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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 {0001} 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,^(1, 2) (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 <1010> directions exceeds^(3, 4) that in the <1120> directions at temperatures up to 870°C, and (b) non-basal line dislocations are responsible^(4, 5) for some of the etch pits. The film shows the "unwinding" of a screw dislocation, i.e., oxidation along the <0001> 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 + O₂ 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⁽⁶⁾ 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 O₂ but entirely absent in CO₂ 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 N₂ atmosphere [3(a)] and 5 min after introducing O₂ [3(b)], show how Mn particles lead to pit production as well as to channelling of the type described^(7, 8) 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 MoO₃ 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 MoO₃, 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.^(1, 2) Upon combustion three products are formed: gaseous CO, gaseous CO₂, 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 O₁₈, that the breakdown of this complex contributes somewhat to the total CO and CO₂ produced during the combustion of carbon.⁽³⁾

Graphite has a unique π 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 (α) 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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