<table>
<thead>
<tr>
<th>ACCESSION FOR</th>
<th>NTIS</th>
<th>GRA &amp; I</th>
<th>□</th>
<th>DTIC</th>
<th>TAB</th>
<th>□</th>
<th>UNANNOUNCED</th>
<th>□</th>
<th>JUSTIFICATION</th>
<th>□</th>
<th>(Oct. 1960)</th>
<th>□</th>
</tr>
</thead>
<tbody>
<tr>
<td>DISTRIBUTION / AVAILABILITY CODES</td>
<td>DIST</td>
<td>□</td>
<td>AVAILABLE AND/OR SPECIAL</td>
<td>□</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DISTRIBUTION STAMP</td>
<td>UNANNOUNCED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DATE ACCESSIONED**

81 5 15 198

**DATE RECEIVED IN DTIC**

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-DDA-2
ETCH PITS IN PYROLYTIC GRAPHITE

TECHNICAL REPORT NO. WAL TR 130.5/1

BY
ARAM TARPINIAN
and
GEORGE E. GAZZA

OCTOBER 1960

O.O. PROJECT: TB4-004, MATERIALS FOR HIGH TEMPERATURE USES
D/A PROJECT: 6B93-32-004

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited
ABTIA miUBIim NOTICI

MT obttit eoplM of tki» raport fro» xU Armd Sarrlcea Techelc»!

■ fomiktloa Af»cj, Arliiftoa H«ll Statlo«, Arlliftoa 11, yir|l*U.

Tkla raport kaa baaa ralaaaad to tkla Offlca of Tackalcal Sarrlcea, D.  Dapartaiaat of Coanarc«, Vaakiaftoa II, D.   C   for atla to tkla gaaaral public.

ASTIA AVAILABILITY NOTICE

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, Arlington Hall Station, Arlington 23, Virginia.

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. for sale to the general public. PB 188817
ETCH PITS IN PYROLYTIC GRAPHITE

TECHNICAL REPORT WAL TR 130.5/1

By
ARAM TARPINIAN
and
GEORGE E. GAZZA

October 1960

O.O. Project: TB4-004, Materials for High Temperature Uses
D/A Project: 5B93-32-004
ETCH PITS IN PYROLYTIC GRAPHITE

ABSTRACT

The observation of pits in pyrolytic graphite after ion bombardment etching is described and their similarity to dislocation etch pits is speculated. Evidence of etch pit multiplication in the form of slip line segments and low angle tilt boundaries is presented.

ARAM TARPINIAN
Physical Metallurgist

GEORGE E. GAZZA
Physical Metallurgist

APPROVED:

J. F. SULLIVAN
Director
Watertown Arsenal Laboratories

REPORT APPROVED
Date: 26 Oct 60
WAL Board of Review
Chairman: W.S.W.
INTRODUCTION

In contrast to metals, the effect of microstructure on the properties of graphitic materials has not been investigated sufficiently to demonstrate which features are most significant. It has been shown in the case of metals and other crystalline materials that the nature of the substructures plays an extremely important role in determining the physical properties of the material. Various techniques such as "decorating" and etch pitting have been used to reveal these substructures in materials. Transmission electron microscopy of thin sections has also been utilized by observing the interference patterns produced by the transmission of the electron beam through the lattice imperfections.

In the case of graphites, the only attempts to identify the substructures have been by transmission electron microscopy. A number of electron microscope observations have been made which are reported to be direct evidence of dislocations in graphite. Although there is no reason to believe that graphite is so perfect that it is free of dislocations, the concept of dislocations in graphite is received by many with some skepticism. However, Grenall's work (Reference 3) with the transmission electron microscopy of graphite thin sections showing the movement of dislocation lines induced by the thermal energy provided by the electron beam is quite convincing. The electron microscope work by Dawson and Follett, (Reference 4) showing edge dislocations in the basal plane consisting of two half planes is also convincing, since one would expect that the atomic arrangement in the hexagonal layer plane would require that two rows of atoms be removed to form the edge dislocation and still maintain the compatibility of the lattice (see Figure 1).

The authors have no knowledge of any published work reporting the use of etch pit techniques and light microscopy for revealing the substructures of graphites. Perhaps the reason for this lack is the fact that until recently there has been little interest in revealing graphite microstructures for metallurgical-type studies. The experience and know-how derived from the study of metal microstructures can be usefully applied to graphite as has already been done in many other nonmetallic and ceramic-type materials. A desire to apply metallographic principles and techniques to graphite prompted our earlier investigations in this area. During the course of these studies, cathodic etching techniques were found to be quite superior to chemical etching for both pyrolytic graphites and graphitized cokes.

Pyrolytic graphite is the term used to describe the graphite deposit derived from the high temperature (> 2000°C) pyrolysis of organic vapors on hot surfaces. The most common raw material used today is methane gas, although there are numerous other organic compounds that will undergo similar pyrolysis reactions. Graphite layers are built up on a hot substrate by the continuous deposition of carbon resulting from the pyrolysis of the organic vapor. The orientation of the crystallites (grains) is such that the basal (00.2) plane lies more or less parallel to the surface of the substrate. Due to the peculiarities of the growth process, the basal planes are bowed with varying degrees of curvature, giving rise to a conical geometry to the
grain structure when viewed parallel to the (00.2) plane.

Graphitized cokes are those graphites that are produced by the heat treatment (> 2000°C) of molded or extruded mixtures of petroleum coke particles and pitch or resin binder. The high temperature heat treatment graphitizes both the binder and the coke filler, resulting in a porous body consisting of fairly randomly oriented graphite crystallites held together by a graphitic pitch or resin bond.

The purpose of this paper is to report some recent work using cathodic etching techniques to reveal the substructures in pyrolytic graphite. Pyrolytic graphite was chosen in lieu of graphitized coke because of its closer approach to single crystal behavior due to the preferred orientation of the grain structure. Etch pit arrays have been observed which we believe may be direct evidence of dislocation sites.

EXPERIMENTAL PROCEDURE

In the case of graphites, chemical etching presents a problem because of the relative inertness of graphite with respect to chemical reaction. The choice of chemical reactions for etching is limited to three types: oxidation, formation of lamellar compounds, and carbide formation at high temperatures. Of the three classes, oxidation seems to be the most feasible for use as a means of etching, since the reaction product is gaseous and does not require removal or solution away from the underlying structure.

In previous work by the authors (Reference 6), a mixture of potassium dichromate - phosphoric acid was found to be the most promising oxidizing etchant for graphite. Subsequent work (Reference 5) showed that cathodic etching (ion bombardment) was much more satisfactory. Consequently, cathodic etching techniques were used in the work reported in this paper.

Pyrolytic graphite specimens were sectioned in a transverse manner so that the basal planes are viewed on edge. The sectioned surface was polished, using standard metallographic polishing techniques, and cathodically etched with argon ions. Details of the construction and operation of the cathodic etching apparatus are given in Reference 5. In general, satisfactory etching was accomplished within a half hour, using a voltage drop from 3000-4500 volts at 5-10 ma/cm². A constant leak of argon at 20 M of Hg was maintained during etching so that continuous evacuation of the etching chamber could be accomplished without depletion of the argon supply.

RESULTS AND DISCUSSION

Examination of the etched pyrolytic graphite surfaces using light microscopy revealed conical etch pits in arrays reminiscent of those that have been observed in other materials. Figures 2 through 6 show some of the etch pit arrays that have been observed. All photographs are oriented such that the basal plane runs horizontal across the page.
Figures 2 and 3 show linear arrays of etch pits in the form of slip line segments. Microcracks predominantly along the basal planes are also seen. The interruption of what appears to be slip at a grain boundary is shown in Figure 3. Figure 4 shows the initiation of slip at the tip of microcracks along the basal planes. The occurrence of single pits lining up to form what appears to be low angle tilt boundaries is seen in Figures 5 a and b.

Whether or not mechanical polishing prior to etching is responsible for the observed structures has not been resolved at present. It is more likely that due to the anisotropic behavior of the graphite crystal lattice, thermal expansion in the c and a axes differs to such an extent as to create thermal stresses in the deposited layers (during high-temperature deposition and during cooling after deposition) which are high enough to initiate plastic flow and propagate microcracks.

Nevertheless, the purpose of this paper is only to report an etching technique which has been successful in producing preferential attack in the form of etch pits in the surface of pyrolytic graphite. This technique has previously been used for etching graphitized petroleum cokes (Reference 5). A type of pitting was also observed on these materials and explained on the basis that they may be due to the sublimation of impurities during the high temperature heat treatment of the coke. These recent observations with pyrolytic graphite suggest that the pitting observed in the graphitized petroleum coke might be explained in terms of dislocation sites. A comparison of the graphitized petroleum coke structures with those of pyrolytic graphites shows numerous similarities. The similarity between the wavy and bowed lines seen in graphitized coke microstructures and in pyrolytic graphites suggests that the same growth mechanism responsible for the pyrolytic graphite structures is responsible for those seen in graphitized cokes. Figure 6 is a photomicrograph of a graphitized petroleum coke particle showing pitting along the curved basal planes.

**SUGGESTIONS FOR FURTHER WORK**

Since this investigation was of an exploratory nature, the significance of the results lies in the fact that it has revealed the existence of substructures in graphite which might be explained in terms of dislocation theory.

An obvious extension of this work would be the controlled application of stress to the pyrolytic graphite in order to determine whether there is motion of the etch pit sites due to the stress. This movement of etch pit sites would be expected if they represented dislocation sites.

The question should be resolved as to whether the mechanical polishing of the specimen prior to etching has created a cold worked layer. An attempt should be made to remove the polished layer by chemical means. Perhaps the oxidizing solution of potassium dichromate - phosphoric acid (Reference 6) used previously for etching graphites can be modified and used as an electropolishing chemical for this purpose.
ATOMIC MODEL OF EDGE DISLOCATION IN GRAPHITE\(^{(3)}\)

X - DENOTES MISSING ATOMS
FIGURE 2: Multiplication of etch pits which form slip line segments (indicated by arrows).

FIGURE 3: Interruption of slip at the grain boundary indicated by arrow.

FIGURES 2 & 3
CATHODIC ETCH 2000X

INITIATION OF SLIP AT THE TIP OF MICRO-CRACKS ALONG THE BASAL PLANE (INDICATED BY ARROWS)
LOW ANGLE TILT BOUNDARIES ALONG THE BASAL PLANE

FIGURE 5
CATHODIC ETCH 2000X
PITTING ALONG THE BASAL PLANES OF AGRAPHITIZED PETROLEUM COKE

FIGURE 6
REFERENCES


5. TARPINIAN, A., Crystallographic and Microstructural Changes Occurring during the Graphitization of a Petroleum Coke, Watertown Arsenal Laboratories, WAL TR 825.5/1, January 1960.

The observation of pits in pyrolytic graphite after ion bombardment etching is described and their similarity to dislocation etch pits is speculated. Evidence of etch pit multiplication in the form of slip line segments and low angle tilt boundaries is presented.

I. Tarpinian, Aram
II. Gazza, George E.
III. O0 Proj TB4-004
IV. DA Proj 5893-32-004
<table>
<thead>
<tr>
<th>To:</th>
<th>No. of Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commanding Officer</td>
<td>5</td>
</tr>
<tr>
<td>Watertown Arsenal</td>
<td></td>
</tr>
<tr>
<td>Watertown, Mass.</td>
<td></td>
</tr>
<tr>
<td>Attn: ORDBE-LXM, Tech. Info. Section</td>
<td></td>
</tr>
<tr>
<td>OMRO, RPD</td>
<td>1</td>
</tr>
<tr>
<td>Authors</td>
<td>2</td>
</tr>
<tr>
<td>Office, Chief of Ordnance</td>
<td></td>
</tr>
<tr>
<td>Department of the Army</td>
<td></td>
</tr>
<tr>
<td>Washington 25, D. C.</td>
<td></td>
</tr>
<tr>
<td>Attn: ORDTB-Res. &amp; Materials</td>
<td>1</td>
</tr>
<tr>
<td>Director</td>
<td></td>
</tr>
<tr>
<td>Army Research Office</td>
<td></td>
</tr>
<tr>
<td>Department of the Army</td>
<td></td>
</tr>
<tr>
<td>Washington 25, D. C.</td>
<td>1</td>
</tr>
<tr>
<td>Commanding General</td>
<td></td>
</tr>
<tr>
<td>Ordnance Weapons Command</td>
<td></td>
</tr>
<tr>
<td>Rock Island, Illinois</td>
<td></td>
</tr>
<tr>
<td>Attn: ORDOW-IX</td>
<td>1</td>
</tr>
<tr>
<td>ORDOW-TX</td>
<td>2</td>
</tr>
<tr>
<td>Commanding General</td>
<td></td>
</tr>
<tr>
<td>Aberdeen Proving Ground</td>
<td></td>
</tr>
<tr>
<td>Aberdeen, Maryland</td>
<td></td>
</tr>
<tr>
<td>Attn: Ballistic Research Lab.</td>
<td>1</td>
</tr>
<tr>
<td>ORDBG-LH, Tech. Library, Bldg. 313</td>
<td>1</td>
</tr>
<tr>
<td>Commanding General</td>
<td></td>
</tr>
<tr>
<td>Army Ballistic Missile Agency</td>
<td></td>
</tr>
<tr>
<td>Redstone Arsenal, Alabama</td>
<td></td>
</tr>
<tr>
<td>Attn: ORDAB-DRF, Mr. W. A. Wilson</td>
<td>1</td>
</tr>
<tr>
<td>ORDAB-DSN, Dr. W. R. Lucas</td>
<td>5</td>
</tr>
<tr>
<td>Commanding General</td>
<td></td>
</tr>
<tr>
<td>Army Rocket &amp; Guided Missile Agency</td>
<td></td>
</tr>
<tr>
<td>Redstone Arsenal, Alabama</td>
<td></td>
</tr>
<tr>
<td>Attn: ORDAB-DV</td>
<td>1</td>
</tr>
<tr>
<td>ORDXR-OCP, Mr. R. L. Wetherington</td>
<td>5</td>
</tr>
<tr>
<td>Transmitted Date: <strong>Oct 26, 1960</strong></td>
<td></td>
</tr>
<tr>
<td>To:</td>
<td>No. of Copies</td>
</tr>
<tr>
<td>-----</td>
<td>--------------</td>
</tr>
</tbody>
</table>
| Commanding Officer  
Detroit Arsenal  
Center Line, Michigan  
Attn: ORDMX-BMW  
ORDMX-AL | 1 |
| Commanding Officer  
Diamond Ordnance Fuze Laboratories  
Washington 25, D. C.  
Attn: ORDUTL 06.33, Tech Ref. Sec. | 1 |
| Commanding Officer  
Frankford Arsenal  
Bridge-Tacony Streets  
Philadelphia 37, Pa.  
Attn: ORDBA-1300 | 2 |
| Commanding Officer  
Ordnance Ammunition Command  
Joliet, Illinois  
Attn: ORDLY-AR | 1 |
| Commanding General  
Ordnance Tank-Automotive Command  
1501 Beard Street  
Detroit 9, Michigan  
Attn: ORDMC-RM.1 | 1 |
| Commanding General  
Ordnance Tank-Automotive Command  
Detroit Arsenal  
Center Line, Michigan  
Attn: ORDMC-RM.1, Mr. Charles Salter | 1 |
| Commanding Officer  
Picatinny Arsenal  
Dover, New Jersey  
Attn: FREL | 1 |
| Commanding Officer  
Redstone Arsenal  
Redstone Arsenal, Alabama  
Attn: Technical Library | 1 |
| Commanding Officer  
Rock Island Arsenal  
Rock Island, Illinois  
Attn: Laboratory | 1 |
To: No. of Copies

Commanding Officer
Springfield Armory
Springfield 1, Mass.
Attn: ORDBD-TX

Commanding General
U.S. Army Ordnance Special Weapons
Ammunition Command
Dover, New Jersey

Commanding Officer
Watervliet Arsenal
Watervliet, New York
Attn: ORDBF-RT

The Director
Jet Propulsion Laboratory
California Institute of Technology
Pasadena 3, California
Attn: Dr. L. Jaffe

Commanding Officer
Office of Ordnance Research
Box CM, Duke Station
Durham, North Carolina
Attn: ORDOR-ED
Dr. Peter Kosting

Army Reactor Branch
Division of Research Development
Atomic Energy Commission
Washington 25, D. C.

Commander
Armed Services Tech. Info. Agency
Arlington Hall Station
Arlington 12, Virginia
Attn: TIPDR

Chief, Bureau of Aeronautics
Department of the Navy
Washington 25, D. C.
Attn: TD Division

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.
Attn: Rep-3
<table>
<thead>
<tr>
<th>To:</th>
<th>No. of Copies</th>
</tr>
</thead>
</table>
| Chief, Bureau of Ships  
Department of the Navy  
Washington 25, D. C.  
Attn: Code 592 | 1 |
| Chief, Naval Eng. Exp. Station  
Department of the Navy  
Annapolis, Maryland | 1 |
| Commander, Naval Proving Ground  
Dahlgren, Virginia  
Attn: A&P Lab. | 1 |
| Director  
Naval Research Lab.  
Anacostia Station  
Washington 25, D. C.  
Attn: Tech. Info. Officer | 1 |
| Chief, Office of Naval Research  
Department of the Navy  
Washington 25, D. C.  
Attn: Code 423 | 1 |
| Commander  
Wright Air Development Center  
Wright-Patterson Air Force Base, Ohio  
Attn: WCTRO  
WCRL | 1 |
| U.S. Atomic Energy Commission  
P.O. Box 62  
Oak Ridge, Tennessee | 1 |
| National Aeronautics & Space Admin.  
1520 H Street, N. W.  
Washington 25, D. C. | 1 |
| Defense Metals Information Center  
Battelle Memorial Institute  
Columbus, Ohio | 1 |
| Research Division Library  
Raytheon Company  
28 Seyon Street  
Waltham 54, Massachusetts | 1 |

TOTAL COPIES DISTRIBUTED - - 82
Total number of copies printed: 10
Extra copies to authors: 10
Copies sent to OTH 2/6/60: 2
Copy for Publ. Editor: 1
Extra copies sent to Tech Dep. Sec.: 6

Cpt. Astronautical Systems Div. Allan ASRCEM-1
McKliger, USAFB, Ohio Retirement