UNCLASSIFIED

ISC-480

**AMES
LABORATORY
IOWA STATE
COLLEGE**

**DO NOT
PHOTOSTAT**

ETCHING METALS BY IONIC BOMBARDMENT

This document is
PUBLICLY RELEASABLE
Hugh Kinnor H. Kinnor
Authorizing Official
Date 9/13/02

UNCLASSIFIED

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.

15C-480

U N C L A S S I F I E D 0

UNITED STATES ATOMIC ENERGY COMMISSION

no 43558

ETCHING METALS BY IONIC BOMBARDMENT

by

A. J. Carlson, J. T. Williams, B. A. Rogers and E. J. Manthos

LEGAL NOTICE

May 30, 1954

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, express 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 will not infringe privately owned rights; or

B. Accepts any liability 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 to the extent that such employee or contractor provides, prepares or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng-82

U N C L A S S I F I E D

980 001

This report is distributed according to the category
Metallurgy and Ceramics as listed in M-3679, April 15, 1954.

ETCHING METALS BY IONIC BOMBARDMENT

A. J. Carlson,* J. T. Williams, B. A. Rogers and E. J. Manthos

ABSTRACT

This paper is devoted to a description of apparatus for etching metallographic specimens by ionic bombardment in an electrical discharge tube and to some results obtained with the equipment. Previous papers are cited to show that the method is not new. A drawing shows the construction of the apparatus and a circuit diagram gives information concerning the electrical power unit. Photomicrographs of brass and steel show that ionic bombardment gives no better results on these common metals than ordinary etching methods. However, photomicrographs of uranium, thorium and two thorium alloys indicate that bombardment has advantages for these metals. (over)

INTRODUCTION

Preparation of metallic specimens for microscopic examination requires some type of etching action that will reveal their structure. Usually, the etching is done by chemical or electrochemical means. The discovery of a suitable reagent and method for a

*Deceased.

specific metal or alloy usually occurs as the result of a little scientific knowledge and a great deal of trial and error. The procedure finally adopted depends upon whether it reveals the features in which the metallographer is interested. In some instances, the metallographer has extreme difficulty in finding a reagent that is satisfactory. Such a situation led the authors to investigate bombardment by gaseous ions as a means of producing etched surfaces.

SURVEY OF PREVIOUS WORK

About a hundred years ago, studies of the action of the electrical discharge in a partially evacuated glass tube provided with two electrodes showed that metal was removed from the negative electrode, or cathode, and deposited near by on the wall of the tube.¹ In the intervening years, many investigations of the behavior of such discharge tubes have been made. Some of them have been concerned with the loss of weight of the cathode as related to the metal used and the kind of gas in the tube.^{2,3,4,5} Kohlschütter⁶ demonstrated that bombardment by rapidly moving ions was a major factor in the removal of metal. In a convincing experiment, he placed his specimen a short distance behind a perforated cathode. He found that the "Kanal" rays coming through the perforations affected the specimen much as if it had been part of the cathode.

A few experimenters^{7,8} made microscopic studies of the metal deposited on the walls. In at least three investigations,^{9,10,11} made during the '1920's, ionic bombardment was demonstrated to be a

practical means of etching specimens for metallographic examination. As the investigators did not claim marked advantages for the method, no further work appears to have been done until McCutcheon and Pahl¹² used bombardment in some special studies.*

CONSTRUCTION AND OPERATION OF THE APPARATUS

The etching apparatus in current use is the third that has been constructed at the Ames Laboratory. It is more compact and generally more satisfactory to use than either of the previous models.

The apparatus is essentially a glow discharge tube provided with means for regulation of the pressure of argon gas used in the tube and of the potential drop between electrodes. The electrical circuit is shown in Fig. 1. A diagram of the discharge tube and its associated pressure control system appears in Fig. 2. Figure 3 is a photograph of the apparatus.

The diagrams and their accompanying legends give most of the information necessary but a few additional facts will be presented. The high voltage unit provides a maximum of 10,000 volts. As Fig. 1 indicates, the power unit gives half wave rectification. Current through the tube is controlled by the voltage and the pressure of the argon. It is limited by the allowable rise in temperature of the specimen under the bombardment of the ions.

*Other recent papers on this method of etching have been published by T. R. Padden and F. Cain, Jr. and B. A. Rogers, J. T. Williams and E. J. Manthos in Atomic Energy Commission Report No. TID-5147 (December 8, 1953).

LEGEND

- A - Female amphenol connector
- B - Male amphenol connector
- C - Conduit (shield for anode lead)
- D - Test lead wire (anode lead)
- E - Female amphenol connector
- F - Polystyrene tubing perforated for air cooling
- G - Anode
- H - Cathode
- L₁ - Vacuum pump pilot light
- L₂ - High voltage pilot light
- M₁ - 0-25 D.C. milliammeter
- M₂ - 0-200 D.C. microammeter, calibrated 0-10 kilovolts
- P₁ - Outlet for vacuum pump power
- P₂ - Outlet for vacuum gauge power
- R₁ - 60 second time delay relay for filament warm up
- S₁ - Vacuum pump switch
- S₂ - High voltage switch
- S₃ - Safety switch on door to high voltage compartment
- T₁ - Filament transformer for 8020 rectifiers
- T₂ - Autotransformer for high voltage control
- T₃ - High voltage transformer
- V - 8020 rectifier tube

Fig. 1 - The circuit of the power unit of the apparatus for ionic bombardment.

LEGEND

- A - 3/16" copper rod silver-soldered to B, 10-24 thread on lower end
- B - 1/4" Kovar glass-to-metal seal
- C - 14/35 pyrex standard taper
- D - Aluminum anode drilled for two-prong spanner wrench
- E - 60 mm pyrex tubing
- F - Aluminum cathode
- G - 1 1/4" standard brass pipe cap soldered to J, threaded outside
- H - 60/50 pyrex standard taper
- I - 2" Kovar metal-to-glass seal
- J - 1 1/4" copper pipe soldered into L
- K - 2" copper pipe silver-soldered into L, soldered to I
- L - 2" x 1 1/4" x 1 1/4" brass reducing tee
- M - 1 1/4" standard brass pipe cap drilled for N, soldered to J and N
- N - 1/4" soft copper tubing
- O - Thermocouple gauge
- P - Ionization gauge
- Q - Argon flushing valve (1/4" vacuum type)
- R - Variable leak
- S - 1 1/4" copper pipe soldered into L and vacuum lead T
- T - Vacuum line of copper pipe

Fig. 2 - The apparatus for etching by ionic bombardment.

Fig. 3 - Photograph of the apparatus for ionic bombardment.

The discharge tube and cathode cooling system are constructed of standard pyrex glass and copper and brass plumbing parts. Copper pipe and tubing are used throughout the vacuum system. Aluminum electrodes are used because of the low sputtering rate of this element. They are sufficiently small in diameter, 1.75 inches, that they do not constrict the discharge tube and thus reduce pumping speed unreasonably, but large enough to shield the brass and copper parts behind them from the discharge. The spacing of electrodes is not critical and the distance of 4 inches between electrodes used in this apparatus was established on the basis of convenience.

Operation of the apparatus is relatively simple. With a specimen on the cathode, polished face upward, the tube is evacuated to a pressure of about 1μ Hg. Then, with the vacuum pump still operating, the cooling water is turned on, the variable leak in the argon line is adjusted to give about 15μ Hg pressure and the potential raised slowly to about 5000 volts. After an induction period of a few minutes, etching starts and the wall of the tube begins to darken because of deposited metal. Usually the current through the tube decreases at this point. When visual observation indicates that the etching is completed, the high voltage switch is opened and the argon supply is shut off. As soon as the specimen is estimated to have reached room temperature, the pump is shut off and the argon flushing valve (Fig. 2, Q) opened. When the pressure of argon in the system approaches atmospheric value, the discharge tube may be lifted up and the sample removed. The entire operation requires about 45 minutes of which approximately 3 minutes are occupied by the actual etching.

As an insurance against breakage of the discharge tube, the pressure in the argon line should be kept low. Otherwise, if the argon flushing valve is opened too rapidly, with the vacuum pump not running, the pressure may increase sufficiently to propel the discharge tube upwards from its seat with consequent breakage. This difficulty may be avoided by the introduction of an extra valve that remains unchanged when the flow of gas is adjusted for a run. The extra valve is set when a new tank of argon is connected.

RESULTS OBTAINED WITH THE APPARATUS

The Nature of the Etching Action

Early in the investigation an experiment similar to Kohlschütter's was tried. The specimen was placed on the cathode inside a nearly closed container within which, presumably, no electric field could exist. The arrangement is illustrated in Fig. 4 which shows the low-carbon steel specimen resting upon the cathode within a short copper cylinder. On top of the cylinder is a perforated sheet of molybdenum. The etching of the specimen below the holes and the absence of attack under the remainder of the sheet is shown at low magnification in Fig. 5. That the boundary between the etched and unetched areas is not sharp is evident from Fig. 6 which shows a section of boundary region at a magnification of 160 diameters. Such a condition is to be expected as some ions come in at an angle.

The Etching of Some Common Metals

Etching experiments were conducted on a few of the common metals. Figure 7 shows a piece of low carbon steel in which

Fig. 4 - Arrangement for shielding specimen from electrical field during bombardment.

A. Perforated molybdenum sheet

C. Specimen

B. Copper ring

D. Aluminum cathode

Fig. 5 - Steel specimen etched by ions passing through holes in perforated sheet. 2X

Fig. 6 - Boundary area of one of spots on Fig. 5. 160X

Neumann bands had been produced by a sharp blow with a hammer. Both the bands and the grain boundaries appear much as if the specimen had been etched by one of the usual chemical procedures. Attempts to etch a specimen of pearlitic steel did not yield satisfactory results because of lack of contrast in the surface and because of difference of level of different areas. Figure 8 illustrates the impossibility of getting the entire field of view in focus at once if a high magnification is used. Brass can be etched without difficulty, as illustrated in Fig. 9. The surface of this specimen appears much as it did when etched with a nitric acid solution. Twin boundaries and grain boundaries have come out clearly, but no shading of the grains is evident. Figure 10 shows a patch of eutectic in an inhomogeneous zinc-rich magnesium-zinc alloy prepared in the laboratory. Etching by bombardment has no advantage in this instance.

Zirconium can be etched readily by ionic bombardment. A piece of arc-melted zirconium sponge produced by the Kroll process is presented in Fig. 11. The pattern on it probably represents residual transformation areas.

The Etching of Thorium and Uranium

Etching by bombardment usually has given satisfactory, and sometimes superior, results on thorium and uranium. Figure 12 shows a piece of thorium that was made by the iodide process and then melted in a tungsten-electrode, helium-atmosphere arc furnace. Figures 13 and 14 are photomicrographs of a thorium-iron alloy containing 2 per cent iron. The surface in Fig. 13 had been etched electrochemically with a solution of $3N\ HNO_3$ to which 0.1 per cent of KF had been added. This reagent was the most

Fig. 7 - Neumann bands in a piece of low carbon steel. 500X

Fig. 8 - Pearlitic steel showing different areas etched to different depths. 1200X

Fig. 9 - Brass piece from scrap box heated 30 minutes at 575°C. 120X

Fig. 10 - Eutectic area in zinc-rich magnesium-zinc alloy cast in laboratory. 1200X

Fig. 11 - Etched surface of zirconium. Bureau of Mines sponge melted in tungsten-electrode arc furnace. 120X

Fig. 12 - Iodide thorium melted in tungsten-electrode arc furnace. 120X

Fig. 13 - Cast thorium-iron alloy containing 2% iron etched electrochemically. 500X

Fig. 14 - Same specimen as in Fig. 13 repolished and etched by bombardment. 500X

satisfactory one that the authors had found after a reasonable amount of experimentation. Figure 14 shows the same alloy etched by ionic bombardment. In this instance the new method has produced the more satisfactory surface.

Thorium-carbon alloys appear to be particularly suitable subjects for ionic bombardment if one may judge from the results obtained in Fig. 15. Uranium also can be etched satisfactorily. Figures 16 and 17 show, respectively, surfaces obtained on uranium in the cast and in the worked conditions.

General Comments

Surfaces etched by bombardment are likely to have little contrast. On the other hand, staining seems to be absent. One advantage is that the method produces a usable result on most metals and may eliminate the need for an extended search for a suitable reagent. Etching by bombardment is relatively time-consuming but not difficult. The time for a complete cycle could be shortened considerably by alterations in the apparatus.

SUMMARY

This revival of a method of metallographic etching that was demonstrated about 30 years ago to give usable results has proved to be advantageous in etching thorium and uranium and some of their alloys. Used on some of the more common metals, it has shown little advantage over chemical and electrochemical methods of etching and in one case, at least, gave unsatisfactory results.

REFERENCES 980 017

1. Plücker, "Ueber die Einwirkung des Magneten auf die elektrischen Entladungen in verdünnten Gasen," Ann. der Physik und Chemie, Vol. 103, 1858, 1p2288p. 60.

Fig. 15 - Arc-melted thorium-carbon alloy containing 1.2 per cent carbon. 1200X

Fig. 16 - Cast uranium. 500X

Fig. 17 - Fabricated uranium. 500X

2. William Crookes, "On Electrical Evaporation," Proc. Roy. Soc. (London), Vol. 50, 1891-1892, p. 88.
3. V. Kohlschütter, and Rud. Müller, "Über Kathodische Verstäubung von Metallen in Verdünnten Gasen," Z. für Elektrochemie, Vol. 12, 1906, p. 365.
4. Research Staff of the General Electric Company, Ltd., "Cathode Disintegration," Phil. Mag., Vol. 45, 1923, p. 98.
5. A. Güntherschulze, "Kathodenzerstäubung," Z. für Physik, Vol. 36, 1926, p. 563.
6. V. Kohlschütter, "Zur Kenntnis der Kathodischen Metallverstäubung in Verdünnten Gasen," Z. für Elektrochemie, Vol. 12, 1906, p. 869.
7. J. P. Gassiot, "On the Deposit of Metals from the Negative Terminal of an Induction Coil During the Electrical Discharge in Vacuo," Report of the British Association for the Advancement of Science, Transactions Section, 1861, p. 38.
8. Josef Mazur, "Pulverisation Cathodique des Alliages," Bull. Acad. Polonaise, 1925A, p. 81. [See Chem. Abs., Vol. 20, 1926, p. 2811.]
9. W. Feltknecht, "Über den Angriff von Kristallen durch Kanalstrahlen," Helvetica Chim. Acta, Vol. 7, 1924, p. 825.
10. Cyril S. Smith, "Note on Cathodic Disintegration as a Method of Etching Specimens for Metallography," J. Inst. Met., Vol. 38, 1927, p. 133.
11. Luigi Belladonna and Mauro de Martino, "La Polverizzazione Catodica Applicata allo Studio Micrografico delle Leghe Metalliche," La Metallurgia Italiana, Vol. 21, 1929, p. 18.
12. Don M. McCutcheon and William Pahl, "Cathodic Vacuum Etching of Metals," Metal Progress, Vol. 56, 1949, p. 674.