STRUCTURAL CHARACTERIZATION OF FINE MORPHOLOGY IN CARBON USING HIGH RESOLUTION ELECTRON MICROSCOPY

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Introduction

In 1973, the above Laboratories were offered financial support from the Science Research Council to advance our theoretical and practical experience in the use of phase contrast, high resolution electron microscopy in which the constituent lamellar molecules of carbon are projected as lines or fringes on to the screen of the microscope, a technique which owes much to Ban (Ref. 1). When studying graphitic materials, there appears to be less of a problem with interpretation as parallel fringes, extending over considerable distances, can be focussed onto the screen. It is with isotropic carbons and anisotropic carbons of HTT <1500 K, that problems of interpretation arise. The detail of the relative positions of short, non-linear fringes appears to be (at least) a function of focal position adopted during imaging, of specimen thickness and of extent of exposure of the carbon specimen to the electron beam. This investigation is now complete and consists of an appraisal of semi-theoretical aspects and several structural analyses of carbonizations and graphitisations which form part of the overall studies of the Laboratories. The following is a summary of the essential findings.

The Technique of Phase-Contrast Electron Microscopy

The potential benefits of defocus phase-contrast electron microscopy in terms of elucidation of structural detail are such that no other technique can seriously be considered. However, the attendant contrast-transfer difficulties inherent in this type of work appear to be prohibitive in terms of the extraction of realistic information (Ref. 2, 3). Hence, the major problem is whether or not it is possible to arrive at a working compromise of using an optimum contrast transfer window which does not exclude relevant information. The approach to the problem is one of establishing an acceptable experimental basis for microscopy as distinct to the complementary theoretical analyses (Ref. 3).

For phase objects, purely geometrical considerations alone, in demanding a minimal phase difference between waves scattered from the top and bottom of the specimen (Ref. 4) give a thickness limitation requiring $t \ll 25$ nm for a resolution of $d=0.3$ nm. More exacting requirements are evident in the weak-phase approximation. Values of $t < 15$ nm for disordered carbons and $t < 7.5$ nm for crystalline carbons probably represent upper limits. For disordered carbons, a complicated super-imposition of image detail could well prove the ultimate limitation to specimen thickness. Generally, for carbons, the sample should preferably be as thin as is consistent with the probable microstructure.

For the JEOL 100C TEM, a specification of the spherical aberration constant of 1.4 mm, i.e. C_s (this parameter defines the contrast transfer properties of the microscope and hence the efficiency of imaging) is inadequate for the range of lattice spacings in the range 0.30 to 1.0 nm of importance in disordered carbons.

Hence, because detail within this range cannot be imaged in a consistent manner an optical working situation requires the choice of the most suitable defocus position. This can only be done by observing an image on the microscope viewing screen and hence decisions based on the visibility of detail would seem to be reasonable. It is considered that at a defocus position (Δf) of −90 nm the range of reasonable imaging is for lattice spacings (d) of 0.34 to 1.5 nm. A dip in intensity occurs at d = 0.46 nm. At a defocus position of −130 nm the range of imaging is for lattice spacings of 0.3 to 0.56 nm which covers the graphite basal-plane spacing of 0.335 nm. However, there is an information gap in the range d = 0.56 to 0.72 nm and information in the range d = 0.31 to 0.56 nm is presented with reversed (negative) contrast. It is concluded that the near-Scherzer optimum underfocus of Δf = −90 nm should be used wherever possible for all carbon imaging when a disordered component is apparent. It is considered that at Δf = −90 nm typical images of large carbon crystallites, small carbon crystallites and systems of defective graphitic sheets indicate that a sensible direct interpretation (in terms of a projected charge-density distribution) is possible for thin samples of carbon. With a Δf of −130 nm, fringe-contrast is reversed within crystallites so presenting difficulties in measuring the crystallite width for microcrystalline carbon. Also for disordered carbons the transfer gap operating at this level of defocus induces loss of information vital to the characterization of microstructure and overestimates of the degree of crystallinity.

The Elucidation of Structure in Carbon

Catalytic Graphitization of Carbons: Chemical catalysis of graphitization carried out under vacuum in an Fe-doped polyfurfuryl alcohol carbon results in the formation of relatively well-developed turbostratic-graphite sheets at unusually low temperatures (873 K). Without catalysis, temperatures in excess of 2000 K would normally be required to initiate the ordering necessary in the production of similarly 'developed' material (Ref. 5).

Voids in Carbons and Graphites: It is concluded that optimum-defocus images represent the only means of obtaining information concerning void character-

istics in disordered carbons . The voids, as
observed, can be classified in terms of struc-
tural classifications. Primary voids are formed
by deviations from a favoured interlayer or inter-
molecular spacing. Secondary voids are formed
by morphological aspects of crystallites and
associations of crystallites. For example,
sharp-edged space can be created bounded by intact
graphitic sheets. Needle-shaped primary voids,
0.4 nm width and 1 to 3 nm in length often occur
with non-twinned tilt boundaries, twist bound-
aries etc. relieving induced crystallographic
stress. In three-dimensions the void is more
likely to be "penny-shaped". Other types of void
which have been imaged include tapered, isometric,
constricted, inter-connecting, bottle-shaped,
closed-ended, slit and wedge shapes. Essentially,
the void character is closely dependent upon the
crystallographic structure of the carbon or graphite.

Heat-treatment of Graphitizing Carbons: Changes
have been examined in anisotropic carbon from its
formation following coalescence of the mesophase
(HTT 750 K) to anisotropic cokes (HTT 1148 K)
Orgreave lean coal-tar forms mesophase, at 750 K,
composed of stacked lamellar molecules about 1.2 nm
in length but with smaller molecules present between
the orientated molecules and misorientated with
respect to the major axis of preferred orientation.
At HTT 945 K these smaller molecules interlink with
the larger ones causing disruptions within locally
pre-orientated material. A strained structure is
created within the semi-coke which now contains
micro-inclusions of inhomogeneous material, 2.0 nm
in size, and also grains about 20 nm in diameter.
Further heat-treatment initiates the annealing of
the strain so increasing molecular size, planarity
and local preferred orientation. (Ref. 6).

In a study of a graphitizing carbon from poly-
vinyl chloride the preferred stacking of basal planes
(HTT 923 K) confirms the model of equatorial stack-
ing of molecules predicted from optical microscopy
and electron diffraction. Secondary structure of
crystallites from the lamellar molecules developed
at an HTT of 1373 K being completed at 1573 K. An
ordering into strips or sheets of material is
initiated at 1773 K and develops continuously to
2273 K when they can be 20 nm in width and may
extend for distances greater than 400 nm in the
L_a direction. They are composed of closely-
linked micro-crystallites. Three-dimensional
ordering appears at 2273 K and at 2673 K the micro-
crystallites have now formed a single large
crystallite with dimensions of the strips. These
strips are linked by narrow, long crystals of carbon
or by a disordered, three-dimensional array of basal
planes. This linking matrix re-crystallizes at
temperatures of about 2673 K. Voids appear between
the crystallites.

Beam Sensitivity of Graphitizable Carbons: Samples
of low HTT (<1000 K) are sensitive to the electron
beam. The (002) diffraction peak loses form and
becomesdiffuse as a result of thermal and irradia-
tion damage. This is marked for a sample of coke
(HTT 750 K), the damage being less critical in
cokes of HTT 945 K. Damage can be reduced by
using lower magnifications for as long as possible,
and prefocussing the objective lens so reducing
exposure times to less than 10 seconds.

Heat-treatment of Non-graphitizing Carbons: Poly-
vinylidene chloride carbon (HTT <1073 K) is
characterized by a mean apparent layer length of
1.1 nm and an apparent spacing of 0.68 nm. In
the temperature range 1073 to 1973 K a growth of
deformed inter-twining graphitic layers occurs
to establish a ribbon model. The growth of
turbostratic crystallites at HTT > = 1973 K
and the progression to a thin-walled, isotropic
three-dimensional closed foam-structure is now
postulated. These structural changes explain
the complexity of the mechanism of loss of
porosity and surface area (>1000 m^2g^{-1}) in these
PVDC carbons, by heat treatment (Ref. 7, 8, 9).

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