Argonne National Laboratory

ELECTRON-MICROSCOPIC STUDIES OF
FUNDAMENTAL PHYSICAL AND CHEMICAL PROCESSES
IN SINGLE CRYSTALS OF GRAPHITE

by

G. Montet, F. Feates,
and G. Myers

MASTER

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.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	The University of Iowa	Northwestern University
Carnegie Institute of Technology	Kansas State University	University of Notre Dame
Case Institute of Technology	The University of Kansas	The Ohio State University
The University of Chicago	Loyola University	Purdue University
University of Cincinnati	Marquette University	Saint Louis University
Illinois Institute of Technology	Michigan State University	Washington University
University of Illinois	The University of Michigan	Wayne State University
Indiana University	University of Minnesota	The University of Wisconsin
Iowa State University	University of Missouri	

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.

Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ELECTRON-MICROSCOPIC STUDIES OF
FUNDAMENTAL PHYSICAL AND CHEMICAL PROCESSES
IN SINGLE CRYSTALS OF GRAPHITE

by

G. Montet, F. Feates, and G. Myers

Solid State Science Division

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.

June 1967

THIS PAGE
WAS THIS PAGE ALLY
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	5
DISPLACEMENT ENERGY IN GRAPHITE	10
OPTICAL DENSITY AND THICKNESS OF GRAPHITE LAMELLAE	18
REACTIONS OF GASES WITH SINGLE CRYSTALS OF GRAPHITE	23
ACKNOWLEDGEMENTS	46
REFERENCES	48

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Typical Appearance of Etched and Decorated Graphite Surface	9
2.	Annealed Crystal-Etched and Decorated	13
3.	Lightly Irradiated Crystal-Etched and Decorated	14
4.	More Heavily Irradiated Crystal-Etched and Decorated	15
5.	Variation of Displacement Energy with Angle of Incidence	17
6.	Cleavage Step on Graphite Crystal, Shadowed with Gold	20
7.	Optical Densities of Graphite Crystals of Various Thicknesses	22
8.	Rates of Vacancy Expansions in Chlorine-Oxygen Mixture	25
9.	Catalytic Channeling in Carbon Dioxide	28
10.	Expansion of Etch Pit in Water Vapor	32
11.	Activation Energy of the Water-Graphite Reaction	33
12.	Apparent Order of the Water-Graphite Reaction at 950°C	34
13.	Radiolytic Oxidation by Carbon Dioxide	37
14.	Controlled Geometry Figure - Basic Sandwich	39
15.	Rates of Recession and Vacancy Formation in Radiolyzed Carbon Dioxide	40
16.	Correlation between α_1 and α_{1-1} (Eq. 6)	43
17.	G(-C) at start of oxidation	44
18.	Alignment of vacancies	45
19.	Influence of Radiolyzed Methane	47

ELECTRON-MICROSCOPIC STUDIES OF FUNDAMENTAL PHYSICAL AND CHEMICAL PROCESSES IN SINGLE CRYSTALS OF GRAPHITE

by

G. Montet, F. Feates, and G. Myers

INTRODUCTION

This article summarizes recent studies of fundamental processes occurring in single crystals of graphite as a result of certain physical and chemical changes. These studies utilized the etch-decoration technique for the detection of defects in graphite by electron microscopy. This method is very useful in the investigation of solid state phenomena, but certain precautions must be observed to avoid misleading results. The viewing of a sample in the electron microscope reveals a vast amount of information from which the essential data must be selected through a judicious use of statistical analysis. Conversely, the area visible in the field of the microscope is a very small fraction of the area of the crystal; hence, it is necessary to ascertain that the sample is representative. In the experiments to be described herein, we have attempted to select a random sample by repeated cleaving of the original crystal; the entire surface area of the cleaved section was examined and an appropriate averaging of the data made. Usually several duplicate samples were run, and only those observations which occurred repeatedly in several samples were retained. In the study of chemical phenomena it is necessary, and often difficult, to avoid catalytic effects.

These investigations were carried out on selected crystals from the area around Ticonderoga, New York. These crystals are found in Precambrian limestone, near contact areas where the limestone has been metamorphosed by igneous intrusions. The formation of graphite under conditions of high pressure and low temperature, which are presumed to have prevailed near the contact areas, should lead to low concentrations of vacancies. Determination of the vacancy concentration using the etch-decoration technique yields a value of 10^{-8} to 10^{-7} vacancies, or vacancy clusters, per carbon atom.¹ Presumably these defects are fossil radiation damage from radioactive impurities in the rock matrix. For those experiments for which this vacancy concentration is too high, the crystals were annealed at 2300°C by electron bombardment in vacuo; this treatment reduces the concentration to less than 10^{-10} vacancies per carbon atom,² the lowest concentration observable by the etch-decoration technique. It is unfortunate that no independent determinations of these concentrations exist.

The etch-decoration method consists of three distinct steps: cleavage, etch, and decoration. All of these steps exploit the peculiar physical and chemical properties of graphite. The layer structure of graphite with weak bonding between the layer planes facilitates the cleaving of single crystals into thin lamellae; in etching the lamella, advantage is taken of the anisotropy of oxidation of graphite; and decoration of surface imperfections is a result of the high mobility of metal atoms on clean surfaces of graphite.

Graphite crystals may be cleaved by any of several procedures. Consistent results are usually obtained by fastening crystals to a microscope slide with Duco cement, and using a second slide covered

with a thinly spread layer of not quite dry cement to pull off slices of the crystal. This operation can be repeated until the desired section of the crystal has been reached. The desired lamella is then removed from the slide by dissolving the cement, reversed, attached to another slide by using a water soluble polyvinyl cement, and repeatedly cleaved until a thickness of a few hundred angstroms is reached. This final cleaving is usually done by using Scotch tape.

The successful etching of defects in the cleavage surface of single crystals of graphite depends on the fact that carbon atoms are much more easily removed from the edges of layer planes than from the surface of these planes. As will be seen later, these rates of removal may differ by as much as 10^{13} . It has been found that many gases and solutions may be successfully used to etch the cleaved surface, but many of the etchants are susceptible to catalytic impurities. Since it is known that many catalysts are inactivated by adding halogens to the reacting gases, a mixture of chlorine and oxygen has been adopted as the standard etchant. This mixture, which is prepared by saturating dry oxygen with carbon tetrachloride and decomposing in a silica tube at 950°C , has proved to be a reliable etchant for a variety of graphite crystals.

Etching converts the lattice defects into circular surface steps which include the same number of layer planes as the original defect; thus, are only a few angstroms deep. In order to render such shallow steps visible in the electron microscope, a special staining or decoration technique is required. The decoration of graphite surfaces is based on Bassett's observations on the decoration of cleavage surfaces of alkali halides by gold.³ He found

that the gold did not form a continuous film, but consisted of a nonuniform distribution of small nuclei aggregated preferentially at surface steps, even when these steps were only one atom high. After some experimentation it was found that equivalent results could be obtained for gold on graphite, if organic compounds were vigorously excluded from the cleavage surface, and prolonged contact with water was avoided. Routine decorations are carried out in a bell jar at a pressure of about 10^{-5} torr. The samples, which are supported on sapphire plates for etching, are floated off on water and caught on copper grids which have been carefully washed in acetone to remove organic contaminants. The grids containing the samples are placed in recesses in a nickel plate which is an integral part of a resistively heated nickel furnace. After evacuating the bell jar, the samples are heated to about 250°C and a quantity of gold sufficient to deposit a monolayer on the graphite (~ 2 mg) is rapidly evaporated from a tungsten filament placed about 20 cm from the samples. In these studies the etched-decorated graphite lamellae were then examined in a Siemens Elmiskop I electron microscope. An electron micrograph of a typical etched-decorated cleavage surface of graphite is shown in Fig. 1.

A more complete description of the etch-decoration technique with observations on the mobility of metals on graphite and the mechanism of nucleation may be found in the review article by Hennig.⁴

Fig. 1. Typical Appearance of Etched and Decorated Graphite Surface

DISPLACEMENT ENERGY IN GRAPHITE

When a fast particle traverses the lattice of a crystalline solid, it may lose energy by several processes, depending on the nature of the particle and its energy. In the case of displacement of atoms, the most important means of energy loss is by elastic collisions with atoms of the lattice. If in an elastic collision the lattice atom receives an energy in excess of E_d , the displacement energy, it is displaced from its normal site. The displacement process, therefore, creates a lattice vacancy and, since in most circumstances the recoiling atom comes to rest in a nonequilibrium site, an interstitial atom. The value of E_d is usually considerably larger than the energy required to form an interstitial-vacancy pair by a thermodynamically reversible process; this is because the recoil takes place before the neighboring atoms have time to relax.

The process just described is the primary process, but in most cases of bombardment with heavy particles the primary recoil is also of importance to the damage process. If the energy of the primary is considerably greater than E_d , the primary causes further atomic displacements by secondaries, etc., until the energy of each particle has been degraded below E_d . Such displacement cascades account for most of the defects produced during bombardment with heavy particles. If one is interested in determining E_d these displacement cascades introduce severe experimental difficulties; for this reason electrons of an energy sufficiently low to minimize secondary displacements are usually chosen as the bombarding particle. This choice excludes complex localized regions of damage and the

vacancy-interstitial pairs are randomly distributed throughout the affected portion of the sample; this portion is usually of sufficient extent to allow reasonably convenient measurements of property changes. The measurement of such property changes is, nevertheless, an indirect determination of the displacement energy and depends on various parameters occurring in the theoretical expression for the cross section for atomic displacement. The etch-decoration technique, described above, permits a direct observation of the vacancies resulting from the primary process, hence a direct determination of the displacement energy in graphite. A redetermination of this value for graphite is desirable since the two prior indirect determinations^{5,6}--both based on measurements of changes in electrical resistance--of the displacement energy, E_d , differ by a factor of about two.

An electron of energy sufficient to eject a carbon atom from its lattice position is in the relativistic range, and the equation governing the energy transfer from electron to target atom is

$$E_t = \frac{2(E_e + 2mc^2)}{Mc^2} E_e \quad (1)$$

In this equation, E_e and E_t are the energies of the electron and ejected atom, respectively, and m and M their respective rest masses; c is the velocity of light in vacuum. The displacement energy E_d is the minimum value of E_t , which corresponds to a value of E_e just sufficient to produce primary vacancies. The initial appearance of the vacancies is detected by the etch-decoration method and the displacement energy E_d is calculated from the observed value of E_e (minimum) by use of Eq. (1).

The irradiations were carried out on annealed ($V/C < 10^{-10}$) single crystals of graphite potted in silver and placed on a rotating target assembly which fitted into the acceleration tube of a Van de Graaff accelerator. A typical bombardment employed a low current of electrons in the energy range from 100 to 500 keV; the charge deposited was usually 6 millicoulombs--typically a current of 10-15 μ a for 7-10 minutes. Irradiations were carried out at various temperatures in the range from 77°K to 600°K, and the angle between the electron beam and the c-axis of the crystal varied from 0 to 90 degrees.

If an annealed crystal is cleaved, etched, decorated and examined in the electron microscope, it appears as shown in Fig. 2. Note that the globules of gold appear to be rather randomly distributed on the surface of the graphite. When a crystal is lightly irradiated with low energy electrons ($\sim$ 180 keV) the appearance in the electron microscope is as shown in Fig. 3. Note that the circles outlining the vacancies are single and reasonably widely spaced. A somewhat heavier irradiation of high energy ($\sim$ 400 keV) produces a distribution of circles as shown in Fig. 4. Note that some of the circles overlap and that there are circles within circles which indicates that these electrons were energetic enough to displace atoms in two successive layers.

When the experiments described above are carried out at room temperature with the electron beam parallel to the c-axis of the graphite crystal, it is found that for energies less than 150 keV the etch-decorated flakes appear as in Fig. 2; that is, no vacancy loops are found. When the energy of the electrons exceeds 160 keV, the etch-decorated flakes appear as in Fig. 3; that is, a low

Fig. 2. Annealed Crystal-Etched and Decorated

Fig. 3. Lightly Irradiated Crystal-Etched and Decorated

Fig. 4. More Heavily Irradiated Crystal-Etched and Decorated

concentration of vacancy loops is found. This electron energy corresponds to a displacement energy,

$$E_d = 33 \text{ eV} \quad (2)$$

This energy is about 10% higher than the preliminary value reported² and results from a calibration of the energy of the Van de Graaff electron beam by passing the electrons through a known magnetic field.

The value of 33 eV for the displacement energy in graphite is in rough agreement with that of Eggen,⁵ but is not in agreement with the recently reported value of Lucas and Mitchell.⁶ The value reported here and that of Eggen refer to displacements taking place at room temperature; whereas, that of Lucas and Mitchell refers to displacements occurring at low temperatures ($\sim 15^\circ\text{K}$). Experiments run at various temperatures from 77°K to 600°K indicate, however, that the temperature of irradiation has little effect on the value of the displacement energy--at least at these low temperatures.

It appears plausible intuitively that the threshold energy for atom displacement in graphite should increase as the direction of the impinging electrons deviates from the c-direction. Accordingly several measurements have been made in which the electron beam was inclined with respect to the c-axis. There appears to be no appreciable change in the value of the displacement energy until an angle of 80° is reached; at this angle where the electrons are almost parallel to the layer planes of the graphite lattice, the displacement energy appears to be about 60 eV. An illustration of the variation of displacement energy with angle of impingement is given in Fig. 5.

Fig. 5. Variation of Displacement Energy with Angle of Incidence

A more complete description of this experiment with a discussion of the results may be found in Ref. 7.

OPTICAL DENSITY AND THICKNESS OF GRAPHITE LAMELLAE

In many studies of the properties of single crystals of graphite in which the etch-decoration method is used, it is useful, and sometimes necessary, to know the thickness of the cleaved sections; for this reason an effort has been made to develop a method by which this thickness may be readily determined on a routine basis. A determination of the optical density of a nonopaque substance is one of the simpler nondestructive measurements of thickness, and it was decided to exploit this procedure. In view of the fact that reflectivity measurements on natural graphite crystals have yielded conflicting values for the optical constants,^{8,9} a more direct technique for determining the optical density was sought.

In these experiments annealed single crystals of graphite were cleaved into transparent sections by the method described above, and those lamellae with apparent cleavage steps when viewed in transmitted light in the optical microscope were selected for further investigation. These lamellae were placed on sapphire plates and etched at 600°C with wet oxygen to make sloped steps more nearly vertical,¹⁰ and to facilitate the handling of these fragile samples, which were then floated on water and caught on carefully cleaned microscope cover glasses.

Measurements of optical density were made with a microdensitometer consisting of an optical microscope (Leitz Ortholux), a selected-area viewing unit (Leitz), and a photometer-densitometer

(Photovolt) utilizing a photomultiplier tube. The light source used was the illumination system of the microscope, powered by a constant voltage transformer, in conjunction with various interference filters to restrict the wavelengths of the light to narrow bands. The densitometer was adjusted to read zero on the low side of a step, so that the reading taken on the high side represented the optical density of the thickness of graphite contained in the step. This procedure was repeated several times and the average optical density computed. The samples were then shadowed with gold particles impinging at an angle of 45° with respect to the crystal planes; the evaporation source was positioned behind the step so that the width of the shadow was equal to the height of the step. Such a shadowed step is shown in Fig. 6. After shadowing, the crystals were again floated on water and caught on electron microscope specimen grids and the width of the shadow measured, at 10^5 diameters magnification, on photographic plates taken in the electron microscope.

Most of the samples were etched at 600°C for 10 minutes; to check the influence of etching on shadow width, a few samples were etched for 20 minutes, but no effect was observed. Occasionally, a step would exhibit a shadow much wider than expected; in these cases a close examination in the electron microscope revealed that the edge of the step had curved upward, or, in some cases, exfoliated. This effect occurred only in those steps greater than $500 \text{ \AA}$ in height. In no instance was a shadow width observed which was appreciably smaller than that expected.

The loss in intensity I of light of wavelength λ passing through at thickness t of material may be expressed as

Fig. 6. Cleavage Step on Graphite Crystal, Shadowed with Gold.

$$I = I_0 \exp \left(- \frac{4\pi kt}{\lambda} \right) , \quad (3)$$

where k is the extinction coefficient in the complex index of refraction $N = n - ik$. Huntjens and Van Krevelen⁸ and McCartney and Ergun⁹ have obtained values for the refractive index n and the absorption index κ by reflectivity measurements on the cleavage surfaces of graphite crystals, and Ergun and McCartney¹¹ have determined extinction coefficients (the product of n and κ) by a transmission method. The optical density at 578 m μ has been calculated, using Eq. (3), for the three sets of data and the results plotted in Fig. 7. It is evident that the direct measurements of the step heights are consistent with the reflectance data of Huntjens and Van Krevelen and the transmission data of Ergun and McCartney. As an independent check, two samples were prepared with steps high enough to be measured by interference microscopy. These measurements, which were expertly made by W. L. Primak of this Laboratory, are shown as crosses in Fig. 7; it is seen that they are in good agreement with our results.

No numerical values may be assigned to the optical constants from this work, but a value of ~ 1.15 (in good agreement with the reported value 1.14¹¹) may be assigned to the product, $n\kappa$. This method of correlating optical density with film thickness should be applicable to other substances suitable for study by electron microscopy.

A more complete version of this report has appeared.¹²

Fig. 7. Optical Densities of Graphite Crystals of Various Thicknesses

REACTIONS OF GASES WITH SINGLE CRYSTALS OF GRAPHITE

This section summarizes the results obtained for reaction rates of single crystals of graphite with various gaseous agents. The rates have been expressed in units such that the rate gives the probability that any given surface atom is removed in one minute; i.e., a rate of unity means a monolayer of surface atoms is removed per minute. As a result of the large structural anisotropy of graphite, reaction rates differ widely depending on whether the reaction is proceeding parallel to or perpendicular to the c-axis of the crystal. In general those reactions which remove edge atoms from the plane (perpendicular to the c-axis) proceed more rapidly than those which remove face atoms from the planes (parallel to the c-axis). It appears that this distinction in reaction rates cannot be made in experiments carried out on polycrystalline graphite, although indications of this anisotropy appeared in early studies of single crystal reactions by optical microscopy.¹³ The rates of reactions proceeding perpendicular to the c-axis have been determined by measuring the diameters of the etch loops produced from lattice vacancies in the cleaved surface. This method rests on the assumption that the rate is independent of curvature of the surface step; this assumption has been tested--for most etchants--by measuring the rate of growth of loops, and the results are discussed under the appropriate etchant. The rates of reactions parallel to the c-axis have been determined by measuring the rate of production of vacancies in the cleaved faces of annealed crystals.

Reactions in chlorine-oxygen mixtures--The reaction rates in Cl_2/O_2 have been carefully studied because this agent has been adopted as a "standard etchant"; nevertheless, the reactions are

not well understood since standardizing the procedure has resulted in a complex system. The gas mixture is prepared by passing dry oxygen through a wash bottle containing CCl_4 , then through a fused silica tube packed with silica wool and heated to 950°C , and, finally, into a second silica tube maintained at the desired reaction temperature. The graphite samples were supported on sapphire plates, air-dried at 110°C , then placed on silica carrier plates and inserted directly into the reaction tube.

The reaction perpendicular to the c-axis was measured over a wide range of time and temperature. The rate of growth of the loops, shown in Fig. 8, was linear, showing that the effect of step curvature was insignificant. The rate of reaction parallel to the c-axis was estimated by counting the number of resolvable loops produced per unit time in a sample originally free of vacancies. This necessarily neglects those loops which have not yet reached a resolvable size, and it is estimated that these rates are about 10% low. The activation energies have been estimated from Arrhenius plots of $K = K_0 \exp(-\Delta H/RT)$. These, and other reaction data, are given in Table I.

Reactions in air--The reactions in air were carried out in a vacuum line. The samples were supported on sapphire plates and outgassed at 10^{-6} torr at 900°C ; they were then reacted with air which had been dried by passage through and storage over magnesium perchlorate, and further passed through liquid nitrogen at 50 torr pressure. The rates reported in Table II have not been corrected for nonlinearity of reaction rate, although preliminary results indicate that the rate varies inversely with curvature of surface steps.

Fig. 8. Rates of Vacancy Expansions in Chlorine-Oxygen Mixture

TABLE I. Reactions of Graphite with Cl_2/O_2

	Reaction $\perp$ c-axis	Reaction $\parallel$ c-axis
Temp. Range, $^{\circ}\text{C}$	500-850	700-850
K_{O} , atom-atom $^{-1}$ -min $^{-1}$	7.1×10^{-6}	2.5
ΔH , kcal-mole $^{-1}$	16.7	46
Rate at 725°C , atom-atom $^{-1}$ -min $^{-1}$	1.7×10^3	2.5×10^{-10}

TABLE II. Reactions of Graphite with Air

	Reaction $\perp$ c-axis	Reaction $\parallel$ c-axis
Temp. Range, $^{\circ}\text{C}$	600-900	800-950
K_{O} , atom-atom $^{-1}$ -min $^{-1}$	4×10^{17}	5.6×10^6
ΔH , kcal-mole $^{-1}$	77	84
Rate at 900°C , atom-atom $^{-1}$ -min $^{-1}$	2.2×10^3	1.6×10^{-9}

The rates of oxidation measured by conventional methods can be compared with those of Table II, if the surface area of the sample is known. Lang et al.¹⁴ have investigated the oxidation of a large number of polycrystalline graphites and concluded that the oxidation rates for particularly pure samples are nearly equal, when referred to B.E.T. areas. Assuming that this constancy reflects the fact that, in all the graphites investigated, the edge atoms constitute a constant fraction, about 1/10, of all surface atoms, Lang's rate constant of $1.3 \times 10^{-3} \text{ g-m}^{-2}\text{-hr}^{-1}$ at 625°C may be compared with the data of Table II. The weighted average area per atom of $3.2 \text{ \AA}^2$ converts this rate to $3.5 \times 10^{-2} \text{ atoms-atom}^{-1}\text{-min}^{-1}$ or 0.35 when referred to edge atoms. The single crystal rate constant, calculated at 625°C from the perpendicular rate constants of Table II, is 0.10 at a pressure of 50 torr, or 0.39 at one atmosphere, utilizing the fact that the reaction rate is proportional to the square root of pressure.

Reactions in carbon-dioxide--These reactions were studied in a double-walled fused silica vacuum system, the annular space being evacuated to reduce leakage of oxygen. It proved to be very difficult to minimize catalytic effects; after reaction, most samples contained some areas where channeling had occurred - see Fig. 9. The carbon dioxide used was resublimed several times and stored over P_2O_5 . The reactions were carried out at a pressure of one atmosphere, and no attempt was made to remove the small amounts of carbon monoxide produced.

The rate of reaction perpendicular to the c-axis depended greatly on the curvature of the step; hence, these rates were measured by first burning the vacancy containing samples in air

Fig. 9. Catalytic Channeling in Carbon Dioxide

to produce loops of a diameter of about $1000 \text{ \AA}$, outgassing at 1200°C , then reacting with carbon dioxide. The results presented in Table III thus refer to reactions taking place at steps of low curvature. No evidence was found for reaction parallel to the c-axis in the temperature range 1000°C - 1200°C ; even when samples were re-etched in the Cl_2/O_2 mixture after exposure to CO_2 , no loops were developed in the cleavage surface.

The values given in Table III may be compared with Lang's measurements¹⁴ of the reaction of polycrystalline graphite with carbon dioxide. His rate of $4 \times 10^{-4} \text{ g-m}^{-2}\text{-hr}^{-1}$ at 900°C is converted to $0.11 \text{ atom-edge atom}^{-1}\text{-min}^{-1}$ by means of the assumptions stated above; this is to be compared to a rate of $0.07 \text{ atom-edge atom}^{-1}\text{-min}^{-1}$, calculated for 900°C from the data of Table III.

Reactions in water vapor--These studies utilize highly purified annealed crystals which have been irradiated with electrons of 267 KeV energy to produce vacancies to a concentration of 2×10^{-7} per carbon atom. After a preliminary etching in the standard chlorine-oxygen mixture to produce an etch pit of known diameter, the cleaved crystals were reacted with a known concentration of water vapor carried in a highly purified (minimum purity 99.997%) stream of helium. The apparatus was constructed of metal and Pyrex and the reactions carried out in a double-walled fused silica vessel surrounded by a tubular furnace. As it is known that oxygen interferes with the desired reaction, extensive care was taken in the construction of the apparatus and rigorous leak-testing was employed; all solutions were carefully degassed and saturated with helium. In spite of these precautions, catalytic effects (similar to those of Fig. 9) were prominent on most of the earlier samples and statistical

TABLE III. Reactions of Graphite with CO₂

	Reaction $\perp$ c-axis	Reaction $\parallel$ c-axis
Temp. Range, °C	1000-1150	---
K_O , atom-atom ⁻¹ -min ⁻¹	2.1×10^{16}	---
ΔH , kcal-mole ⁻¹	94	---
Rate at 1100°C, atom-atom ⁻¹ -min ⁻¹	25	---

methods were used to insure that areas representative of non-catalytic oxidation were studied. These catalytic effects, which apparently were due to the entrainment of microscopic particles of mercury, have been minimized in recent experiments by a more efficient trapping procedure. All of the oxidations were carried out with reference to a "control" lamella which was subjected to only the preliminary etch, and the diameters of the oxidized and "control" samples were measured on photographic plates taken in the electron microscope. Electron micrographs of an oxidized crystal and its "control" are shown in Fig. 10.

The most complete set of data so far accumulated were taken with the helium stream saturated with water at room temperature to give a concentration of about 2.2×10^4 VPM. Runs made at 25 degree intervals in the range from 800°C to 950°C inclusive yield data points which fall on a fairly straight line with a slope corresponding to an activation energy of $70.4 \text{ kcal-mole}^{-1}$.

Other concentrations studied over more limited temperature ranges were 4×10^3 VPM, 2×10^3 VPM, 10^3 VPM, and 500 VPM. These concentrations could be monitored by an electrolytic hygrometer (CEC "moisture monitor") and are more accurately known and more uniform over the duration of an experiment than the saturated value above. Arrhenius plots of the data are given in Fig. 11.

The apparent order of the reaction at 950°C is 0.71 over the concentration range measured, as is shown in the plot of the reaction rates given in Fig. 12. This is in good agreement with results obtained by Overholser and Blakely.¹⁵

Fig. 10. Expansion of Etch Pit in Water Vapor

Fig. 11. Activation Energy of the Water-Graphite Reaction

Fig. 12. Apparent Order of the Water-Graphite Reaction at 950°C

The reaction rates obtained herein may be compared with those of Overholser and Blakely, on the same basis as that used above. When oxidizing Speer Moderator-2 graphite with a BET surface area of $0.3 \text{ m}^2\text{-g}^{-1}$, they found a rate at 950°C of about $2.5 \times 10^{-4} \text{ g-g}^{-1}\text{-hr}^{-1}$ for a water vapor concentration of 460 VPM. On the basis of a one gram sample, this rate corresponds to the removal of 1.3×10^{19} carbon atoms per hour. The same authors found, for ATJ graphite with a BET surface area of $0.1 \text{ m}^2\text{-g}^{-1}$, a rate of about $1.8 \times 10^{-4} \text{ g-g}^{-1}\text{-hr}^{-1}$ (extrapolating their data) for the same conditions, corresponding to the removal of 9.4×10^{18} carbon atoms per hour. The area occupied by edge atoms in the Speer graphite is $3 \times 10^{18} (\text{\AA})^2\text{-g}^{-1}$; using this area of edge atoms in single crystal graphite and the observed rate of recession of this edge at 950°C and 500 VPM of $75 \text{ \AA-hr}^{-1}$ (see Fig. 12), a volume of $2.25 \times 10^{20} (\text{\AA})^3$ of graphite is consumed per hour. In single crystal graphite each atom occupies a volume of $8.85 \text{ \AA}^3$, so this rate corresponds to the removal of 2.5×10^{19} carbon atoms per hour. A similar comparison for the ATJ graphite yields a rate of removal of 8.5×10^{18} atoms per hour. Such close agreements in rate are probably fortuitous.

Some of these results have been included in a review article⁴ and a complete description of the reaction of graphite and ozone, as studied by the etch-decoration technique, has been published.¹⁶

Radiolytic Oxidation--Graphite can be oxidized by exposure to a number of gases excited by radiation. The resulting reactions are complex, and, with a controlled radiation source, slow. Investigations have been made using gas analysis techniques,¹⁷ C-14 labeling¹⁸ and conventional electron microscopy,¹⁹ but although all have yielded important information, little knowledge of the atomic processes

involved has been obtained. Outstanding problems include identification of active species responsible for gasification (or determination of some of their properties), measurement of the efficiency with which radiation produces oxidation (represented by $G(-C)$) and its dependence on gas pressure, geometrical arrangement of specimen and gas, etc., evidence for particular structural features in graphite which have reactivities different from bulk material, and the means by which certain gaseous additives can reduce the oxidation rate. The etch decoration technique, with its ability to identify sites from which individual carbon atoms have been removed has been used with considerable success to look at these problems.

Procedure--Specimens were prepared by the normal method,⁴ and were subjected to a short thermal etch to develop rings ($\sim 1,000 \text{ \AA}$ diameter) around all existing vacancies. While still resting on the sapphire support used for the etch, they were transferred to silica tubes which were filled with the oxidizing gas and were sealed off. Radiolysis was carried out using a Co-60 γ -source, and the capsule was finally opened, the specimen recovered and decorated with gold.

After exposure to CO_2 or O_2 and decoration, the appearance of the specimen was similar to that shown in Fig. 13 (CO_2 , 90 hours irradiation at dose rate of $1.2 \text{ M Rad hr}^{-1}$). The rings fall into two distinct groups, a population of large rings all about $7,000 \text{ \AA}$ diameter and another population in which rings vary in size from the smallest measurable ($\sim 400 \text{ \AA}$ diameter) up to about $6,000 \text{ \AA}$. The large rings arose from the "natural" vacancies which were given a $1,000 \text{ \AA}$ start in growth by the original thermal etch, whereas

Fig. 13. Radiolytic Oxidation by Carbon Dioxide

the rest have developed from vacancies produced and etched entirely by reaction with radiolyzed gas. By a careful count of the rings and their diameters it is possible to deduce the vacancy formation rate (VFR) and ring etch rate (RER) under a range of conditions. In a silica tube providing an excess of gas around the specimen, $VFR = 4.2 \times 10^{-10}$ and $3.7 \times 10^{-10} \text{ M.Rad}^{-1} \text{ mm Hg}^{-1}$ and $RER = 0.8$ and $6.2 \text{ atoms M.Rad}^{-1} \text{ mm Hg}^{-1}$ for CO_2 and O_2 respectively. No other influence of pressure (1 mm Hg - 800 mm Hg) or temperature (20°C - 350°C) was observed.

Nature of active species--Although VFR and RER are constant in a large tube, this is no longer true if the gas space above the specimen is reduced. This can be achieved using a small cell (Fig. 14) made of two microscope cover glasses separated by a small gap made with aluminum foil spacers, the specimen being placed in the center of the lower glass. Adequate mixing is achieved by diffusion from the cell and the gas gap can be measured easily and varied by altering the thickness of aluminum. Typical results for CO_2 are shown in Fig. 15. With very small gaps (at low pressure) the rates become directly proportional to gap, indicating a limiting rate with a negligible number of active species deactivated in the gas before reaction with the graphite. The limiting rates for CO_2 are $VFR = 8.6 \times 10^{-11}$, $RER = 46$ and for O_2 , $VFR = 7.9 \times 10^{-11}$ and $RER = 250$.

With increasing gaps some species become deactivated and the net rate falls. The point at which curvature commences therefore gives a qualitative measure of the range of the active species. For CO_2 and for oxygen at 6 cm Hg. pressure this starts at a gap of about 600 μ . However, there is slight evidence that linearity

Fig. 14. Controlled Geometry Figure - Basic Sandwich

Fig. 15. Rates of Recession and Vacancy Formation in Radiolyzed Carbon Dioxide

is maintained to a larger gap for VFR than for RER. This suggests that different active species may be responsible for the two modes of attack.

Calculation of $G(-C) \rightarrow G(-C)$, the number of carbon atoms gasified per 100 eV of energy absorbed by the gas, has little significance in the early stages of reaction which can be detected by the etch decoration technique, for as vacancies are formed and expand the G-value varies considerably. It is only in the steady state, when oxidation is occurring through many planes, that a constant value can be expected.

The steady state value can be assessed by extrapolating data using the initial values of VFR and RER given above. By analogy with crystal growth²⁰ in the top plane¹⁷ of an oxidizing surface the fraction of the surface (α) removed for a dose D can be deduced from:

$$\alpha_1 = 1 - \exp\left(-\frac{1}{3} k_1 k_2^2 N_0 \pi D^3\right), \quad (4)$$

where $k_1 = \text{VFR}$

$k_2 = \text{RER}$

$N_0 = \text{atom density in the plane.}$

Now the removal of α of the top plane exposes α of the second plane which becomes available for vacancy formation, and so on for each successive layer.

For the i 'th layer, the fraction of material oxidized

$$\alpha_i(D) = \sum_{n=0}^{D/\Delta D} \left[\alpha_{i-1} \left(\frac{2n+1}{2} \Delta D \right) - \alpha_{i-1} \left(\frac{2n-1}{2} \Delta D \right) \right] \alpha_i(D-n\Delta D) \quad (5)$$

and for all layers

$$\alpha_{(D)} = \sum_{i=0}^{i=\infty} \sum_{D=0}^{D=D} \alpha_i (D-u) d \alpha_{i-1} (u) \quad (6)$$

where $\alpha_i(u) = 1 - \exp(-\frac{1}{3} k_1 k_2^2 N_0 \pi D^3)$.

The above expression can be solved by computer and a steady state reaction rate obtained. Figure 16 shows the values of α_i as a function of α_{i-1} . It is clear that when the tenth and subsequent layers are oxidizing essentially steady state conditions are obtained. The summed reaction rates are shown in Fig. 17. The rapidly rising rate at the start of oxidation corresponds to the expansion of vacancies on the first layer. As the rings begin to overlap, the rate falls, but at the same time the rate is rising in the second layer, leading to a series of damped oscillations eventually settling to the steady state rate. For CO_2 this yields a value of $G(-C)$ of 2.4 and for O_2 of 9.5, which are very similar to values deduced from measurements on bulk material.^{26,27}

Effect of structural features--In general, no influence of structural features was observed. However, in a few cases, using very low radiation doses followed by a thermal etch to develop vacancies, some lining up of reactive sites was seen. In Fig. 18, a line of such sites have reacted and coalesced up on etching to produce a channel. At present no explanation of this behavior can be given.

Effect of gaseous additives--Methane is known to reduce the rate at which radiolytic oxidation occurs. It is believed²² to be effective by surface adsorption processes. This was tested by carrying

Fig. 16. Correlation between α_i and α_{i-1} (Eq. 6)

Fig. 17. $G(-C)$ at start of oxidation

Fig. 18. Alignment of vacancies

out an oxidation in CO_2 in the usual manner, and then exposing the specimen to irradiated methane before decoration. After decoration no evidence of ring structure was visible, the gold having remained on the surface as a fine granular deposit, particle size 20 A. However, by carefully heating the specimen, mobility of the gold commenced at 700°C and the etch rings appeared (Fig. 19). In experiments where methane was present during the attempted oxidation, no rings developed at all. This is therefore compelling evidence that radiolyzed methane is indeed adsorbed by the graphite, and that the adsorbed layer is stable at temperatures up to 700°C .

ACKNOWLEDGEMENTS

We are grateful to Dr. D. A. Woodward of the Applied Mathematics Division for assistance in the programming of the computer calculations. One of us (FSF) wishes to express his appreciation to Dr. O. C. Simpson, Director of the Solid State Science Division, for making laboratory facilities available.

Fig. 19. Influence of Radiolyzed Methane

REFERENCES

1. G. R. Hennig, Appl. Phys. Letters 4, 55 (1964).
2. G. L. Montet, Proc. 7th Carbon Conference, Cleveland, Ohio, June, 1965
3. G. A. Bassett, Phil. Mag. 33, 1042 (1958).
4. G. R. Hennig, Chemistry and Physics of Carbon, Vol. 2, 1 (1966), (Marcel Dekker, N. Y.).
5. D. T. Eggen, Report NAA-SR-69 (1955).
6. M. W. Lucas and E. W. J. Mitchell, Carbon 1, 345 (1964).
7. G. L. Montet, Carbon 5, 19 (1967).
8. F. J. Huntjens and D. W. Van Krevelen, Fuel 33, 88 (1964).
9. J. T. McCartney and S. Ergun, Fuel 37, 272 (1958).
10. G. R. Hennig, J. de Chimie Physique 58, 12 (1961).
11. S. Ergun and J. T. McCartney, Proceedings of the Fifth Conference on Carbon (Pergamon Press, London, 1963), Vol. 2, p. 167.
12. G. E. Myers and G. L. Montet, J. Appl. Phys. 37, 4195 (1966).
13. G. R. Hennig, Z. Electrochem. 66, 629 (1962).
14. F. M. Lang, P. Magnier, and S. May, Proc. Fifth Conf. on Carbon (Pergamon, London, 1962), p. 171
15. L. G. Overholser and J. P. Blakely, Carbon 2, 385 (1965), Carbon 3, 269 (1965).
16. G. R. Hennig, Carbon 3, 107 (1965).
17. R. Anderson, et al., Proc. 2nd U. N. Int. Conf. on Peaceful Uses of Atomic Energy, Vol. 7, p. 335.
18. T. B. Copestake and F. S. Feates, Proc. I.A.E.A. Symposium on Corrosion in Reactor Materials, Salzburg, (1962), p. 313.
19. I. Y. Adamson, I. M. Dawson, F. S. Feates, and R. S. Sach, Carbon 3, 393 (1966).

20. K. L. Mampel, Z. F. Physik Chemie, A187, 43, 1940.
21. P. C. Davidge, AERE Report CR.1450 (1959).
22. D. A. Dominey, Unpublished work (1966).
23. F. S. Feates, AERE Report R.4819, (1964).