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### The Influence of Solid Catalysts on the Etching of Graphite Single Crystals—A Motion Picture Study\*

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By using a 16 mm movie camera mounted on a Leitz Panphot microscope fitted with a hot-stage, it has been possible to observe directly the oxidation of purified natural graphite (Ticonderoga) single crystals. The motion picture shows the oxidation of four types of  $\{000\}$  graphite surfaces: (i) the as-purified faces which often contain rough patches owing to sublimation and inadvertent oxidation during purification, (ii) the pre-oxidized faces which contain a number of hexagonal etch pits and surface steps,<sup>(1,2)</sup> (iii) cleaved surfaces and (iv) cleaved surfaces on to which have been added metallic impurities. The impurities, which were invariably added as the free metal, were introduced from an acetone suspension and were never greater than a few microns in diameter except where unavoidable aggregation had occurred. The impurities included Fe, Ni, Co, Mn, Ta, Ti, Ag, Mo and B.

So far as the uncatalyzed reaction is concerned, this study confirms that (a) oxidation in the  $\langle 10\bar{1}0 \rangle$  directions exceeds<sup>(2,3)</sup> that in the  $\langle 1120 \rangle$  directions at temperatures up to 870°C, and (b) non-basal line dislocations are responsible<sup>(4,5)</sup> for some of the etch pits. The film shows the "unwinding" of a screw dislocation, i.e., oxidation along the  $\langle 000 \rangle$  direction to give a spiral pit.

Significant differences in the behaviour of various metal catalysts are readily apparent. Thus Fe in the initial stages of the graphite + O<sub>2</sub> reaction functions as an efficient catalyst, each particle giving rise to an etch pit as shown in Fig. 1(a). As oxidation continues, the Fe particles lose<sup>(6)</sup> their catalytic efficiency. Figure 1(b), which shows the same region as that shown in Fig. 1(a) 20 min later at 720°C, illustrates how particles of Fe no longer stimulate etch pit production and how well-defined hexagonal pits characteristic of an uncontaminated surface develop in the later stages of the oxidation. Ni, unlike Fe, retains a considerable degree of catalytic efficiency even after oxidation has continued for 105 min at 650°C. Particles of Co, after their initial period of catalysis, tend to rotate on, and migrate over, the surface. Figures 2(a), (b) and (c), which are three successive frames taken at intervals of 0.6 sec, show the nature of the cluster of partially oxidized particles of Co and how they rotate at 750°C. This rotation and clustering process depends critically upon the nature of the ambient gas; it is pronounced in O<sub>2</sub> but entirely absent in CO<sub>2</sub> both at 750°C.

Mn and Ag are extremely efficient catalysts, and Figs. 3(a) and (b), taken with the temperature at 720°C in a N<sub>2</sub> atmosphere [3(a)] and 5 min after introducing O<sub>2</sub> [3(b)], show how Mn particles lead to pit production as well as to channelling of the type described<sup>(7,8)</sup> previously for other metals. Ti is also a good catalyst, but Ta

appears not to affect the oxidation in any discernible manner. Mo metal first forms molten MoO<sub>3</sub> which is a remarkable catalyst as can be judged from Figs. 4(a), (b) and (c), which show the same region of the surface at roughly 2 min intervals at 720°C. Figure 4(a) shows the graphite surface, with its highly strained twin, and a few Mo particles. Figures 4(b) and (c) show the marked channel formation of the molten MoO<sub>3</sub>, together with the "straightened" twin: it appears likely that the exothermicity of the oxidation reaction is sufficient to relieve mechanical strain in the graphite crystal.

### REFERENCES

- HUGHES E. E. G., WILLIAMS B. R. and THOMAS J. M., *Trans. Faraday Soc.* **58**, 2011 (1962).
- THOMAS J. M. and HUGHES E. E. G., *Carbon* **1**, 209 (1964).
- THOMAS J. M., WILLIAMS B. R. and HUGHES E. E. G., *Phil. Mag.* **8**, 1513 (1963).
- HUGHES E. E. G., THOMAS J. M., MARSH H. and REED R., *Carbon* **1**, 339 (1964).
- THOMAS J. M., ROSCOE C., JONES K. M. and RENSHAW G. D., *Phil. Mag.*, in press.
- ANDERSON R. C., Ph. D. Thesis, Pennsylvania State University (1963).
- HENNIG G. R., *J. Inorg. & Nuclear Chem.* **24**, 1129 (1962).
- HUGHES GLENDA, Ph. D. Thesis, University of Wales (1963).

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### Chemisorption of Oxygen on Graphite as Followed by Thermoelectric Power Measurements\*

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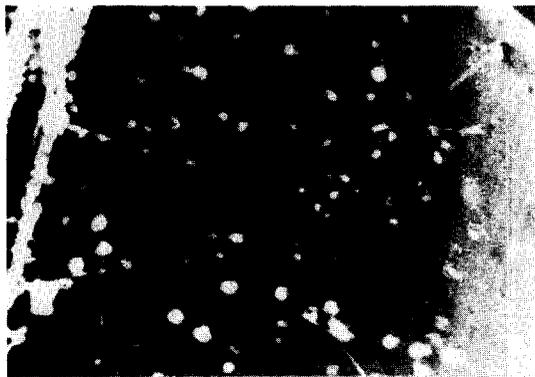
CARBON-OXYGEN surface complexes play a significant rôle in the combustion of carbon at temperatures up to, at least, 675°C.<sup>(1,2)</sup> Upon combustion three products are formed: gaseous CO, gaseous CO<sub>2</sub>, and a stable carbon-oxygen complex. The complex builds up on the active sites of the carbon undergoing combustion, resulting in a decrease in reaction rate. Recently, it has been shown, by using O<sub>1s</sub>, that the breakdown of this complex contributes somewhat to the total CO and CO<sub>2</sub> produced during the combustion of carbon.<sup>(3)</sup>

Graphite has a unique  $\pi$  electron band structure, with the positive and negative carriers balanced closely in concentration and the total concentration small relative to metals. These factors make the thermoelectric power ( $\alpha$ ) very sensitive to any process which results in the trapping of negative carriers; for example, the formation of a carbon-oxygen surface complex. Therefore, we

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OF GRAPHITE SINGLE CRYSTALS—A MOTION PICTURE STUDY



1(a)



1(b)



2(a)



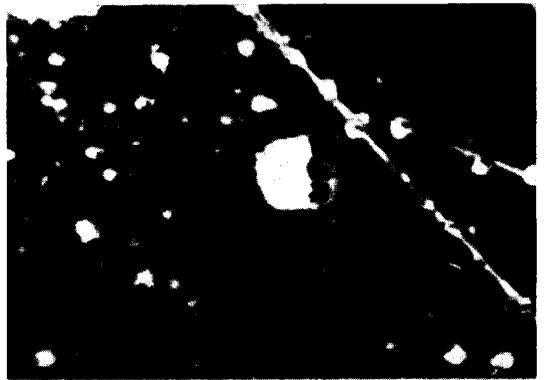
2(b)



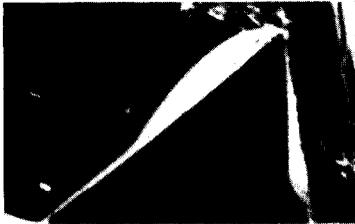
2(c)



3(a)



3(b)



4(a)



4(b)



4(c)

should be able to study the kinetics of oxygen chemisorption by following the change in  $\alpha$  upon exposure of graphite to  $O_2$  at different temperatures for various periods of time. This paper considers this possibility.

A natural graphite, having  $< 6$  ppm total impurity and a surface area of  $1.8 \text{ m}^2/\text{g}$  was used.† The graphite particles had a mean diameter of *ca.*  $30 \mu$  and a thickness of *ca.*  $0.5 \mu$ . Each particle was essentially a single crystal. Either the pure graphite or graphite plus 0.3 per cent by weight of  $3 \mu$  Fe powder was molded into bars at  $100,000 \text{ lb/in.}^2$   $\alpha$  was measured against Pt, with the temperature gradient imposed  $\perp$  to the molding direction.

All molded samples were first degassed at  $995^\circ\text{C}$  in He to remove most of the complex present on the original graphite. Wide variations in molding pressure and the introduction of 0.3 per cent Fe had a negligible effect on  $\alpha$  of the degassed samples. Degassed samples were then exposed to 1 atm of  $O_2$  at temperatures between  $608$  and  $725^\circ\text{K}$  to form various amounts of oxygen complex. (Gasification of carbon was negligible.)  $\alpha$  was then measured on each sample in 1 atm of He over temperature ranges where the oxygen complex was stable, prior to each sample being heated to  $950^\circ\text{C}$  to recover quantitatively the complex as CO and  $\text{CO}_2$ . Figure 1 shows the change in  $\alpha$  with measurement temperature for a series of pure graphite samples containing various amounts of oxygen complex. Figure 2 shows the dependence of  $\alpha$ , measured at  $720^\circ\text{K}$ , on the amount of chemisorbed oxygen ( $n$ ); obviously negative carriers are being trapped. The relation between  $\alpha$  and  $n$  is independent of chemisorption temperature.

With this correlation, the kinetics of oxygen chemisorption could be studied. Figure 3 shows the results upon exposure of the pure graphite to 1 atm of  $O_2$  at different temperatures. If it is assumed that the velocity of chemisorption is first order with respect to both reactants, the rate equation may be expressed as  $dn'/dt' = kC(1-0)n_\infty$ , where  $n'$  is the amount of oxygen chemisorbed on the graphite surface at time  $t'$ ,  $k$  is the rate constant,  $C$  is the concentration of  $O_2$  in the gas

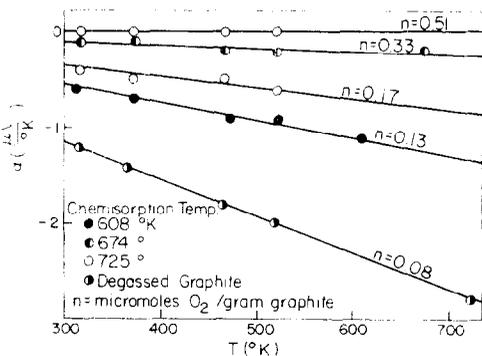


FIG. 1. Temperature dependence of the thermoelectric power of SP-1 graphite as a function of varying amounts of oxygen chemisorption.

†SP-1 graphite from Carbon Products Division, Union Carbide Corporation.

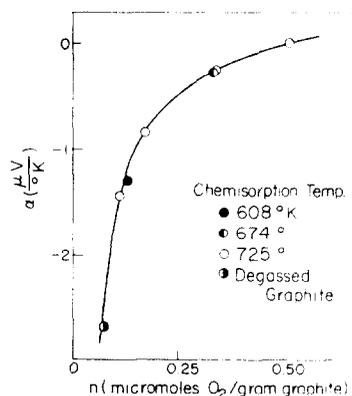


FIG. 2. Dependence of the thermoelectric power of SP-1 graphite at  $720^\circ\text{K}$  on the amount of chemisorbed oxygen.

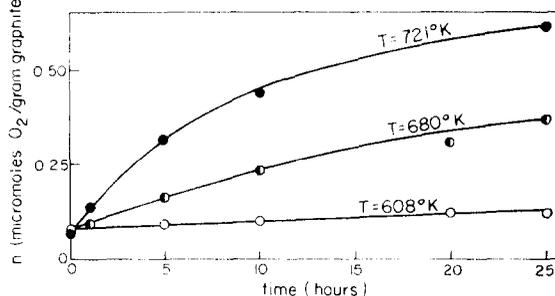


FIG. 3. Rate of oxygen chemisorption on SP-1 graphite.

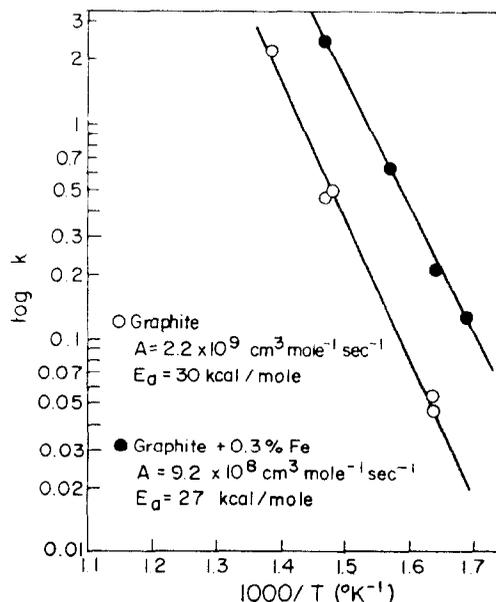


FIG. 4. Arrhenius plots for the catalyzed and uncatalyzed chemisorption of oxygen on SP-1 graphite.

phase,  $\theta$  is the fraction of active surface area covered at time  $t'$  and  $n_\infty$  represents the saturation amount of chemisorbed oxygen. Since  $\theta = n'/n_\infty$ , this equation can be integrated between the limits of  $n' = n_0$  at  $t' = 0$  and  $n' = n$  at  $t' = t$  to give  $n = n_\infty - [(n_\infty - n_0) \exp(-kCt)]$ . Curves calculated from the above equation by adjusting the values of  $n_\infty$  and  $k$  are shown in Fig. 3.  $n_\infty$ , which was independent of chemisorption temperature and the presence of Fe, equalled  $0.67 \pm 0.04 \mu$  mole  $O_2/g$ . It is estimated that this amount of  $O_2$  would be chemisorbed on *ca.* 3.7 per cent of the total surface area of the graphite, which corresponds closely to the percentage of the graphite particle surface which is edge area.

Figure 4 presents Arrhenius plots for  $k$ . Activation energies ( $E_a$ ) and preexponential term values ( $A$ ) are included. Since the uncertainty in  $E_a$  is  $\pm 2$  kcal/mole, nothing can be said about the possibility of Fe affecting  $E_a$  for  $O_2$  chemisorption. From the magnitude of  $A$ , it is concluded that the activated complex for  $O_2$  chemisorption loses all three translational degrees of freedom and part of one degree of rotational freedom.

#### REFERENCES

1. LAINE N. R., VASTOLA F. J. and WALKER P. L., JR., *Proceedings of the Fifth Carbon Conference*, Vol. 2, pp. 211-217. Pergamon Press, Oxford (1963).
2. LAINE N. R., VASTOLA F. J. and WALKER P. L., JR., *J. Phys. Chem.* **67**, 2030 (1963).
3. VASTOLA F. J., HART P. J. and WALKER P. L., JR., *Carbon* **2**, 65 (1964).

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#### Improvement of Surface Activity of Acetylene Black by Explosive Shock Loading

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It is reported in this note that the surface activity of a sample of acetylene black is largely improved by an explosive shock loading.

The sample of acetylene black was treated with benzene and then with acetone by using Soxhlet extractor, after which it was dried at  $120^\circ\text{C}$ . Using the experimental arrangement illustrated in Fig. 1, 2 g of the sample was shocked explosively with 68 g of a tetryl charge.

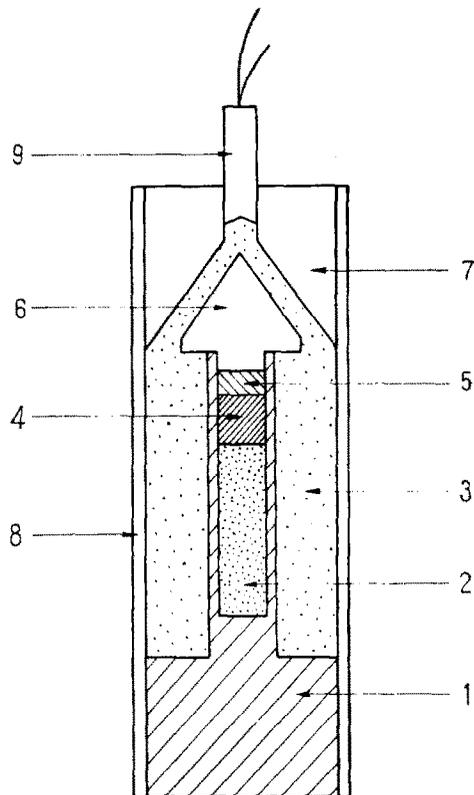


FIG. 1. Schematic diagram of an experimental arrangement. 1, sample holder of mild steel; 2, sample of acetylene black; 3, charge of tetryl; 4, plug of mild steel; 5, plastic clay; 6, wooden cone; 7, wooden plug; 8, plastic tube of vinyl chloride; 9, electric detonator.

After the shock loading, the sample retained its free-flowing state, the apparent density increased remarkably however. Electron micrographs of the original and the shocked samples (Fig. 2) indicate that shock loading converts the spherical shape of the original particles into an irregular one, and breaks the carbon structure.

The chemical properties of the shocked sample were examined in comparison with those of the original sample. The surface area was determined by the amount of iodine adsorbed in an iodine-potassium-iodide

TABLE 1. EFFECT OF EXPLOSIVE SHOCK LOADING ON THE SAMPLE OF ACETYLENE BLACK

Sample	Apparent density $\text{g/cm}^3$	Ignition temperature, $^\circ\text{C}$	Surface area, $\text{m}^2/\text{g}$	Amount of carbon dioxide evolved in 10 min $\text{cm}^3/0.1 \text{ g}$	$k \times 10^5$
Original	0.080	677	65.8	70.6	2.7
Shocked	0.308	581	110.4	97.6	38.2