A NEW SUBSTRATE FOR SURFACE STUDIES

M. B. Dowell
Union Carbide Corporation, Carbon Products Division
Parma Technical Center, Parma, Ohio 44130

Expanded graphite foil is a novel substrate for studies of adsorbed films because its large surface, ~16 m^2/g, consists of homogeneous basal planes. [1,2] The accuracy of diffraction studies and heat capacity measurements of films adsorbed on graphite foil are often limited by the size of the basal plane regions [3] and by the orientation of basal planes with respect to the foil. [4] A substrate made by intercalating and expanding oriented pyrolytic graphite might be expected to exhibit improved basal plane size and orientation because pyrolytic graphite experiences little change in basal plane orientation when it is expanded, [5] and because it can be expanded and recompressed as a monolith rather than as an assembly of flakes. Expanded highly oriented pyrolytic graphite is now being offered as UCAR-ZYX*. Preparation of a highly oriented graphite substrate for adsorption, and an investigation of interlayer disorder resulting from intercalation, expansion, and recompression of highly ordered pyrolytic graphite, may thus be of interest to surface scientists.

Disorder introduced by intercalation is determined by comparing the full width at half maximum intensity of the (002) reflection of pyrolytic graphite specimens before intercalation with that of the comparable (00ℓ) reflection of the same specimens after intercalation. A specimen of UCAR-ZYA* stress annealed HOPG having a "mosaic spread" 0.24 to 0.31 deg (FWHM), exposed to HNO_3 vapor to form Stage II $C_{48}{}^{+}NO_3{}^{-}\cdot 3HNO_3$ and further exposed to air for 20 hours to form a stable "residue compound" consisting of a mixture of stages, exhibited a mosaic spread 0.52 to 0.80 deg of the (005) of $C_{96}{}^{+}NO_3{}^{-}\cdot 3HNO_3$ at 3.59Å. Another specimen of stress-annealed HOPG immersed in a hot mixture of sulfuric and nitric acids and rinsed in water to form a graphite bisulphate residue compound exhibited a reflection at 3.15Å having a mosaic spread 0.69 deg. Stress annealed pyrolytic graphites are thus disordered only slightly by intercalation and partial disintercalation.

Intercalated pyrolytic graphites are expanded by placing them in metal molds having closely fitting sides and heating them rapidly to 400°C to 600°C for a few minutes. Mosaic spreads of the expanded specimens of Figure 1 have a mean value 2.1 deg and appear to decrease as the density increases. Specimens recompressed to densities 0.8 to 1.4 g/cm^3 have mosaic spreads averaging 2.2 deg which appear to decrease with increasing density in the same way. Considerable interlayer disorder is thus introduced by expansion; little increase in mosaic spread results from recompression; and mosaic spreads reported here may be compared with values ~ 25 deg for "Grafoil"* flexible graphite.

Transmission diffraction studies of adsorbed monolayers require the fraction of substrate basal planes oriented nearly normal to the foil to be as small as possible. The ratio of integrated intensity of the (002) peak in transmission to that in reflection is much smaller for expanded pyrolytic graphite than for "Grafoil"* as shown in Table I. This "transmission ratio", unlike the mosaic spread, can be increased by compression and is sensitive to the mechanical history of the specimen.

References

1. J. G. Dash, Films on Solid Surfaces, New York, Academic Press, 1975.

2. J. G. Daunt and E. Lerner, eds., Monolayer and Submonolayer Helium Films, New York, Plenum Press, 1973.

3. M. Bretz, J.G. Dash, D.C. Hickernell, E.O. McLean, and O.E. Vilches, Phys. Rev. A8, 1589 (1973).

4. J.K. Kjems, L. Passell, and H. Taub, Phys. Rev. Lett. 32, 724 (1974).

5. L.C. Olsen, S.E. Seeman, and H.W. Scott, Carbon 8, 85 (1970).

Table I

Surface and Structural Properties of Various Graphites

	Density g/cm^3	N_2 Surface Area, m^2/g	Mosaic Spread deg FWHM	Transmission Ratio $I(002)_{tr}/I(002)_r$
Highly Oriented Pyrolytic Graphite	2.25	10^{-3}	< 1.0	0
Expanded HOPG	0.15-0.60	--	~2.1	$(0.12 \pm 0.16) \times 10^{-3}$
Expanded HOPG	0.8-0.4	4	~2.2	$(0.4 \pm 0.6) \times 10^{-3}$
"Grafoil"	1.0	20	~7	$\sim 4 \times 10^{-1}$

*"Grafoil" flexible graphite, UCAR Grade ZYA stress-annealed highly oriented pyrolytic graphite and UCAR Grade ZYX expanded pyrolytic graphite are products of Union Carbide Corporation, 270 Park Avenue, New York, N.Y. 10017. "Grafoil" is a registered trademark of Union Carbide Corporation.

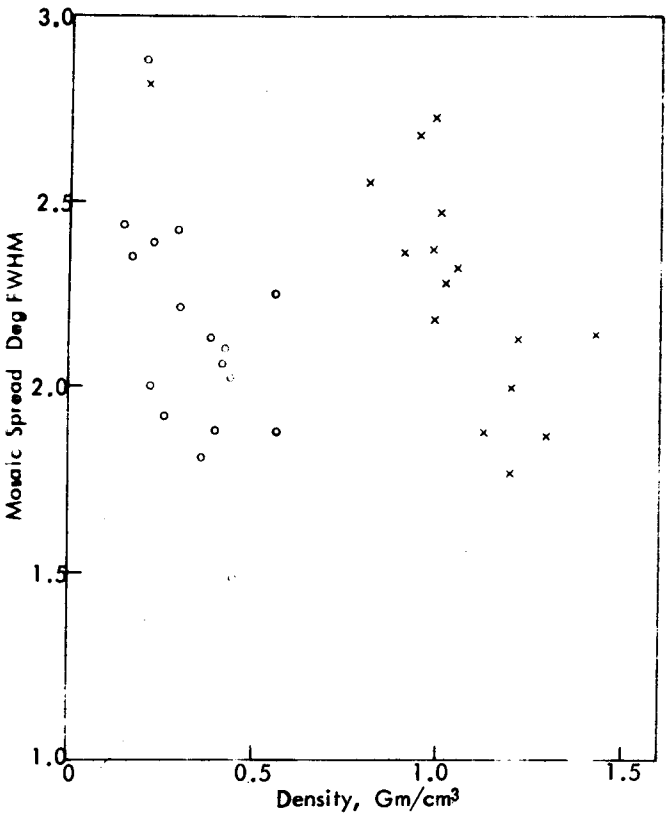

Figure 1. Mosaic spread of (O) expanded and (X) recompressed HOPG of different densities.