence for an etching effect was derived from the statistical analyses. There was no consistent effect for pore density.

The cell pore volume contributions for the two etching periods as a function of cell number (proportional to $\log$ pore diameter i) were calculated (Figure 4). The ordinate, expressed as pore volume fraction per unit cell width i , was obtained by multiplying each cell contribution by the correction factor listed in the Appendix, thereby correlating each ordinate value with a constant abscissa section. The similar shapes of the distribution curves indicate that the two different etching times do not introduce a significant error in the estimates of pore volumes in uranium. This does not preclude the possibility that the original pores change and assume an equilibrium configuration during the initial etching. However, this is not likely. In any event, comparisons of reproducible estimates of pore volume fractions and densities can be made, and should yield valuable information.

CONCLUSIONS

1. During the etching of uranium by ion bombardment, sputtered atoms can deposit on the uranium and form hillocks. The numbers and sizes of these hillocks depend on the pressure of the gas surrounding the specimen. The hillocks are artifacts.
2. Fission gas pores with diameters of 0.08 to 1μ in irradiated uranium do not distort or enlarge during proper etching of the uranium by ion bombardment.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of K. Thomas, A. Bloomstrand, and the radiometallurgy personnel to various phases of this investigation. Special thanks go to J. Figg and W. Nickolson for their help in the statistical testing and programming of data, and to D. Cummings for measuring diameters of hillocks and pores.

Figure 4 - Similarity in pore size distribution estimates derived from measurements of pores on equivalent areas of a specimen which had been etched for 20 minutes and an additional 70 minutes.

APPENDIX
PORE VOLUME FRACTION AND PORE DENSITY FORMULAS*

The following formulas are for calculation of the pore volume fraction (VF) and the pore density (PD) of a single spherical pore randomly distributed in a matrix. The formulas assume that the data are collected on the exponential scale of a 48-cell Zeiss Particle Size Analyzer by scanning a photomicrograph of a negative-shadowed replica.

$$VF = \frac{0.9 \pi}{A} \sum V_i N_i$$

$$PD = \frac{1.111}{\pi A} \sum D_i N_i \text{ (sphere centers/cu mm in enlarged micrograph.)}$$

The summation extends over all 48 cells. A is the area of the photomicrograph (sq. mm). N_i is the number of particles with observed diameters in the i^{th} cell.

$$V_i = \frac{2 r_i^3}{r_i + \sqrt{r_i^2 - b^2}}, \text{ and} \quad D_i = \frac{2}{r_i + \sqrt{r_i^2 - b^2}};$$

where r_i is the midpoint radius (mm) for the i^{th} cell and b is the optical resolution point for sizing spherical particles.

Particles that appear on the negative replica as less than a hemisphere must have an interface radius greater than b to be seen. For cells 1 through 21, $b = 0.605$ mm, the minimum radius resolved by the Zeiss Analyzer. For cells 22 through 48, $b = r_i \sin \theta$. (θ is the angle between the shadow direction and the interface plane.) In this latter range, spheres with interface radii less than b cast no shadow and hence are not observable. With a positive resolution point such as the preceding 0.605-mm, direct estimation of total VF and/or PD (including the contribution from spheres with radii less than 0.605-mm) is not possible. The present formulas estimate VF and PD contributions from spheres with radii greater than 0.605 mm. The addition of the contribution from small spheres is an extrapolation problem which demands knowledge of the functional form of the sphere radii distribution in the matrix.

For particles that appear on the replica as more than a hemisphere, the preceding formulas are averages of two possible extremes: (a) perfect replication -- spherical segment of one base; and (b) replication distorted perpendicular to plane of interface -- right circular cylinder with radius equal to the interface radius. (7)

The 0.9 in the VF formula is the average of 0.8 and 1.0; the 1.111 in the PD formula is the average of $(2\pi)/(2 + \pi)$ and 1.0, which are the respective numerical factors for these two extreme models.

* Formulas and their derivation appear in: Nicholson, W. L. Quantitative Metallography - Estimation of the Characteristics of a Spherical Phase from Two-Dimensional Sections, HW-73178. To be published.

TABLE II
FACTORS FOR PORE VOLUME FRACTION AND PORE DENSITY ESTIMATES
 Shadow Angle $\theta = 15^\circ$

Cell Number	r_i, mm	V_i, mm	D_i, mm	Factor for Converting
				N_1 or D_1 to Constant Cell Width
1	0.625	0.62454	2.55807	6.73
2	0.670	0.62798	2.08794	6.33
3	0.715	0.66699	1.82473	5.95
4	0.760	0.71965	1.63938	5.58
5	0.815	0.79546	1.46942	5.23
6	0.870	0.88082	1.33761	4.90
7	0.925	0.97427	1.23099	4.59
8	0.990	1.09414	1.12763	4.30
9	1.055	1.22362	1.04205	4.03
10	1.125	1.37338	0.96457	3.76
11	1.205	1.55728	0.89003	3.52
12	1.290	1.76731	0.82327	3.33
13	1.370	1.97859	0.76947	3.08
14	1.460	2.23192	0.71717	2.89
15	1.560	2.53271	0.66713	2.72
16	1.660	2.85374	0.62386	2.53
17	1.780	3.26560	0.57903	2.39
18	1.900	3.70646	0.54038	2.23
19	2.025	4.19646	0.50537	2.09
20	2.160	4.76087	0.47242	1.96
21	2.310	5.43088	0.44059	1.83
22	2.465	6.18153	0.41271	1.71
23	2.630	7.03677	0.38682	1.62
24	2.805	8.00438	0.36268	1.51
25	2.995	9.12548	0.33968	1.42
26	3.195	10.38493	0.31841	1.32
27	3.415	11.86433	0.29790	1.24
28	3.645	13.51627	0.27910	1.16
29	3.890	15.39434	0.26152	1.09
30	4.150	17.52097	0.24514	1.02
31	4.430	19.96500	0.22965	0.96
32	4.705	22.52066	0.21622	0.90
33	5.045	25.89311	0.20165	0.84
34	5.385	29.50076	0.18892	0.79
35	5.750	33.63547	0.17693	0.74
36	6.135	38.29050	0.16582	0.69
37	6.550	43.64600	0.15532	0.65
38	6.990	49.70685	0.14554	0.61
39	7.460	56.61604	0.13637	0.57
40	7.965	64.54066	0.12773	0.53
41	8.500	73.50209	0.11969	0.50
42	9.075	83.78285	0.11210	0.47
43	9.685	95.42477	0.10504	0.44
44	10.335	108.66328	0.09844	0.41
45	11.035	123.88152	0.09219	0.38
46	11.775	141.05344	0.08640	0.34
47	12.570	160.74312	0.08093	0.34
48	13.415	183.08097	0.07584	0.32

REFERENCES

1. Bierlein, T. K., H. W. Newkirk, Jr. and B. Mastel. "Etching of Refractories and Cermets by Ion Bombardment", J. Am. Ceram. Soc. 41: 196-200. June 1, 1958.
2. Bierlein, T. K. and B. Mastel. "Improved Method of Etching by Ion Bombardment", Rev. Sci. Instr. 30: 832-833. September, 1959.
3. Bierlein, T. K. and B. Mastel. "Optical and Electron Microscope Examination of Preselected Areas", Rev. Sci. Instr. 28:960-961. November, 1957.
4. Meckel, B. B. and R. A. Swalin. "Selective Delineation of Screw Dislocations by Cathodic Sputtering", J. Appl. Phys. 30:89-93, Jan., 1959.
5. Wehner, G. K. "Etching of Germanium Crystals by Ion Bombardment", J. Appl. Phys. 29: 217-221. February, 1958.
6. Pugh, S. F. "Swelling in Alpha Uranium Due to Irradiation," Nuclear Materials 4: 177-199. July, 1961.
7. Bierlein, T. K., B. Mastel and R. D. Leggett. Metallographic Observations of Swelling in Uranium - Interim Report, HW-63848. June, 1960.
8. White, A. D. "New Hollow Cathode Glow Discharge", J. Appl. Phys. 30: 711-719. May, 1959.