GRAPHITIZATION OF THIN CARBON FILMS

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The results obtained by heat-treatment of thin carbon films are somewhat confusing (1) since it cannot be clearly demonstrated if these films are graphitizable or not. The following data were obtained by high resolution electron microscopy (EM) study. The thin carbon films were deposited under vacuum upon a NaCl cleavage. They were then removed from NaCl and laid on carbon supporting grids (these grids are made by heating a cellulose tissue at 3000°C). They were then progressively heat-treated from 1000°C up to 3000°C in a covered crucible in an argon flow. Carbon films deposited at room temperature are amorphous and correspond to a random network model (2). On the contrary, when heat-treated, they become turbostratic carbons.

SAD patterns show that the thin carbon films are progressively graphitizable. Above 2000°C the hk.1 maxima appear and get sharper and sharper as HTT increases, in a way similar to any other soft carbon (fig. 4). L_a crystallite diameter has been measured by using both 10 and 11 dark field images. The N number of parallel layers has been measured, close to the carbon film breaks, since these breakages cause folding and thus 00.2 scattered beams to appear. N has been deduced from 00.2 DF images, SAD patterns and 00.2 lattice fringes.

At 1000°C all the EM techniques show the film to be formed by stacks 2 to 3 layers thick and smaller than 10 Å in diameter (3). Lattice imaging and SAD pattern as well, show a high degree of preferred orientation, therefore, each elementary carbon layer stack is tilted and twisted at random towards its neighbour. Only very small changes occur before 1250°C. Between 1250° and 1850° N increases very quickly and this growth is only limited by the thickness of the film. 00.2 DF images show that the small bright dots less than 10 Å (fig. 1) which are located on the folds are progressively replaced by bands of equal thickness rich in intense Bragg fringes (fig. 2). Over 1850°C whatever the HTT, the 00.2 DF images always show such single or multiple bands (single fold or rolled film). The bands which apparently look single but in fact include many folds are very common. This phenomenon can be easily explained in considering SAD patterns. At 2490°C for instance (fig. 4), as at any other high HTT, the free surfaces which limit both faces of the folds lead to observe in SAD patterns many subsidiary maxima (fig. 5) on both sides of the main 00.2 reflection (or 00.4). Their period allows the measurement of the diffracting domain thickness ; this thickness can also be evaluated in considering the 00.2 reflection width. In fig. 5 it is approximately 80 Å. The arrows in fig. 2 indicate a region where the measured thickness is 40 Å in A and 80 Å in B. If compared to fig. 3 (lattice fringes) the N number of fringes is 12 (≈ 40 Å) or 24 (80 Å). The real thickness of the carbon film is thus 40 Å but the two parts of the fold are parallel enough to induce interferences between the scattered beams of two crystallites (spatial coherence), thus leading to double the values. Noticeably, in the B region of fig. 3, nothing indicates where in the fringes the boundary between the two films can be. Between two experiments the real film thickness varies from 25 to 50 Å at the most, N_{max} thus varies from 7 to 15 at or above 1850°C.

11 DF images (fig. 6), if HTT < 2400°C, show hexagonal domains containing **moiré** fringes. This obviously shows that 2 or 3 crystallites at least are superimposed inside the film. The real L_c thickness cannot thus be related to the N number of parallel planes (equal to the film thickness) and is smaller. It is only at 2490° and above (fig. 6) that domains without any moiré fringes become more and more numerous and look homogeneously bright or out of contrast. At 3000°C all of them are bright or out of contrast. And thus L_c = N = film thickness. These DF images also lead to the measurement of the L_a crystallite diameter, plotted in fig. 7 versus HTT.

SAD patterns show that thin films are graphitizable. L_a values can be precisely measured in highly heat-treated thin films (or thin particles) owing to DF images when other diffraction techniques cannot succeed. Thin films L_a reach 3000-5000 Å. The N number of parallel layers is precisely measured by SAD, DF and lattice fringes and can be related both to film (or particle) thickness and to L_c value. In thin carbon films, N_{max} is equal to the film thickness and L_c remains smaller below 3000°C. At this temperature a unique crystallite extends over the whole film thickness (25-50 Å) which is demonstrated by the lack of moiré fringes. The g graphitization value is thus one.

(1) I.S. Mc Lintock and J.C. Orr. In Chemistry and Physics of Carbon 11, 243 (1973), P.L. Walker, P.A. Thrower ed. Dekker N.Y.

(2) A. Oberlin, M. Oberlin and M. Maubois, Phil. Mag. 32, 833 (1975).

(3) A. Oberlin, G. Terrière and J.L. Boulmier, Tanso (Japan) 80, 29 and 83, 153 (1975).

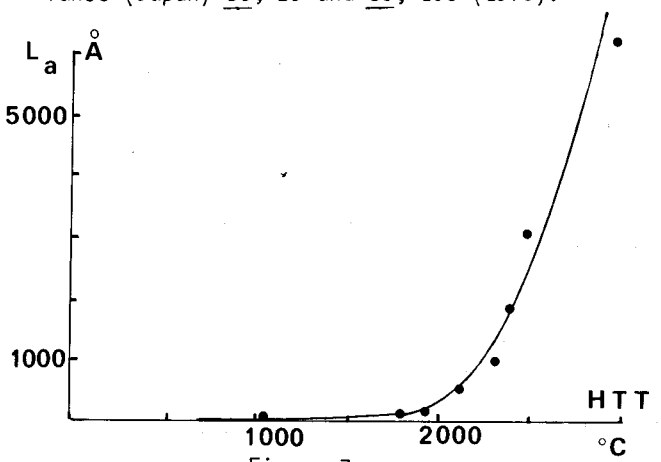

Figure 7.

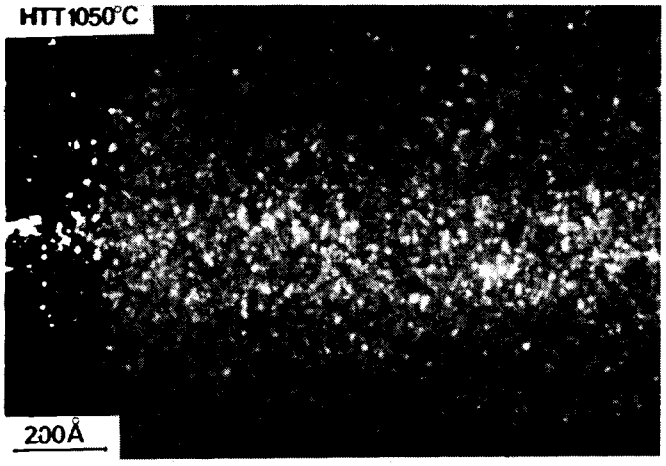

Figure 1

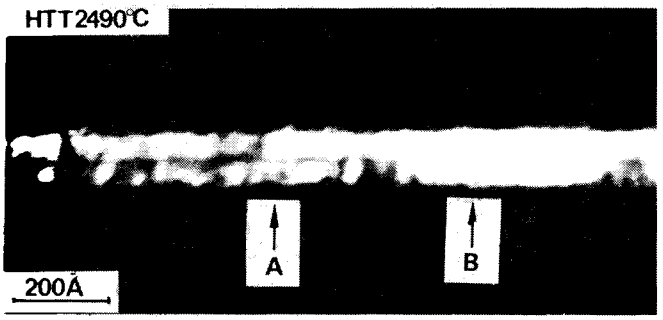

Figure 2

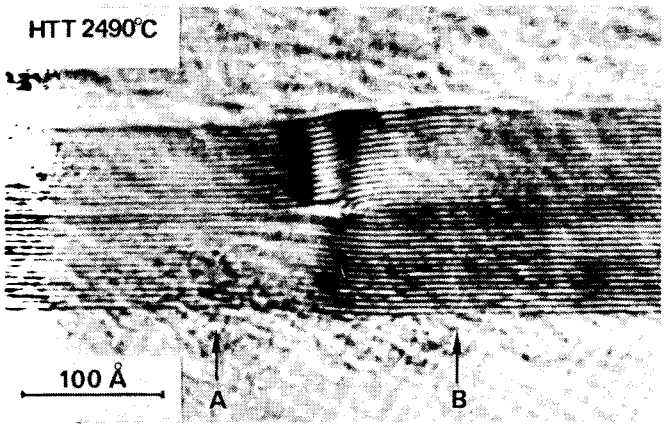

Figure 3

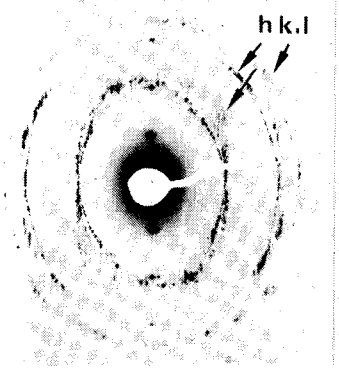

Figure 4

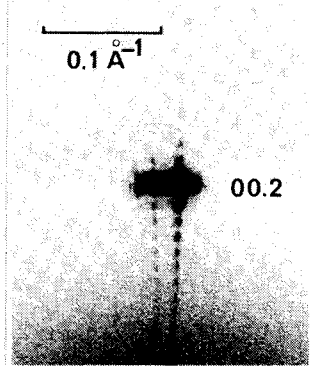

Figure 5

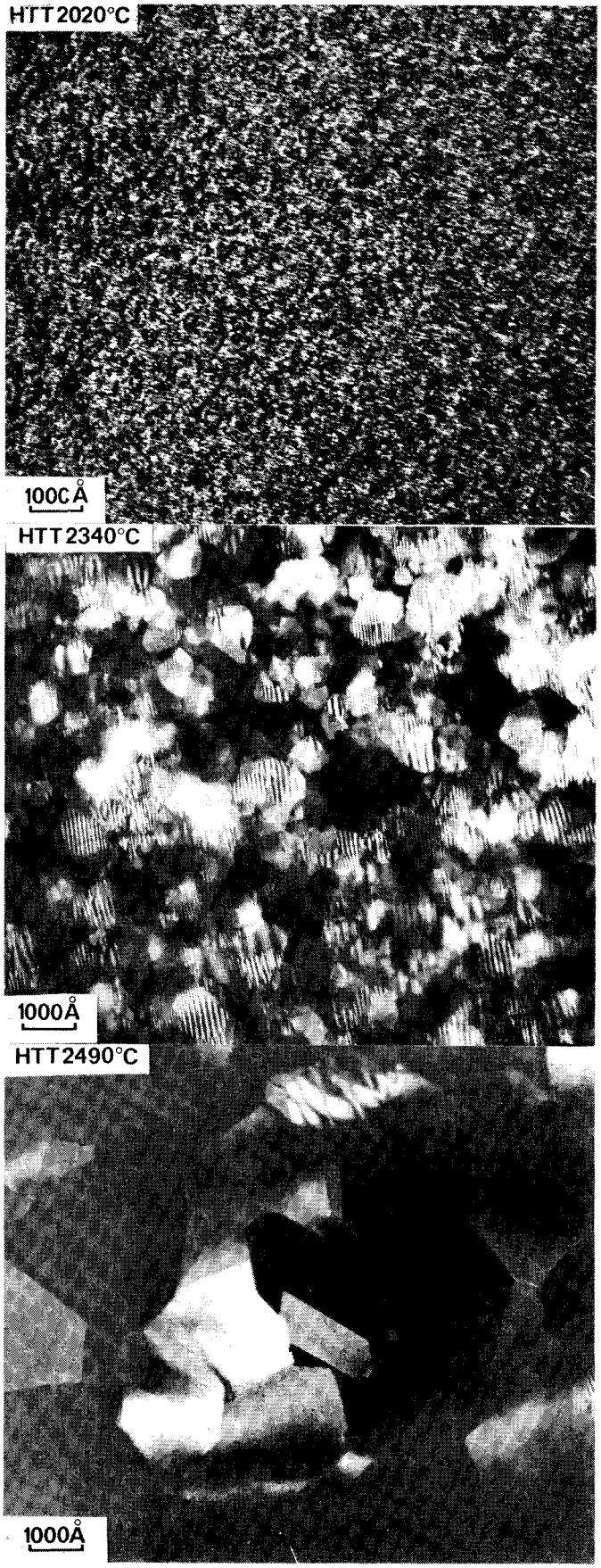

Figure 6