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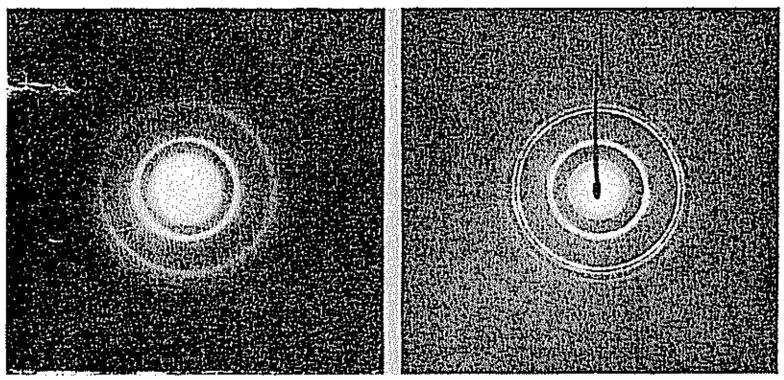
Pyrolytic Carbon Formation from Carbon Suboxide

ALMOST all the extensive work done on the formation of pyrolytic carbon films has consisted of the decomposition of a hydrocarbon on non-metallic substrates like porcelain or artificial graphite. Work is in progress in our laboratory investigating the kinetics and mechanism of carbon film formation on glazed porcelain from carbon suboxide (C_3O_2)[1]. In the course of this work, it was of interest to look briefly, initially, at the effect of some different substrates on the qualitative rate of carbon formation and more particularly on the nature of the film formed.

Very pure C_3O_2, entrained in pre-purified helium, was pyrolysed at 713° C. for about 3 hr. over porcelain, electrolytic nickel and copper foils, and reagent grade platinum foils. The concentration of C_3O_2 at the pyrolysis temperature was about 6×10^{-6} mole/l. Tenacious and hard carbon films were obtained, with the rate of film formation on nickel being roughly four times that on the other substrates.

The carbon films were separated from the metal substrates by acid treatment prior to studying their structure by transmission electron diffraction and transmission electron microscopy. 50-kV. electrons, having a beam width of 10μ, were used. Fig. 1 (*a*) shows the diffraction pattern for the film carbon resulting from deposition over a copper substrate.



a *b*

Figs. 1 *a* and *b*. Transmission electron diffraction patterns of film carbon deposited from C_3O_2 on to a substrate at 713° C.; *a*, copper substrate; *b*, nickel substrate

Table 1. SPACINGS OF (*hkl*) LINES OF FILM CARBON DEPOSITED FROM C_3O_2 ON TO A NICKEL SUBSTRATE AT 713° C.

(*hkl*) Graphite	d_g, Å	d_{fc}, Å	Intensity of experimental halos
002	3·370	3·370	medium
100	2·102	2·091	broad ring with very strong intensity
101	2·036		
110	1·232	1·230	very strong
112	1·150	1·155	strong
200	1·063	1·060	medium
210	0·804	0·799	medium
310	0·709	0·704	medium

Diffuse halos, corresponding to the (10) and (11) reflexions of a polycrystalline, turbostratic carbon[2], are observed. The absence of a strong (002) reflexion when the incident electron beam is normal to the film surface is indicative of preferred orientation of the basal planes parallel to this surface. Diffraction patterns very similar to Fig. 1*a* were obtained from the film carbon deposited on a porcelain or platinum substrate.

On the other hand, the diffraction pattern (Fig. 1*b*) of the film carbon deposited on the nickel substrate is characteristic of a material of substantial crystallite size, in which the crystallites have extensive three-dimensional ordering. Table 1 compares the *d*-spacings for the film carbon (d_{fc}) with comparable spacings calculated from the graphite lattice (d_g). Similar diffraction patterns for carbon films deposited on porcelain, copper, or platinum are obtained only

Fig. 2. Transmission electron micrograph of film carbon deposited from C_3O_2 on to a nickel substrate at 713° C. (× *c*. 4,700)

when the separated films are ultimately heated in excess of 2,000° C.

Fig. 2 is an electron micrograph of the carbon film deposited on nickel. Variations in the thickness of the films are evident. In addition, the presence of small, white circular spots is noted. It is suggested that these spots were formed by the removal by acid treatment of inclusions of nickel and/or nickel carbide which were originally present, but this has not been verified. From work on the interaction of evaporated carbon films with a similar nickel substrate on subsequent heat treatment, it is known that substantial inter-diffusion of nickel and carbon occurs at 500° C. and above (Banerjee, B. C., and Walker, P. L., unpublished results).

These results clearly suggest that more attention might be paid to the effect of the substrate in work on the formation of pyrolytic carbon films. In particular, substrates of nickel and iron are of interest. They are highly active catalysts for the decomposition of carbonaceous gases, apparently because of the incomplete filling of their *3d* bands. In addition, they markedly increase the crystallinity of the carbon formed as a decomposition product. The effect of nickel is clearly evident from this work. The effect of iron, both on rate of formation and structure of carbon, has been previously shown for carbon monoxide decomposition[3].

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