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Electron Microscopy of Pyrolytic Graphite

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A detailed study of heat-treated and deformed pyrolytic graphite has been made using transmission electron microscopy. Single-crystal characteristics are observed in material annealed at 3600° C. Tilt boundaries are shown to be kinks in the basal planes with some twin boundaries which can be described in terms of dislocations, as for natural crystals.

1. Introduction

Transmission electron microscopy has been used to evaluate the crystallinity of various graphites. Dawson and Follet [1] have reported a layer diameter of approximately 3000 Å for micro-crystals in synthetic Calder A graphite. Pyrolytic graphite, because of its high degree of preferred orientation, is well suited to transmission techniques although there is little published evidence of such studies. Stover [2] was able to illustrate the removal of tilt boundaries between crystallites in the deformed material and the appearance of moiré patterns on samples deformed at high temperatures. Furthermore, numerous dislocations have been observed after hot pressing pyrolytic graphite [3]. In both cases the grain size was considerably enlarged. Coy [4] and Kotlensky and Martens [5] have reported that as-deposited pyrolytic graphite has a sub-grain size of approximately 0.1 μm. Replica and transmission studies of layer planes have shown that annealing at 3000° C causes an increase in the sub-grain diameter to approximately 0.4 μm [6] and to as much as 4 to 5 μm [7]. Replica studies on surfaces normal to the *a*-axes [8] show a tilted laminar structure although fine detail has not been resolved. Flame polishing of these same surfaces enables foils for transmission microscopy to be obtained but few results have been published [9, 10].

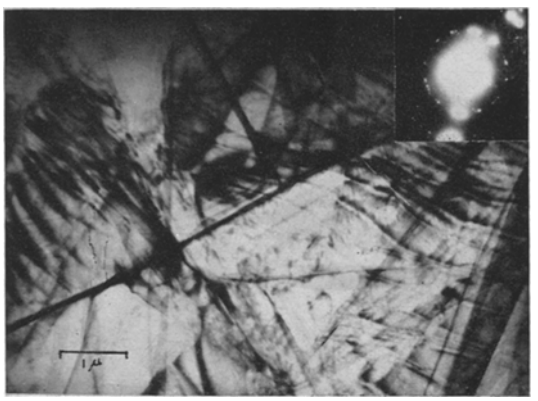

Figure 1 Tilts and basal dislocations in pyrolytic graphite, annealed at 3600° C.

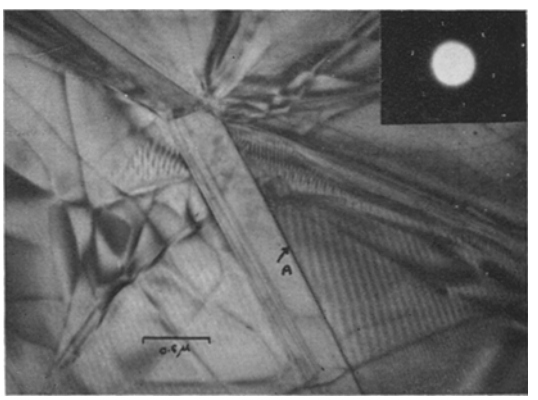

Figure 2 Twin boundary for a very thin specimen of pyrolytic graphite, angle of tilt 35°, axis of tilt about $<11\bar{2}0>$.

2. Material

The pyrolytic graphite was supplied by the General Electric Company, Schenectady, USA,

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and was prepared by techniques developed by Diefendorf [11] which involve the deposition of carbon in layer form on flat plates from methane gas at a temperature of 2100° C. The as-deposited density was 2.14 gm/cm³ and the average layer spacing was between 3.415 and 3.430 Å. Material annealed at 3600° C cleaved readily between glass slides which had been liberally coated with a plastic glue ("Durofix"). The thin foils were then removed from the glass slide by immersing them in acetone. However, all other specimens were cleaved between layers of "Sellotape", the "Sellotape" backing then being dissolved in a solution of trichlorethylene. Some specimens were deformed in tension at temperatures up to 2600° C [12]. All foils were examined at 100 KV in a Siemens Elmiskop I electron microscope.

3. Experimental Results

3.1. Annealing As-Deposited Pyrolytic Graphite

The presence of tilts and basal dislocations in pyrolytic graphite annealed at 3600° C can be observed in fig. 1. The spotty rings in the diffraction pattern indicate that there are rotations about the hexagonal axis. For a very thin specimen, a twin boundary is observed in fig. 2 with a tilt angle of approximately 35° and an axis of tilt about $\langle 11\bar{2}0 \rangle$. The diffraction pattern shows both the matrix and the twin spots.

3.2. Annealed and Plastically Deformed Material

As-deposited pyrolytic graphite showed no plastic extension when tested at temperatures up to 2560° C [12]. Fig. 3 shows the polycrystalline

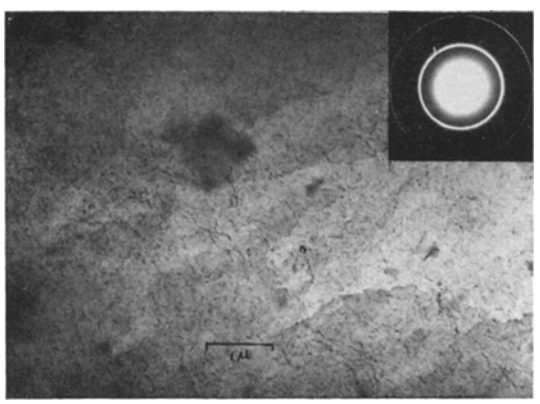


Figure 3 Polycrystalline nature of as-deposited pyrolytic graphite.

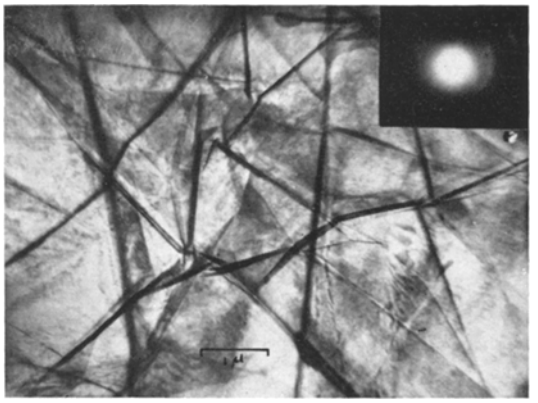


Figure 4 Pyrolytic graphite annealed at 3000° C, strained 5% at 2560° C.

nature of this material. In the same material annealed at 3000° C and strained 5% at 2560° C, there is a marked increase in crystallinity and well defined tilt boundaries are seen (fig. 4). The increase in crystallinity and single-crystal characteristics is further emphasised in fig. 5 for pyrolytic graphite annealed at 3600° C and strained 8% at 2560° C. The tilt density is considerably reduced and basal dislocations and moiré patterns are readily visible.

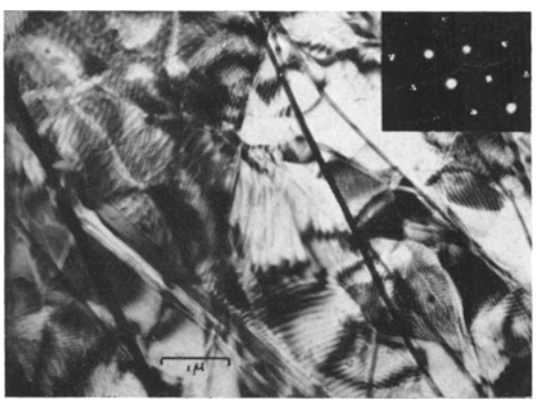


Figure 5 Pyrolytic graphite annealed at 3600° C, strained 8% at 2560° C.

3.3. Foils Normal to the Zone Axis $\langle 11\bar{2}0 \rangle$

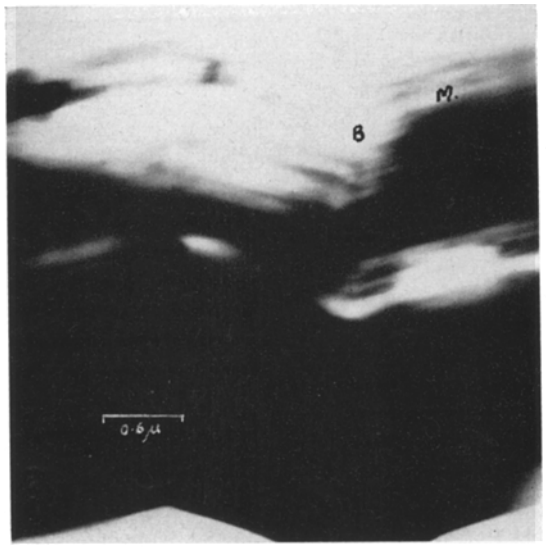
Electron micrographs were prepared from specimens of pyrolytic graphite supplied by E. Stover, General Electric Company, which had been annealed at 3000° C and flame-polished with surfaces parallel to the *c* axis. Fig. 6a shows a tilt boundary with a tilt angle of approximately 35°. The diffraction pattern of the matrix (fig. 6b) shows $\{0002\}$, $\{10\bar{1}1\}$

and $\{10\bar{1}0\}$ reflections and across the boundary there is some splitting of the (0002) spots (fig. 6c) about a zone axis of $\langle 11\bar{2}0\rangle$ type.

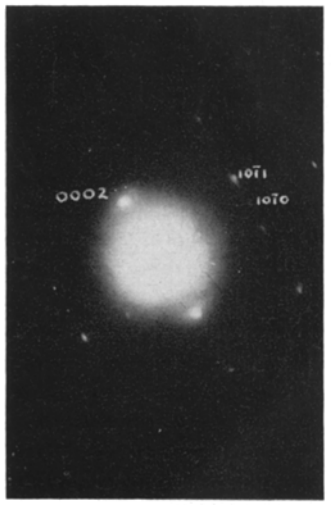
4. Discussion

Pyrolytic graphite annealed at 3600° C shows single-crystal characteristics, the presence of tilts and basal dislocations being similar to that observed by Freise and Kelly [13] and Gillin and Kelly [14] for deformed single-crystal graphite. These observations agree with galvanomagnetic measurements [15] on similar material which also suggested that the synthetic graphite has essentially single-crystal characteristics.

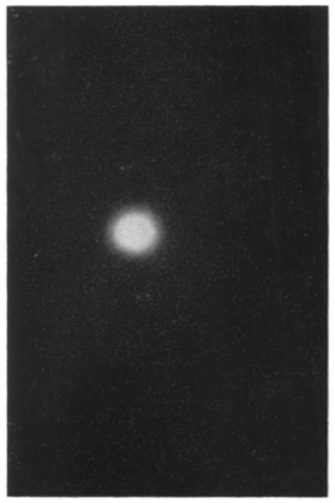
Guentert and Cvikevich [16] have shown pyrolytic graphite to be a polycrystalline material with a high degree of preferred orientation, but with a random stacking order. Furthermore, as particle growth is not associated with progressive graphitisation it is considered that the deposited pyrolytic graphite is composed of essentially parallel but heavily wrinkled sheets of basal layers which are large compared with



(a)



(b)



(c)

Figure 6 Pyrolytic graphite annealed at 3000° C. (a) Tilt boundary, angle of tilt about 35°; (b) diffraction pattern of the matrix; (c) splitting of the (0002) spots about a $<11\bar{2}0>$ axis.

the crystallite dimensions [10, 12]. This wrinkled structure has been shown to arise from crystallites separated by positive and negative tilts approximately 200 Å apart [16]. Both annealing and high-temperature straining reduce this tilt boundary density (figs. 4 and 5) and cause a growth in the crystallite size within the overlapping layers.

It appears that the crystallites are tilted layer planes joined across a continuous atomic tilt boundary. The diffraction pattern (fig. 2) can be indexed on the assumption that the tilt A is a 35° 12′ twin boundary. Also, in fig. 6, the layers appear continuous across the tilt boundary and the associated diffraction pattern corresponds to a tilted atomic structure and not an amorphous one of width greater than 1 to 2 atomic distances as required for cross links between the crystallites [17]. Certainly there is no diffraction evidence for an amorphous structure. It cannot be proved that no amorphous carbon is present but if so it is in a very thin layer. The situation is analogous to a grain boundary in a metal. The twins observed are similar to those found in natural single crystals and an atomic model for the 35° 12′ twins observed in figs. 2 and 6 has been given by Baker, Gillin and Kelly [18].

5. Conclusions

Annealing and high-temperature straining of pyrolytic graphite results in increased crystallinity and the material displays single-crystal characteristics. It is shown that the crystallites are joined by tilts in the basal planes which are continuous across the boundary. These boundaries can be described in terms of dislocations as for simple twin boundaries.

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