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[Plates 1 and 2]

Conditions are recorded under which specimens of graphite deposited from pyrolysis of methane are found to incorporate large strain energy. Methods of relieving strains by annealing have been investigated. Recrystallization under suitable constraint can be made to yield graphite of high crystal perfection. Observations indicate that such recrystallization is a co-operative process, which we have termed 'stress-recrystallization'. It is very rapid at 2700 °C and can become uncontrollable.

INTRODUCTION

Methods of recrystallizing metals to obtain large single crystals have been utilized for a considerable time. Well-known procedures involve incorporating a high degree of strain energy into a polycrystalline sample, by inducing plastic flow under tension, so that on annealing at higher temperatures the energy-rich atoms migrate to form large crystals, starting at one preferred region in the cold-worked sample.

It would be very convenient if a similar procedure could be applied for producing large single crystals of graphite, since these are rare in nature and have interesting electronic properties (e.g. Blackman, Dundas & Ubbelohde 1960). As with polycrystalline metals, simple heating of polycrystalline graphite to very high temperatures leads to only limited growth of perfect grains; moreover, because the elastic and plastic properties of graphite differ from those of metals it does not appear to be feasible to incorporate large amounts of strain energy into polycrystalline graphite in forms that would lead to growth of large single crystals, merely by mechanical working in the cold. The present paper describes some novel procedures, which take advantage of the strain energy incorporated in certain forms of pyrolytic graphite, during their deposition from the gaseous phase.

Early researchers (Pirani & Fehse 1923; Koch Holm 1927; Nishiyama 1932) used carbon filaments heated electrically in the range of temperatures 1500 to 2700 °C. This gave materials in which the graphite crystallites showed marked preferred orientation, with their basal planes (a axis) predominantly parallel to the filament axis. Although the full significance was not realized at the time, it is interesting to note that considerable improvement in graphite character was attained in some cases by heat treatment of the deposits at temperatures up to 3000 °C; Pirani & Fehse (1923) obtained one specimen whose specific resistance ($4.7 \times 10^{-5} \Omega \text{ cm}$) and positive temperature coefficient of resistance matched quite

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closely values reported for single crystals (Soule 1958) in the direction of the a axis. Brown & Watt (1958) obtained flat specimens of pyrolytic graphited by cracking hydrocarbons on to electrically heated rods of rectangular cross-section. They reported that such pyrolytic deposits can exhibit high internal strains, but again no detailed studies were made to elucidate this phenomenon.

In what follows, various experiments are described that were made to characterize the comparatively large amounts of strain energy incorporated in certain samples of well-oriented pyrolytic graphite when these are deposited from gaseous methane under controlled conditions. When the temperature of such samples is raised sufficiently, recrystallization can be made to take place under controlled or under almost explosive conditions, leading to a much higher degree of crystal perfection than is attainable (Blackman, Saunders & Ubbelohde 1961*a*) in pyrolytic graphite as deposited. On occasion, this propagation becomes uncontrollable and may take the form of a 'weak' detonation.

'AS-DEPOSITED' TYPE A GRAPHITE

The starting material for this work, referred to hereafter as type A graphite, was normally obtained by cracking gaseous methane at a pressure of 10 cm Hg in a former ($6 \times 1.25 \times 0.5$ cm) of purified polycrystalline graphite (Morgan EY 9A) heated to 2150 °C. Since different ways of preparing pyrolytic graphite appear to yield material whose structural characteristics differ (see, for example, Colligan & Galasso 1961), it should be noted that for the present work the former was heated by passing 50 c/s a.c. current from a variable voltage transformer (cf. Brown & Watt 1958); the temperature at the middle of the flat surface of the deposit was observed by means of an optical pyrometer (Evershed and Vignoles) uncorrected for emissivity changes of the graphite surface and was kept to within ± 10 °C by hand control of the voltage. Deposition was fairly slow, a deposit 1 mm thick being formed in approximately 30 min.

Because of its large coefficient of thermal expansion normal to the surface on which it has been formed, the deposit forms a distinct sleeve which separates fairly easily from the substrate. Segments were cut from the sleeves of pyrolytic graphite thus obtained, by means of a jeweller's saw blade; smaller pieces for X-ray diffraction studies were usually cut from such segments by an 'airbrasive' blast of corundum particles, in order to minimize mechanical working at the edges. When required, the segments were separated into successive strips parallel to the flat surface, by gentle cleavage using a sharp razor blade.

Mechanical stresses in 'as-deposited' pyrolytic graphite

Stresses in deposited sleeves of pyrolytic graphite become evident when these are segmented:

(1) When a single longitudinal saw cut is made through the sleeve with the former still in position, and the former is then pushed out, the sleeve contracts so as to close the cut. Considerable force is required to prise the hollow sleeve open again.

(2) When a segment is separated from the flat part of the deposit by making two longitudinal cuts, it curves spontaneously with its concave aspect towards the deposition plane.

(3) When such a segment is cleaved into several thinner strips parallel to the deposition plane, the innermost strip reverts to a flat piece, while the outermost strip increases in curvature. This is illustrated in figure 1. Qualitatively similar results are obtained if a segment (for example $1 \times 0.1 \times 0.1$ cm) is cut from the

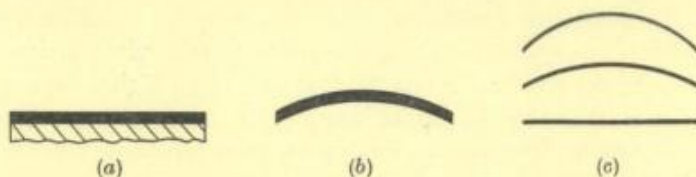


FIGURE 1. Schematic representation of change in curvature of a strip of 'as-deposited' graphite. (a) Still in contact with former; (b) released from former; (c) subdivided into thinner strips.

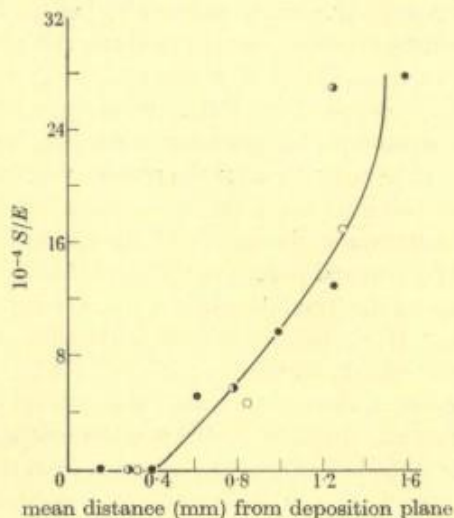


FIGURE 2. Variation of the ratio stress/Young's modulus (S/E) in successive layers of 'as-deposited' graphite for deposits of initial thickness 0.149 (○), 0.153 cm (×), and 0.19 cm (●).

flat part of the deposit at right angles to the previous direction and is separated into strips. These observations point to an effectively isotropic compressive stress in the pyrolytic deposit, increasing from its inside surface outwards.

More quantitative information was gathered from measurements (by means of a travelling microscope) of the principal radius of curvature (R) of strips subdivided from three different deposits of initial thicknesses, 0.149, 0.153 and 0.190 cm. The reciprocal of the curvature (R) assumed by a strip is proportional to the average compressive stress S in the piece of material. The gradient of S/E , where E is

Young's modulus, was determined by a simple modification of a method described by Barrett (1944). If, when a strip of thickness Δt is removed from the deposit thickness t the remainder assumes a radius of curvature R , then

$$\frac{S}{E} = \frac{4}{3} \left(\frac{1}{R} \right) \frac{t^2}{\Delta t}.$$

Up to six thin strips were removed successively from the inside of each segment and the curvature of the remainder was measured. Values of S/E calculated in this way for the three segments are plotted in figure 2. Without knowledge of the value of Young's modulus for each strip, it is not possible to determine the absolute values of the compressive stress. However, on the reasonable assumption that for the various strips E varies by less than one order of magnitude, the curve of S/E in figure 2 effectively represents the gradient of stress. Any allowance for the change in E from the values for highly disordered graphite, for which it is low, to those for more perfect graphite, for which it is higher (Davidson, Losty & Ross 1958), would increase the slope of figure 2.

Though the points are unavoidably somewhat scattered, the plot shows that an innermost layer of the deposit, approximately 0.4 mm thick, is relatively free from strain; beyond this layer the compressive stress S , assessed as above, increases roughly in linear dependence with the distance from the inside of the sleeve.

Crystallographic measurements

Other quantitative information was obtained from Debye-Scherrer X-ray diffraction patterns of material taken from the six strips of the segment 0.19 cm thick, a conventional 19 cm radius camera and filtered Cu $K\alpha$ radiation being used. Microphotometer traces of the middle region of the spectra for strips numbered 1, 4 and 6 (cf. table 1) are illustrated in figure 3. These traces have not been corrected for instrument broadening and Lorentz-polarization effects; the intensities are given as ratios relative to an arbitrary peak value for the (100) reflexion.

Mean interlayer spacings (d) were calculated from the (00 l) reflexions applying the Nelson-Riley (1945) extrapolation, and corresponding values of the stacking disorder factor (p) of nearest neighbours were computed by means of the Bacon-Franklin equation (Bacon 1951). These parameters, which again indicate the progressive increase in disorder from the inside outwards, are listed in table 1. Relevant

TABLE 1. PROGRESSIVE CHANGE IN DISORDER FROM THE INSIDE OUTWARDS
IN A DEPOSIT OF PYROLYTIC GRAPHITE

no.	thickness of strip (mm)	mean distance from inside (mm)	$d(\text{\AA})$	p	$I/R \text{ (cm}^{-1}\text{)}$
1	0.33	0.16	3.3565 ± 5	0.075	0
2	0.15	0.41	3.3572 ± 2	0.125	0
3	0.24	0.60	3.3595 ± 2	0.16	0.005
4	0.49	0.97	3.3688 ± 4	0.34	0.027
5	0.10	1.26	3.370 ± 1	0.36	0.052
6	0.59	1.61	3.395 ± 5	0.65	0.057

values of I/R are also given. Figure 3, and the numerical results recorded in table 1, show to what extent the structural disorder increases on passing from the inner to the outer layers of the deposit.

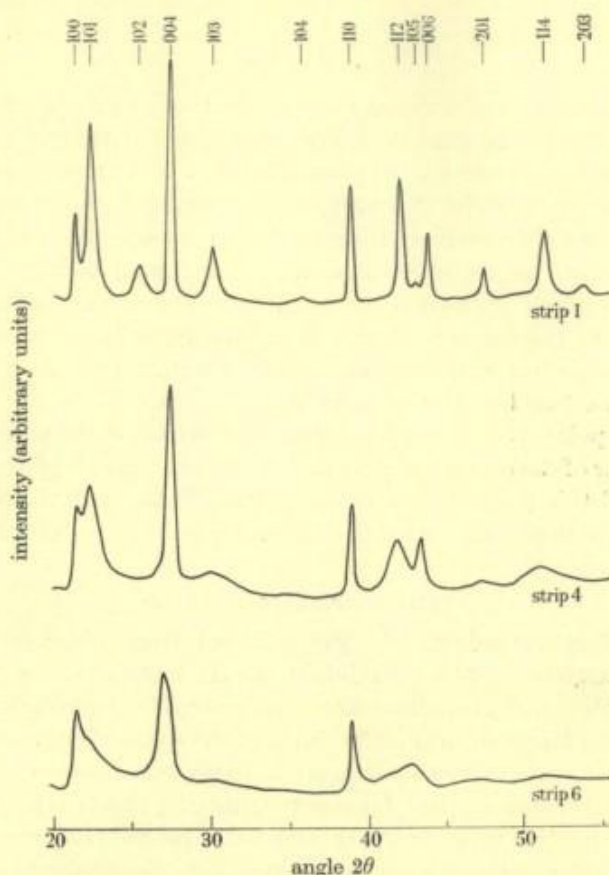


FIGURE 3. Microphotometer traces of X-ray reflexions from strips at various depths from 'as-deposited' graphite (cf. table 1).

The decrease in intensity and increase in breadth of the $(h0l)$, (hkl) and $(00l)$ reflexions show that there is a progressive decrease in three-dimensional order on passing from the inside outwards of a deposit. In contrast, the near-constant line width of the (110) reflexion indicates that there is relatively little change in the structure of the individual carbon hexagon layers throughout the deposit.

The p -factors reveal that in the innermost layers approximately only one layer in thirteen is misoriented with respect to its nearest neighbour, whereas in the outermost layers there is almost complete stacking disorder as in turbostratic graphite ($p = 1$).

Electrical measurements

Measurements of the electrical resistivities and of the Hall coefficients (extrapolated to infinite field) in the predominant a axis direction were made on a similar

series of strips from another specimen of pyrolytic graphite (table 2) and substantiate the trends recorded in table 1.

In yet another specimen of type *A* deposit the thermoelectric power at room temperature in the direction of the *a*-axis was observed to change from -2 to $+10 \mu\text{V}/^\circ\text{C}$ in successive strips from the inside to the outside of a segment of the deposit. These findings point to increasing predominance of positive carriers of electricity on proceeding outwards, indicating that the sites of structural disorder act as electron traps in the general sense that they decrease the concentration of electrons in the upper band. This trend is also illustrated by the decrease in field dependence of the Hall effect (not shown).

TABLE 2. PROGRESSIVE CHANGE OF ROOM TEMPERATURE *a*-AXIS ELECTRICAL PROPERTIES IN A DEPOSIT OF PYROLYTIC GRAPHITE

location of strip in deposit	electrical resistivity ($10^{-5} \Omega \text{ cm}$)	Hall coefficient (cm^3/C)
inner	7.85	-0.17
middle	14.1	-0.12
outer	16.9	-0.10

Origins of the trend in disorder

Although such findings show that the outermost layers of a pyrolytic deposit are under the greatest compressional stress and are the most disordered, they do not indicate the origin of this trend. At the pressures of methane gas used, the general orientation of a deposited crystallite is more or less independent of the structure of the substrate, in so far as no epitaxial growth is found (Diefendorf 1960). The progressive increase in structural disorder observed in the present work would not be expected on these grounds.

By varying the deposition time from 1 to 30 min, keeping other conditions constant, a series of deposits was prepared whose thickness ranged from 0.05 to 1.05 mm. Segments were cut as before, and their average curvature I/R when released from the sleeves of deposit was determined. Results recorded in figure 4 show that very thin deposits, far from being near to ideal graphite, show gross stacking disorder ($p \sim 0.85$) and their curvature indicates very high compressive stresses. It is noteworthy that a critical decrease of stress and increase of order appears for deposits that are allowed to grow thicker than about 0.5 mm. This suggests that the relatively stress-free innermost layers found in the thicker deposits result from a secondary recrystallization process which only occurs after sufficient graphite has been deposited to attain a critical compressive stress. Indeed, as soon as the thickness of a deposit exceeds about 0.5 mm, the disorder of the outermost layers (cf. table 1, $p \sim 0.65$) is below that observed for very thin deposits; apparently recrystallization of the innermost layers begins to influence the outer skin.

To test this view further, an even thicker deposit (2.7 mm) was prepared. When this was segmented, it was observed that the innermost layer (about 0.5 mm thick)

was extremely soft, resembling natural graphite in appearance. The layer spacing $3.3540 \pm 0.0003 \text{ \AA}$ and other physical properties corresponded with the near-ideal type *B* graphite described below. In striking contrast, the outermost strip (0.3 mm) of this thick deposit was grossly disordered ($p \sim 0.9$), practically to the limit for turbostratic graphite. Figure 5, plate 1, illustrates the contrast.

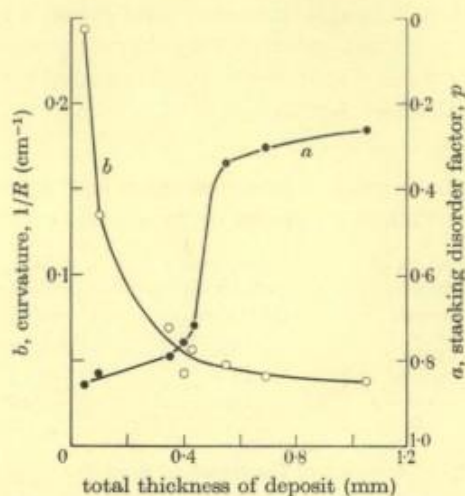


FIGURE 4. Average stacking disorder and stress curvature of 'as-deposited' graphite as a function of thickness of deposit.

STRESS-ANNEALING OF PYROLYTIC GRAPHITE

Although annealing could generally be achieved by raising the temperature of a specimen sufficiently, its course was found to depend in a critical way on the mechanical constraints to which the specimen was subjected.

Without external constraints, when a segment ($5.50 \times 0.5 \times 0.135 \text{ cm}$) of type *A* graphite was heated in argon for about 1 h to 3000°C , its curvature increased from 0.021 to 0.18 cm^{-1} and its length increased by 4.55% . A similar segment divided into three strips showed highly significant changes on annealing. Whereas the innermost strip, which was 0.4 mm thick, became only slightly curved ($1/R = 0.025 \text{ cm}^{-1}$) the middle strip (0.6 mm thick) increased to 0.12 cm^{-1} and the outermost strip showed even greater increase to 0.3 cm^{-1} . Other aspects of annealing have been described by Martens & Kotlensky (1960).

TABLE 3. CHANGES ON CONSTRAINED ANNEALING OF PYROLYTIC GRAPHITE AT 2800°C

specimen	% change in length	interlayer spacing ($\text{\AA}$)		stacking disorder factor p	
		before	after	before	after
inner	1.95	3.358 ± 1	3.3555 ± 5	0.17	0.05
middle	2.6	3.368 ± 1	3.3545 ± 3	0.35	0.02
outer	4.5	3.376 ± 1	3.3535 ± 5	0.44	0

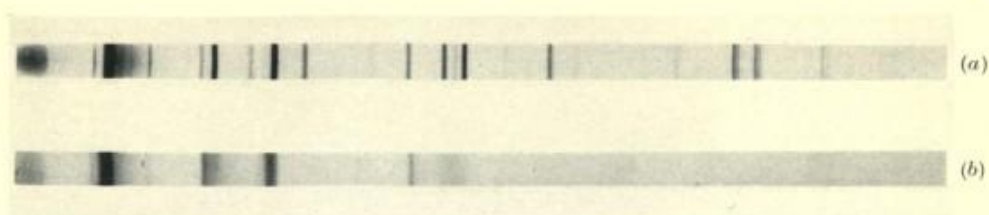


FIGURE 5. Debye-Scherrer X-ray photographs of (a) innermost and (b) outermost layers from a thick (2.7 mm) pyrolytic deposit.



FIGURE 8. Electron micrograph of type B graphite showing Moiré fringe patterns.

(Facing p. 26)

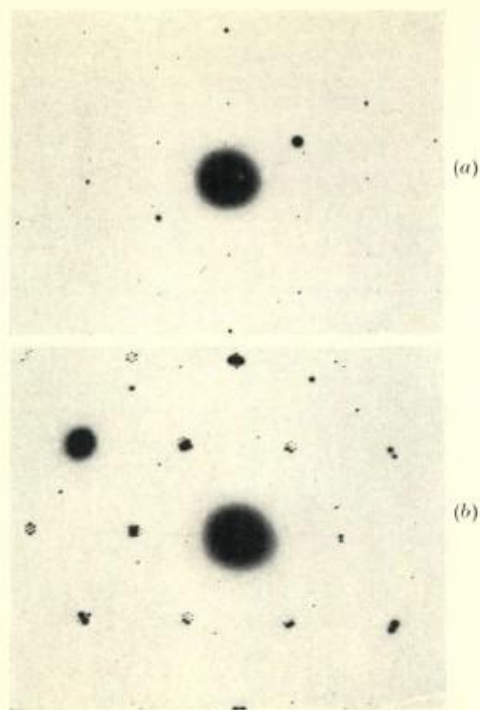


FIGURE 9. Electron diffraction patterns from type *B* graphite. (*a*) Single crystal region; (*b*) pattern from two overlapping crystals.



FIGURE 11. (*a*) Specimen of 'as-deposited' type *A* pyrolytic graphite. (*b*) Product after detonative 'stress-annealing'.

The effect of an external constraint which prevents specimens from curving during annealing was investigated as follows: a segment from a deposit 1.5 mm thick was separated into three strips, and these were then held parallel in a slot cut in a block of polycrystalline graphite. Annealing was carried out for 1 h as before, but the temperature was lowered to 2800 °C to avoid possible deformation of the polycrystalline block.

Table 3 on p. 26 records the changes in order observed.

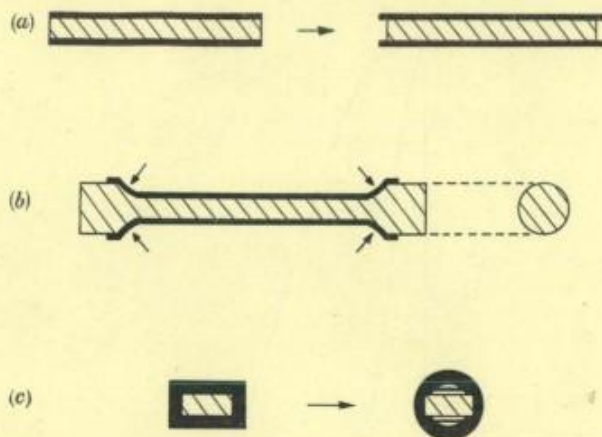


FIGURE 6. Schematic representation of (a) expansion of sleeve of pyrolytic graphite on annealing to around 3000 °C to form type *AB*; (b) the regions where the expansion of the sleeve of pyrolytic graphite exerts pressure on the former if ends are left uncut; (c) change in cross-section of sleeve of deposit from rectangular to circular when annealed under constraint.

The striking conclusion from these results is that on annealing, the innermost layer though initially fairly well ordered attains markedly lower ultimate crystal perfection than the outermost layer which initially incorporated much more disorder and stored energy.

Type AB recrystallized graphite

One application of these findings to the stress recrystallization of graphite is convenient when flat specimens are required, though on account of the incomplete constraint the ultimate crystal perfection is lower than that of type *B* described below. To achieve this partial recrystallization a complete sleeve of pyrolytic graphite (conveniently about 1.5 mm thick), still on the rectangular former but with the ends cut off square, is annealed for an arbitrary period of about 1 h at 3000 °C in a carbon resistivity tube furnace flushed with argon. On cooling, the sleeve is found to have expanded by about 4.3 % in length, whereas the former shows no significant change (figure 6(a)). Material obtained in this way, which is referred to as type *AB* graphite, shows improved three-dimensional order throughout the deposit (observed layer spacings for a number of specimens ranged from 3.3545 ± 0.0005 to 3.3555 ± 0.0005 Å) as well as considerable reduction in angular spread of crystallite *c*-axes normal to the plane of the substrate.

Figure 7 illustrates the change in intensity ratio for the (002) reflexion as a function of the inclination of the deposition plane to an incident beam of Mo radiation. To determine these intensities cylindrical specimens (0.08 cm diameter) were turned from the pyrolytic deposit on a watchmaker's lathe, with an 'air-brasive' jet of corundum particles carried in nitrogen as the cutter. I_0 is the intensity in the direction making an angle of 6.5° to the deposition plane, where crystallites with their basal planes strictly parallel to it would be in the reflecting position.

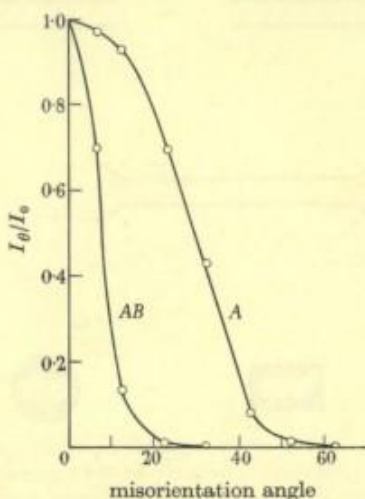


FIGURE 7. Relative misorientation of basal planes of crystallites in types A and AB graphite.

The strong mechanical forces brought into operation during the structural transformation to type AB graphite can be observed if the ends of the former are not cut off square before annealing. On annealing at 3000°C for 1 h, due to the pressure of the expanding sleeve on the shaped ends of the former (figure 6(b)), the former is itself expanded by about 1.5%. The degree of structural transformation produced in this way in the deposit is much less than that for type AB graphite.

Type B graphite

Thicker deposits (about 2.5 cm) incorporate even more strain energy than those just described. When these are heated with the ends of the former cut off square they likewise show a transformation to type AB graphite.

If, however, annealing is carried out under constraint by heating *in situ* in the deposition chamber, much more marked recrystallization occurs. Visually a most striking feature of this method of stress annealing is that the surface of the deposit changes from a rectangular to a cylindrical conformation (figure 6(c)). Momentary heating to a nominal surface temperature of about 2700°C is sufficient to achieve this transformation and visual observations suggest that actual recrystallization is probably completed in less than 1 s.

The highest degree of order in the material transformed under constraint is found in the innermost portions of the sleeve close to the major deposition plane; this dense material is referred to as type *B* graphite. Figure 6(c) illustrates a section of the product. On either side of compact type *B* graphite a layer of graphitic dust is found. The outermost cylindrical skin is crystallographically similar to type *AB* graphite, though some observations indicate residual compressive stresses in this layer. Pieces of type *B* graphite up to $4 \times 1 \times 0.1$ cm have been separated whose properties are close to those of small single crystals of natural graphite. Although it is rather difficult to separate such specimens from the deposit because of their extreme softness, this can be achieved with care. The very softness of the periphery tends to protect the interior portions from mechanical distortions, and it is probably for this reason that comparatively large segments retain their properties as formed. These are close to those of single crystals of natural graphite (see below).

Under the optical microscope plane sheets can be seen right across the thick pieces. Electron microscopy reveals surface structures also found in natural single crystals, such as networks of dislocations and Moiré fringe patterns (figure 8, plate 1). Direct evidence of the presence of single crystal regions is obtained from electron diffraction patterns taken from selected regions of a segment. The pattern shown in figure 9(a), plate 2, is clearly from a single crystal region, while that shown in figure 9(b), with 'double-diffraction' satellite hexagonal reflexions around the main single crystal reflexion, points to two overlapping crystals with only slight mutual misorientation. Corresponding with these electron diffraction records, X-ray diffraction diagrams confirm near-single crystal regions of considerable extent (Blackman, Saunders & Ubbelohde 1961*a*).

In type *B* graphite the degree of misorientation of crystallites about the position parallel to the deposition plane was found to be so small that I/I_0 values cannot be usefully plotted in figure 7.

Further indication of the near-perfect nature of type *B* graphite is illustrated in figure 10 by the close matching of the temperature coefficient of electrical resistivity with that of data reported (Soule 1958) for a 'good single crystal'. For comparison, corresponding typical curves for type *A* and *AB* material are given. The absence of any indication of residual resistivity in type *B* graphite down to the lowest temperature used indicates the extent to which electron scattering centres are removed during the thermal transformation. It is not clear whether the fact that the resistivity of the specimen of type *B* graphite illustrated in figure 10, plate 2, is actually lower than that of the 'good single crystal' implies even greater freedom from crystal defects. Accurate evaluation of the number of charge carriers per unit mass for the two materials under comparison would be required to determine whether type *B* illustrated in figure 10 actually shows less scattering than the 'good single crystal'.

Properties of type *AB* and type *B* graphite are compared in other respects with those of the parent material in another publication (Blackman *et al.* 1961*a*). For convenience some of the principal differences are summarized in table 4. It may be noted that the magneto resistance is a particularly sensitive measure of residual crystal defects.

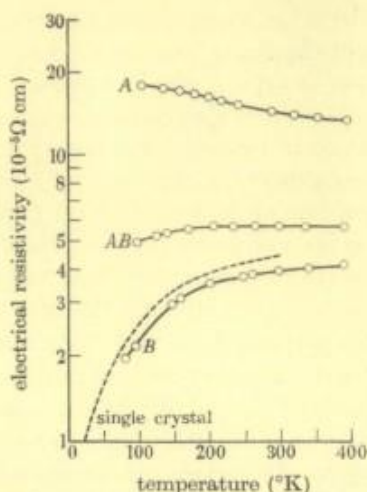


FIGURE 10. Comparison of temperature dependence of the 'a-axis' electrical resistivity of types *A*, *AB* and *B* graphite with that of a single crystal (Soule 1958).

TABLE 4. COMPARATIVE PROPERTIES OF VARIOUS GRAPHITES

property	pyrolytic			'single crystal'	polycrystalline
	<i>A</i>	<i>AB</i>	<i>B</i>		
density (g/cm ³)	2.22	2.24	2.26	2.26	1.6 to 1.9
'a-axis' electrical resistivity (10 ⁻⁴ Ω cm), 293 °K	9 to 20	5 to 9	3.5 to 5	4	80
'a-axis' magneto-resistance, Δρ/ρ ₀ % for 7000 Oe, 77 °K	10 to 30	80 to 900	3050	about 4700	2

Uncontrolled recrystallization

On three occasions, the release of energy during the thermal transformation was so great that the process apparently became 'detonative'. A sharp crack was heard, and both the sleeve and those parts of the former it covered, were found to have completely disintegrated into small fragments (figure 11). In each case it was noted that there was no appreciable liberation of gas since the mercury manometer remained stationary. The particular conditions which determine such uncontrolled stress-annealing are not at present known. The phenomena are under investigation.

DISCUSSION

Specimens of graphite with controlled residual disorder obtained by techniques described above have been used in various researches (Blackman, Dundas & Ubbelohde 1960; Blackman, Mathews & Ubbelohde 1960*a*, *b* and *c*; Blackman *et al.* 1961*a* and *b*) which need not be further discussed in the present paper.

Comment seems warranted on some of the more unusual features observed with the stress-recrystallization of type *A* 'as-deposited' pyrolytic graphite.

Though it seems to be a fairly general observation, not restricted to graphite, that solids deposited from the vapour phase incorporate strain energy, the origin

of the compressive stresses in pyrolytic graphite is not quite clear. 'As-deposited' pyrolytic graphite consists essentially of an assembly of crystallites linked together at their edges but misoriented with respect to the plane of deposition. Obviously the large anisotropy of thermal expansion of graphite would lead to local tensile or compressive stresses when the temperature was raised or lowered away from the temperature of deposition. However, the balance of evidence does not accord with the possibility that such thermally induced stresses can account for the effects observed.

Simple considerations of lattice theory suggest another source of stresses in pyrolytic graphites. In close-packed crystals, the potential energy of attraction between nearest neighbour atoms, regarded as spheres, remains much the same so long as they remain in contact, whether these atoms lie on the points of a perfect crystal lattice, or constitute a more disordered condensed state of matter. But the repulsion energy in unit mass of material is greater, in some cases considerably greater, when the units of structure though in contact are positionally disordered. In graphite, the enhanced repulsion that results from attacking disorder of the carbon hexagon networks leads to well-known expansion of the *c*-axis layer spacing from 3.35 Å to about 3.44 Å on passing from well ordered to turbostratic material.

When close-packed crystals melt, the increased repulsion energy that accompanies positional disorder is generally released by an expansion of volume (Ubbelohde 1960, 1961). However, many disordered solids are insufficiently plastic to allow full release of internal repulsion energy, and thus retain stored compressional energy, distributed more or less homogeneously. Mechanisms of release of such stored energy by recrystallization have certain kinetic analogies with the growth of crystals from a disordered melt, which usually requires migration of atoms or molecules under co-operative conditions of rearrangement. Because this kind of ordering is co-operative, threshold conditions are often found both for nucleation and for crystal growth. The observations on stress recrystallization of graphite recorded above likewise point to the existence of a threshold condition, which appears to involve the storage of enough compressive energy per unit volume to ensure that once recrystallization has started it will be propagated by a co-operative mechanism. When the disordered pyrolytic graphite is raised to a sufficiently high temperature blocked dislocations may well become unpinned. Provided the material is suitably constrained at this stage the compressive energy is not immediately dissipated at the boundary between order and disorder, so that recrystallization can be propagated. In the limit, the velocity of propagation of mechanical displacements in a condensed state of matter, that accompany the propagation of crystal ordering, will be that of a sound wave of corresponding amplitude, i.e. a shock wave in the solid. Such limiting rates of co-operative transformation in solids, that are accompanied by the liberation of the stored energy, have been termed 'weak detonations' (Ubbelohde 1950, 1953). It seems possible that in the course of the observations referred to above the conditions for the propagation of stress-recrystallization in pyrolytic graphite became sufficiently favourable to attain something like weak detonation. This possibility could be of wider importance with regard to other forms of stored strain energy in graphite, for example,

as a result of radiation damage. If such stored energy can likewise be released co-operatively, rates of propagation of recrystallization could attain dangerously high values. Further work is required to determine to what extent different types of stored energy in graphite can in fact undergo comparable modes of co-operative recrystallization.

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