

NOTE

An Electron Microscopy, Electron Diffraction and XPS Study of the Ag-Catalyzed Oxidation of Graphite

The role played by silver particles during the oxidation of single crystal graphite has been studied by transmission electron diffraction and microscopy, and by X-ray photoelectron spectroscopy.

Naturally occurring single crystals of graphite (obtained from Ticonderoga, NY) were purified and cleaved in a manner that has been described previously (1). Specimens suitable for study by transmission electron microscopy, were prepared by basal plane cleavage until they were less than 100 nm thick (2). An amount of silver equivalent to approximately five monolayers was deposited on the basal surface of these graphite samples in a commercial evaporator unit (AEI Metrovac Coating Unit) in a vacuum of $1.33 \times 10^{-3} \text{ N m}^{-2}$ (10^{-5} Torr) with the crystals at room temperature. Some of these coated samples were studied by transmission electron microscopy (Philips EM300) and the remainder were oxidized with molecular oxygen in a double walled quartz furnace. After heating the samples at 750 K *in vacuo* [$1.33 \times 10^{-4} \text{ N m}^{-2}$ (10^{-6} Torr)] molecular oxygen was introduced into the furnace at 1.3 KN m^{-2} (10 Torr) for 600 s. The samples were then cooled *in vacuo* and studied by electron microscopy.

Figure 1a is an electron micrograph showing the silver-coated graphite immediately after deposition of the metal, and Fig. 1b is the corresponding electron diffraction pattern from this selected area. The con-

tribution to the diffraction pattern from the silver film is found to be a series of continuous rings corresponding to a {111} texture superimposed on the single crystal spot pattern of the underlying graphite.

Figure 2a is an electron micrograph showing graphite coated with silver subsequent to high temperature treatment in oxygen and Fig. 2b is the electron diffraction pattern from this region. It is found that the silver clusters have agglomerated into larger particles during the high temperature oxidation process and that catalytic channeling on the graphite surface has occurred, similar to that observed in other investigations (3). It has been shown (4) that the clusters are mobile in the presence of oxygen at high temperatures and on encountering a step on the graphite surface, they catalyze the oxidation of graphite resulting in channel formation. The contribution to the electron diffraction pattern from silver now consists of individual spots indicative of improved alignment of the silver with respect to the graphite. Diffraction spots also appear in the pattern in positions corresponding to interplanar spacings of approximately 0.27 and 0.34 nm which do not correspond to any interplanar spacings in elemental silver. These additional diffraction reflections could be due either to the presence of an oxide of silver such as Ag_2O or to double diffraction of electrons at imperfections such as twin boundaries in the silver par-

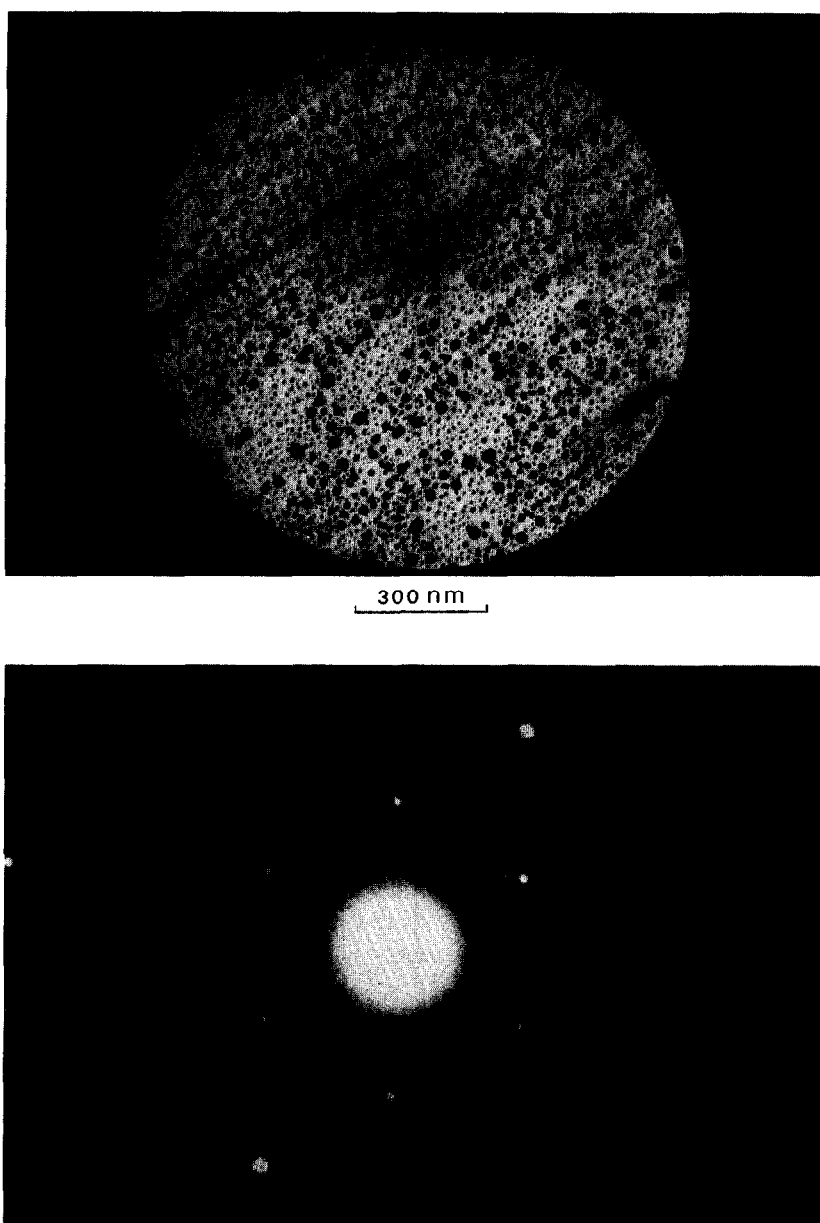


FIG. 1a. Bright-field electron micrograph of graphite coated with silver and (b) the corresponding selected area electron diffraction pattern.

ticles (5). Attempts to establish the cause of these anomalous reflections using dark field electron microscopy were unsuccessful because the small and relatively disordered quantity of silver present on the graphite surface produced only weak and complicated patterns, thus rendering the method particularly difficult.

X-Ray photoelectron spectroscopy has been utilized in an attempt to establish whether a surface oxide was formed during the catalytic reaction. Since relatively large samples (15×5 mm) were required for use in the X-ray photoelectron spectrometer (AEI ES 200) it was not possible to use single crystals of graphite since the

specimens were too small (a maximum diameter of 5 mm); consequently, stress recrystallized pyrolytic graphite (Union Carbide Ltd.) was used, which is known to behave in a similar manner to single crystal graphite during oxidation (6). Samples of pyrolytic graphite with silver deposited on their basal surfaces were

studied by X-ray photoelectron spectroscopy both prior to and subsequent to treatment in molecular oxygen under identical conditions to those described above for single crystal graphite. Figure 3 shows the photoelectron spectra obtained (a) before and (b) after oxidation and no significant differences were apparent between the two

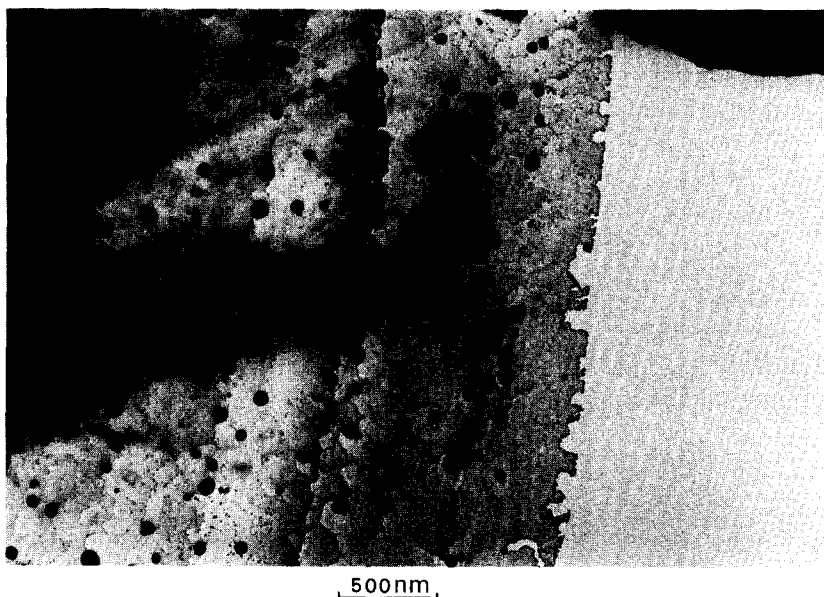


FIG. 2a. Bright-field electron micrograph of graphite coated with silver subsequent to high temperature treatment in molecular oxygen and (b) the corresponding selected area electron diffraction pattern.

spectra. It is believed that the small amount of oxygen present was associated with any exposed prismatic planes of the pyrolytic graphite (7) and the remainder as an adsorbed oxygen layer on the surfaces of the silver particles. Since the surface area of the silver present on the graphite was too small to establish the nature of this oxygen, *in situ* experiments on the oxidation of silver foil were performed inside the electron spectrometer and the results of this investigation have been published recently (8). It was found that the binding energy of oxygen 1s electrons associated with the graphite/silver system was identical to that found for oxygen 1s electrons on a silver surface exposed to molecular oxygen. It would appear from these results that silver does not undergo a permanent chemical change during the silver catalyzed oxidation of graphite, i.e., no bulk oxide is produced, and the additional

anomalous reflections in the electron diffraction pattern of an oxidized sample are probably due to double diffraction at imperfections produced during the coalescence of silver particles. Matthews and Allinson (9) have demonstrated by transmission electron diffraction and dark field electron microscopy that {111} twin bands are formed during the coalescence stage of thin film growth of silver on rock salt, and the present authors, using similar techniques (5), have reached the same conclusions concerning the deposition of gold on graphite. Thus twin formation is the most probable cause of the anomalous reflections in the diffraction patterns.

In conclusion, it is believed that during the catalytic channeling of a silver particle on the surface of graphite in the presence of oxygen at high temperature, the oxygen is transported to the vicinity of the reaction site as a transitory oxide on the sur-

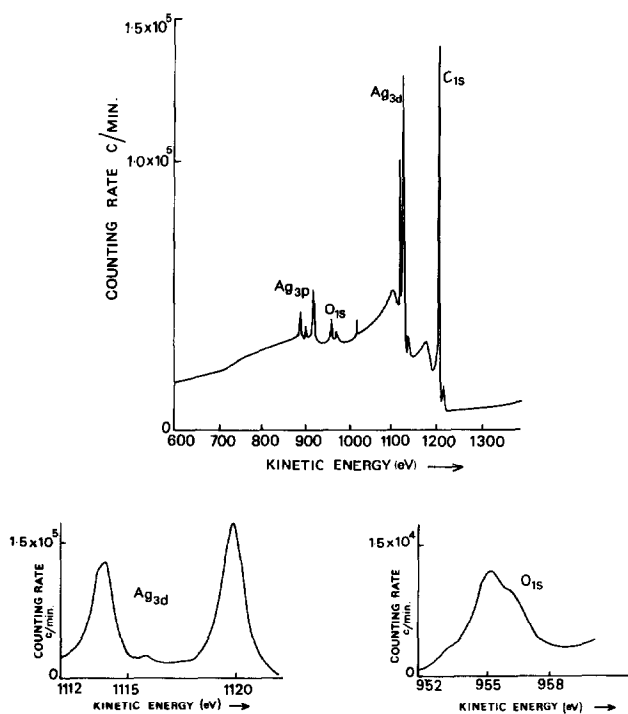


FIG. 3. X-Ray photoelectron spectra of graphite coated with silver obtained (a) before and (b) after oxidation showing that there are no significant differences between the two spectra. (The decrease in intensity of silver peaks results from agglomeration and evaporation.)

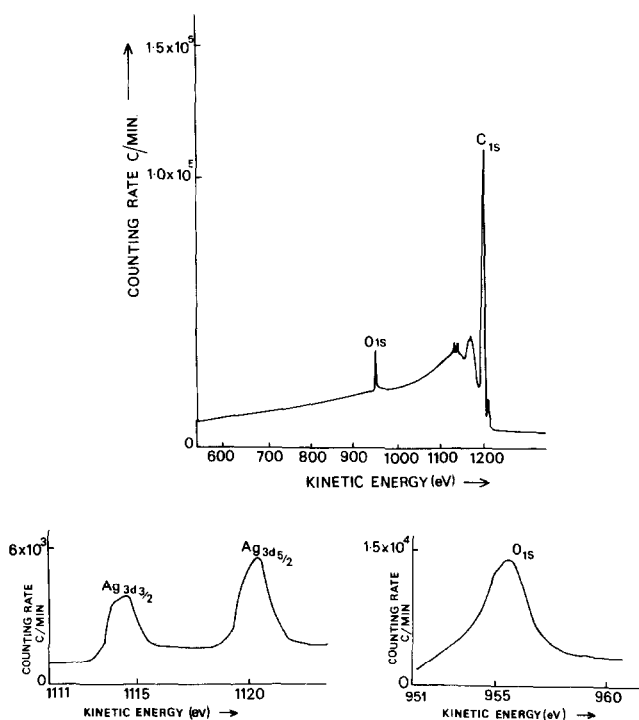


FIGURE 3b

face of the silver particle resulting in enhanced reactivity of the carbon towards the oxygen at the silver-oxygen-carbon interface.

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REFERENCES

1. THOMAS, J. M. "Chemistry and Physics of Carbon," Vol. 1, p. 121. Dekker, New York, 1965.
2. GRIFFITHS, R. J. M., AND EVANS, E. L., unpublished data.
3. HENNIG, G. R., *J. Inorg. Nucl. Chem.* **24**, 1129 (1962).
4. FEATES, F. S., MORLEY, H., AND ROBINSON, P.

S., *Congr. Int. Micr. Electronique*, Grenoble, 1970.

5. EVANS, E. L., AND GRIFFITHS, R. J. M., unpublished data.
6. ROSCOE, C., AND BAKER, J., *J. Appl. Phys.* **40**, 1665 (1969).
7. THOMAS, J. M., EVANS, E. L., BARBER, M., AND SWIFT, P., *Trans. Faraday Soc.* **67**, 1875 (1971).
8. EVANS, E. L., THOMAS, J. M., BARBER, M., AND GRIFFITHS, R. J. M., *Surface Sci.* **38**, 245 (1973).
9. MATTHEWS, J. W., AND ALLINSON, D. L., *Phil. Mag.* **8**, 1283 (1963).

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