HIGH RESOLUTION DARK - FIELD E M APPLIED TO CARBON CHARACTERIZATION PAN FIBER MICROTEXTURE

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Carbon fibers are made of carbon layers more or less parallel to the fiber axis but their a axis is distributed at random. The azimutal disorder of the a axis generates hk cylinders corresponding to the rotation of each set of hk reciprocal lines. These cylinders then rotate around the fiber axis. The SAD pattern thus obtained is schematically represented in fig. 1b or 2b. Two different models of texture (1,2) fit equally well with these patterns since scattering which averages the results forbids any choice. Fig. 1a represents the fibrillar model while 2a represents a part of the lamellar one, i.e a distorted turbostratic carbon layer stack. Lattice-imaging cannot separate between the two models for two reasons. First too many details are superimposed so that no valuable restoration of the real texture can be deduced. The second reason derives from the fact that the 00.2 fringes approximate carbon layers seen edge-on. The kind of artefact which may occur is illustrated in fig. 3 which compares an object (fig. 3a) to its restoration (fig. 3c) obtained from 00.2 lattice imaging (fig. 3b). In longitudinal thin-sections or in ground materials, fibrils or folded parts of distorted lamellae look the same. In the same way, in transverse sections, the continuity of 00.2 fringes can be due either to a real curvature of the layers or to a superimposition of details situated at different levels in the fiber.

To overcome these difficulties dark field has necessarily to be used ; 00.2 DF leads to the same results than 00.2 fringes and may be used to measure the N number of parallel layers (3). Only a careful comparison of both 10 and 11 DF can separate between the fibrillar and the lamellar models. Let first consider the fibrillar model (fig. 1). If the aperture is set on 10 position the ribbons imaged as regions containing bright moiré fringes (fig. 1c) have one of their a axis approximately parallel to the fiber axis (misorientation depending on the aperture opening) and also are more or less tilted, which depends on the aperture opening. If the aperture corresponds to the 11 position more ribbons should light on since the allowed amount of tilting is then practically ± 90°. This no longer depends on the aperture opening but on the diameter of the 11 reciprocal line. Both 10 and 11 DF images show ribbon-like bright domains, variable in width, representing the prjection of the fibrils on the observation plane. On the contrary, for the lamellar model (fig. 2) ribbon-like domains should appear only in 10 DF and 11 should be quite different. Characteristic features to be noticed are the following : first more isometric domains appear which contain bright moiré fringes, then bands without contrast occur at the very location where bright domains were used to appear in 00.2 DF, finally diffuse bright lines (corresponding to moiré fringes seen obliquely) edge these bands. (Similar reasoning may be applied to the a axis of the turbostratic stack lying perpendicular to the fiber axis ; if so, 10 has to be inverted with 11). It can also be deduced from fig. 2 that, if the ρ curvature radius of the stack increases and tends to produce flat isometric lamellar particles, 10 and 11 positions should give identical images.

Such considerations have been applied in the present work to commercial PAN fibers heat-treated at 2500° C (AG 25 produced by SEROFIM, France). The fibers were prepared for EM by thin sectioning (tranverse and longitudinal sections) and by wet-grinding. SAD patterns show a turbostratic material containing a small amount of partially graphitized regions (4,5). Therefore fiber texture has been found homogeneous and entirely lamellar.

The validity of the lamellar model established by high resolution DF has to be confirmed by other experiments. First the occurence of lamellae instead of ribbons, then the homogeneity of the fiber have to be proven. The occurence of lamellae is emphasized by fiber exfoliation. A lamellar compound was made by treating the fibers by a mixture of H_2SO_4 and $K_2Cr_2O_7$ during one hour ; the fibers were then exfoliated by H_2O_2. Very stable water suspensions were thus obtained including mainly small isometric lamellae besides fragments of intact fibers (the suspensions were shown to be graphite oxide free by SAD control). Krypton adsorption isotherms were performed on fiber surface at 77 K(6). They show that the surface is homogeneous and the steps produced at low p/p_0 values are typical of adsorption localized on basal planes of graphite layers and not on their edges. The amount of chemical groups distributed on the surface is also evaluated to be low, which fits well with the lack of reactive carbons i.e edge-carbons. All the experiments agree quite well with the fact that both surface and core of the fibers are lamellar. Homogeneity of the fiber has been tested and confirmed by oxidation kinetic studies using O_2 and CO_2. Oxidation rate was followed by DTG and gas analysis. The curves are all monotonous, sample reactivity does not change when oxidation gets deeper and deeper.

In conclusion it must be kept in mind that lattice-fringes represent only a part of the reciprocal space which can be possibly analysed by imaging. It is absolutely necessary to achieve the exploration of the whole available reciprocal space in using DF techniques especially in using as many reflections as possible.

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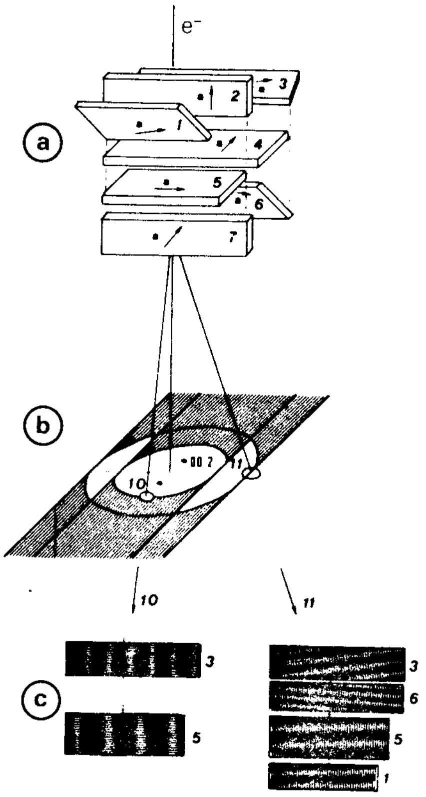

Figure 1

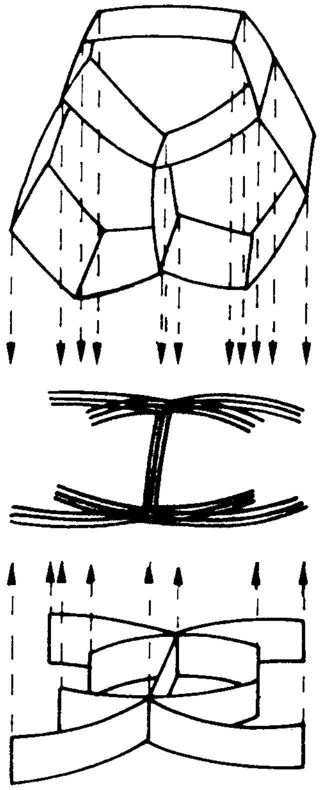

Figure 3

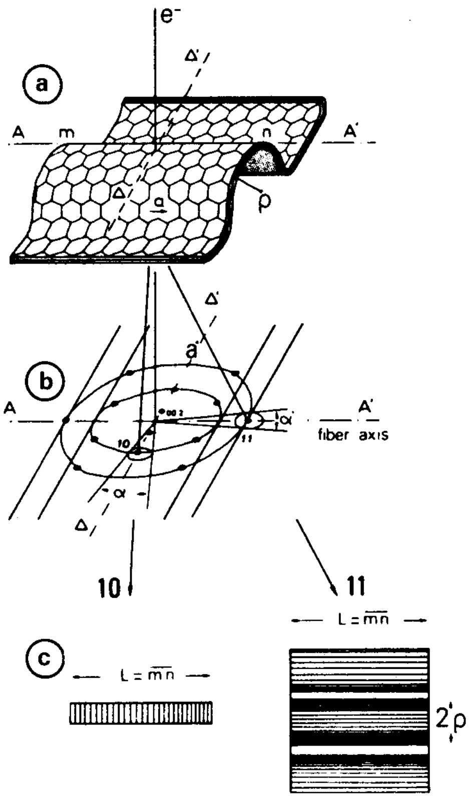

Figure 2