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Effect of Twins on Deformation of Graphite Single Crystals

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A detailed investigation has been made of deformation and fracture in graphite single crystals, between 20 and 2400° C, under a tensile stress parallel to the basal plane. Crystals are shown to be inherently weak when twins are present and the low value of modulus recorded in twinned crystals is attributed to dislocation glide within these regions. A mechanism of fracture is proposed which is consistent with the low strength and the fracture characteristics of graphite.

It has been shown that graphite single crystals exhibit anomalous behaviour in that the tensile fracture strength increases if tests are made at temperatures greater than 2000° C.

This increase in strength is associated with the movement and annihilation of twin boundaries and subsequent reduction in stress concentration. Delamination is also shown to result from twin boundary movement.

1. Introduction

Most studies on the mechanism of deformation and fracture of graphite have been made on complex, polycrystalline, two-phase materials. Freise and Kelly [1] first examined deformed single crystals and found that they had a very low tensile strength of 2 ± 1 kg/mm^2. The highest recorded value for graphite whiskers is 2000 kg/mm^2, corresponding to an elastic strain of 2% [2, 3].

Electron microscope studies have confirmed the movement of dislocations which lie and glide in the basal plane (0001), [4, 5]. Such movement often results in the production of twins and ill-defined tilt boundaries [6] which prevent extensive glide in the basal plane. The twins correspond to regions separated from the matrix by bend planes of a specific angle, and have a low energy.

Freise and Kelly [1] proposed that the existence of twins, with the subsequent formation of microcracks in single crystals of graphite, would account for the absence of ductility at room temperature except for the special case of a shear parallel to the slip plane. For the case of polycrystals no preferred orientation corresponding to the twin has been observed, but kinking is possible [7].

The deformation characteristics of graphite at elevated temperatures are quite different from those of metals, and both pyrolytic and polycrystalline graphites show increased fracture strengths when deformed at temperatures above 2000° C [8, 9]. Stover [10] considered pyrolytic graphite to be composed of tightly packed and wrinkled sheets which straighten during deformation above 2000° C. No atomic displacement model has been suggested to account for these results.

2. Experimental

The graphite crystals used in this investigation came from the Lead Hill mine at Ticonderoga, New York. The crystals occur embedded in pyroxene which was leached away by alternate treatments with concentrated HF and boiling HCl. The ash content of the graphite after this treatment was 2.7% and after annealing at 3000° C for 1 h was reduced to approximately 0.1%. The impurity content of these annealed

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crystals is 30 ppm. The density, as measured by a displacement method, was 2.5 g/cm^3, compared with 2.26 g/cm^3 for the X-ray density [11]. The crystals ranged in size from a few mm to 1 cm in diameter and up to 1 mm in thickness. Tensile specimens were taken from crystals between 0.75 and 1 cm in diameter.

All the crystals exhibited a platelike habit, being thin in the *c*-direction. Fig. 1 shows such a crystal with a large number of well defined striations. Freise and Kelly [1] showed that many of these striations lie in crystallographic directions, the most common angle of intersection being 60°; optical goniometer measurements showed these striations to be tilts in the basal plane with an average angle of tilt of 20° 21′ ± 45′ and a habit plane of $\{11\bar{2}1\}$. Tilt boundaries of other angles occur with a habit plane which is not always $(11\bar{2}1)$ [12].

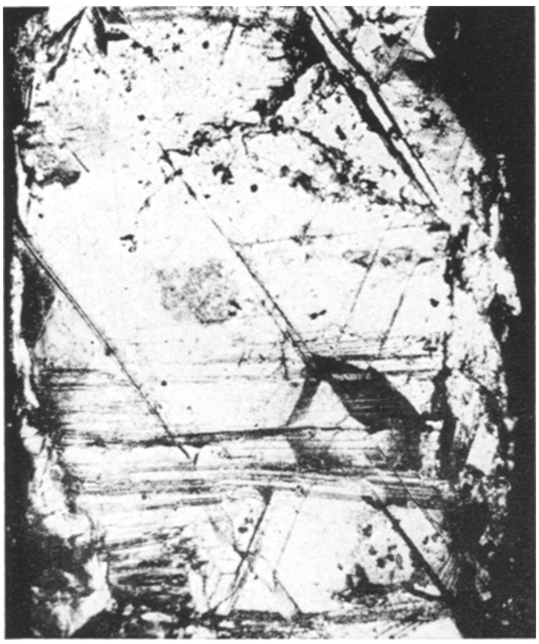


Figure 1 Striations on natural crystals (habit plane $\{11\bar{2}1\}$) (× 75).

Crystal perfection and twin orientation relationships were determined by means of transmission Laue photographs, using unfiltered copper radiation. Most crystals contained twist boundaries of ≈ 3 to 4°, as measured from the observed asterism. Cleaving of these crystals produced macroscopic improvement of the overall perfection. Prior to the tensile and shear tests, all the specimens were annealed in argon at 3000° C for 1 h. Except for a few specimens deformed in a micro-tensile machine [13], testing was performed on an Instron Testing Machine at a crosshead speed of 0.01 cm/min in a water cooled "Polanyi cage" attached to the moving crosshead. Tensile tests were performed at room temperature both in air and in a vacuum of at least 10^{-4} torr and over the temperature range 20 to 2400° C in a vacuum of 10^{-4} torr, using an electron bombardment furnace attached to the Instron Testing Machine [14].

All specimens were tested parallel to (0001) and pulled in graphite grips, machined to provide shoulders against which the matching shoulders of the waisted crystal could be loaded. This form of tensile specimen was obtained using an air/abrasive cutter. The graphite crystal was embedded in beeswax and a polythene pattern placed on the crystal, using a further amount of wax. The cutter could then follow the pattern and the resulting edges were undeformed, as confirmed by X-ray analysis. The gauge length was approximately 3.5 mm and the width 0.75 to 1.00 mm.

3. Results

3.1. Behaviour at 20° C and in Air

The tensile fracture stress of the single crystals is shown in fig. 2 to be a function of the orientation of the twin traces to the tensile axis. Fig. 3 shows typical load/extension curves in which the curve after fracture, and the type of fracture, are related to the orientation and depth of the twins in the crystals. The orientations of twin traces in a crystal prior to the application of a tensile load are indicated, as an example, in fig. 4a. Under load, fracture has occurred along and down these twin traces (fig. 4b), (i.e. across packets of basal planes, and also parallel to the basal planes). Such fracture gives rise to the pulling out of interleaved sheaves of basal layer planes over each other. This type of fracture is associated with an extension of up to 20% and its nature is evident from fig. 5. Interference microscopy indicates the thickness of these packets to be approximately 1000 Å. Further straining initiated small fracture steps, cleavage steps, and river patterns on the sheared basal plane.

If the assumption is made that all layer packets in the graphite specimen are broken after the initial drop in load, and a measurement is made of the area of shear on pulled out sheaves,

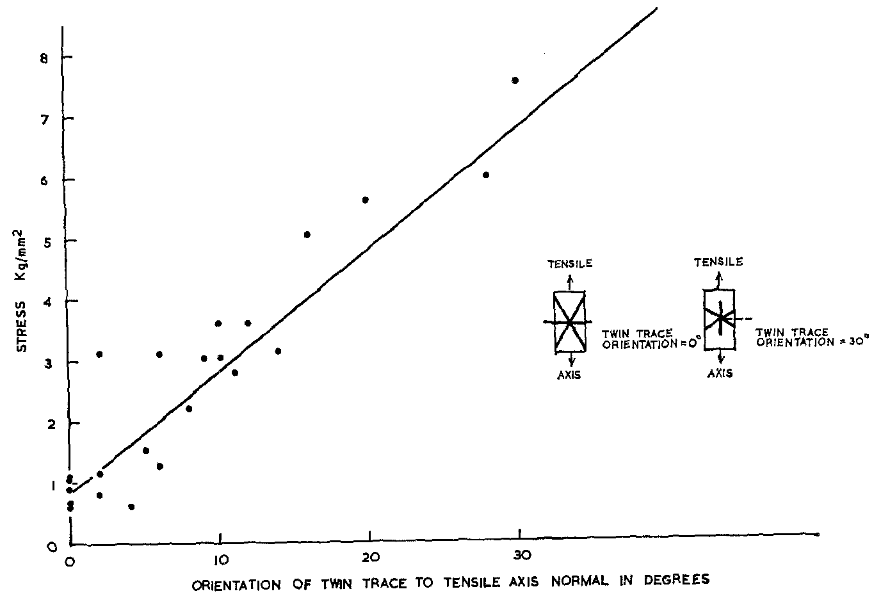
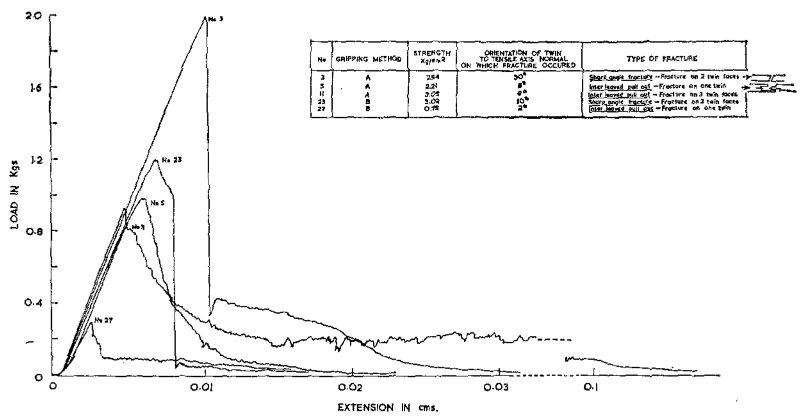


Figure 2 Variation of fracture stress with the angle between the twin trace and the tensile axis.



No	GRIPPING METHOD	STRENGTH Kg/mm²	ORIENTATION OF TWIN TO TENSILE AXIS NORMAL ON WHICH FRACTURE OCCURED	TYPE OF FRACTURE
3	A	7.54	30°	Sharp angle fracture – Fracture on 2 twin faces
5	A	2.21	8°	Inter leaved pull out – Fracture on one twin
11	A	3.04	0°	Inter leaved pull out – Fracture on 3 twin faces
23	B	3.02	10°	Sharp angle fracture – Fracture on 3 twin faces
27	B	0.75	2°	Inter leaved pull out – Fracture on one twin

Figure 3 Typical load/elongation curves.

a shear stress can be calculated at the point of fracture. The average shear stress was 11.4 gm/mm² for the twelve samples measured.

Small rectangular crystals cleaved to a thickness of approximately 0.01 mm have been successfully tested in the Marsh micro-tensile testing machine [14]. Of a number of specimens tested by this method, three were free of twins and were stressed to 75, 104 and 40 kg/mm² respectively, before slip occurred in the grips. The remaining ten specimens all showed the presence of twins in the gauge length and fractured at a twin trace on loading. The fracture stresses varied between 2 and 6 kg/mm². The modulus for the specimens with twins present was $7.5 \pm 1.0 \times 10^{11}$ dynes/cm² and for those free of twins, 10, 8 and 7.5×10^{12} dynes/cm² respectively.

Shearing experiments were performed on the graphite crystals by cementing them to machined aluminium anvils (with an epoxy resin) and compressing them. A lubricated ball bearing was used to transmit the load to the aluminium anvil thus reducing the effect of friction. The angle between the slip plane and the axis of compression was varied. No unique slip direction was found; shear occurred in the direction of maximum stress. The load to cause shear was recorded autographically. The critical resolved shear stress in the direction of maximum shear stress on the slip plane had an average value of 4.8×10^{-2} kg/mm².

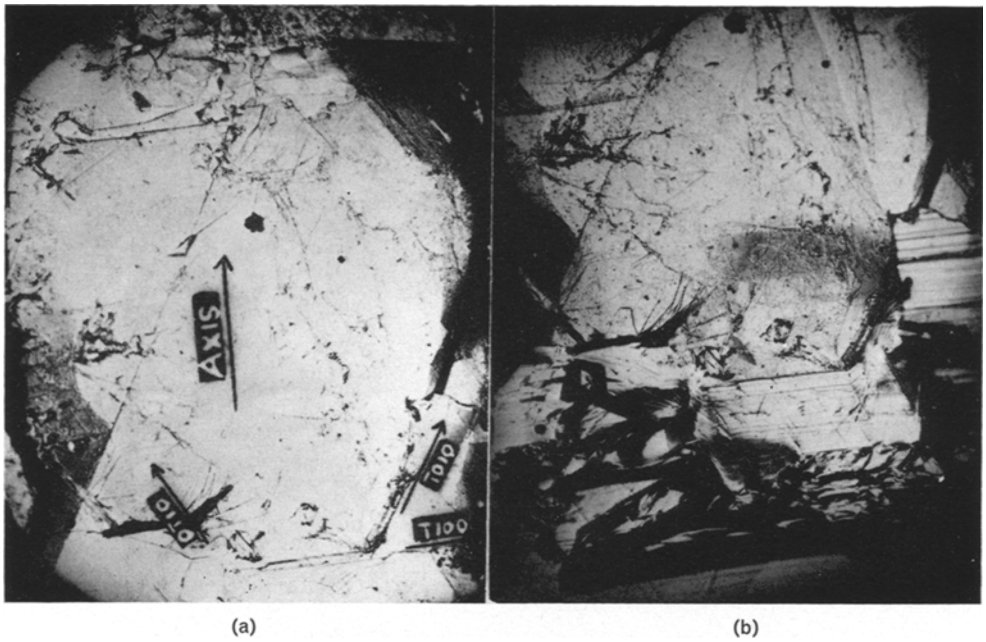


Figure 4 (a) Relation of tensile axis and twin trace before deformation. (b) Fracture surface after deformation (× 52).

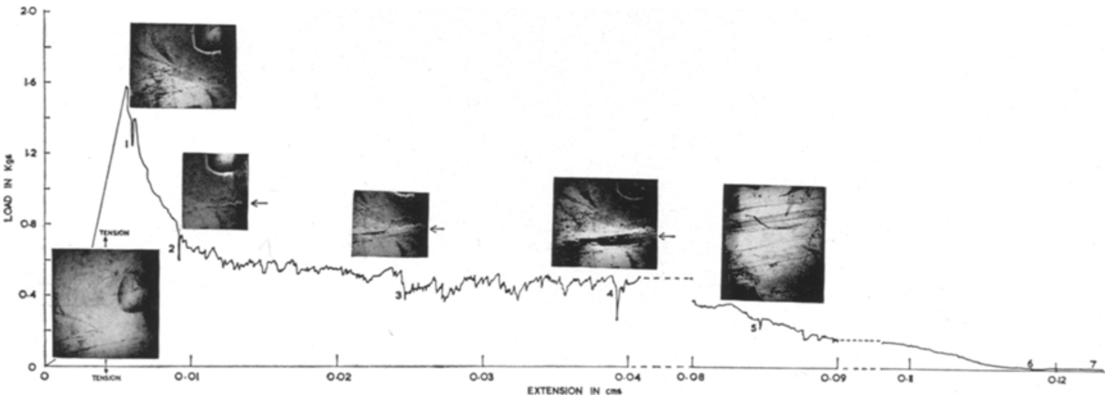


Figure 5 Initiation of fracture at twin trace and subsequent pull-out showing fractured layer packets. Load/elongation curve shows pull-out extension.

3.2. Behaviour at 20° C and in Vacuum

Tensile specimens cleaved from the same crystal and having identical twin orientation were heated to 2200° C for 15 min in a vacuum of 10^{-4} torr. Subsequent tensile testing at 20° C showed no significant variation in fracture strength when tested either in air or in a vacuum of 10^{-4} torr (fig. 6). The change in slope of the initial part of the curve is due to a change in the machine characteristics and is not significant.

3.3. Behaviour at Elevated Temperatures

Fig. 7 shows the variation of fracture strength and yield strength as a function of both the orientation of the twin trace to the normal of the tensile axis, and the test temperature. Above 2200° C there is a marked increase in strength. This is seen in fig. 8 in which two specimens cleaved from the one graphite crystal, and having identical twin orientations, are tested at room temperature in air, and at 2200° C under a vacuum of 10^{-4} torr.

The following comments can be made:

(*a*) There is a change in slope of the linear portion of the stress/strain curve, at 2200° C (see section 3.2).

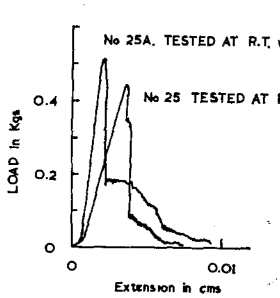


Figure 6 Load/elongation curves for single crystals tested in air and vacuum of 10^{-4} torr.

(*b*) At the temperature of 2200° C, the yield strength is approximately the same as the fracture strength at 20° C.

(*c*) For the sample heated to 2200° C, the load continually increases by a jerky motion until fracture, which occurs with no interleaved pull-out effect as observed at 20° C. This jerky motion is not a function of the applied load acting on the mechanism of the load train; loads exceeding 50 kg have been applied to the load train without any such motion being observed. Moreover, by the use of much harder, dummy specimens the grips have been tested to 2400° C under a load of more than 20 kg without the occurrence of jerky motion. Finally, no deformation of the shoulders of the specimen is observed as a result of tensile loading.

Fig. 9a shows, prior to tensile deformation, the surface of a graphite crystal, in which a number of twin traces are evident. After loading at 2350° C there is a decrease in the width of the twins and the disappearance of some (fig. 9b), particularly of those twins which subtend large angles to the tensile axis. Loss by evaporation of the surface layers did not amount to a significant fraction of the thickness. Associated X-ray examination of this crystal confirms the elimination of some twin boundaries, since asterism is reduced.

Strain measurement proved difficult. However, by utilising twin markings in the shoulder areas of the specimen, and providing the specimen was removed before fracture, a measurement of the strain could be made.

Extensions of up to 3% were recorded. Concomitant with twin movement on the basal planes, delamination occurs during extension (see below). With increasing temperature a decrease was observed in the stress at which the load/elongation curve became jerky. Fig. 10 shows this with three specimens, each having an angle of 8° between the twin trace and the tensile

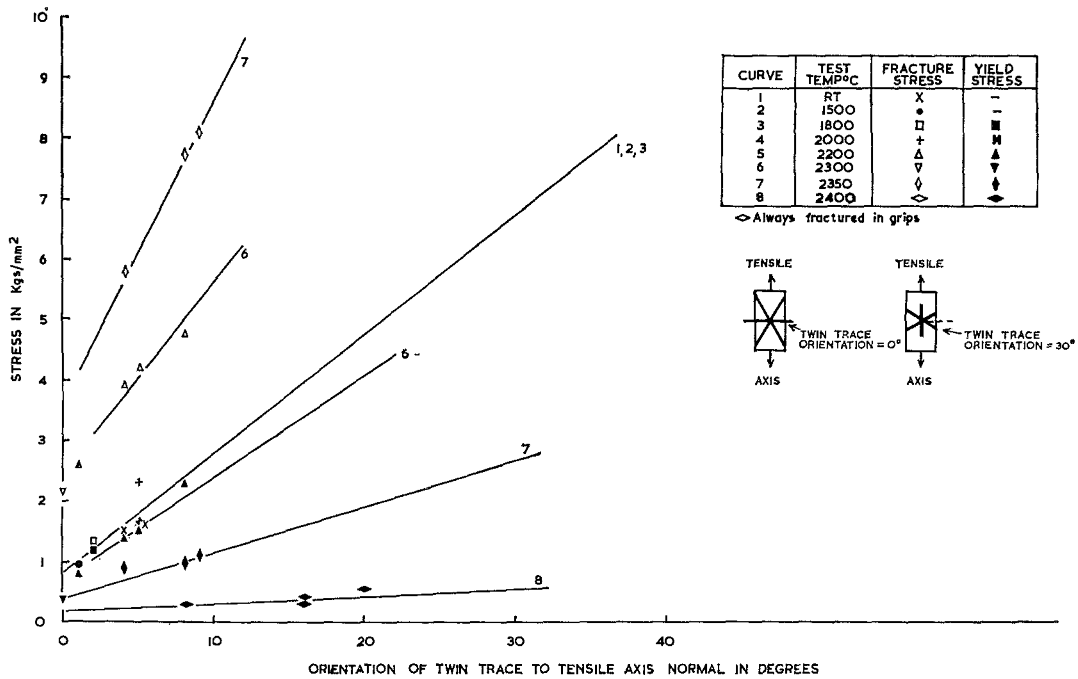


Figure 7 Variation of fracture stress and yield stress as a function of temperature at orientation of twin trace.

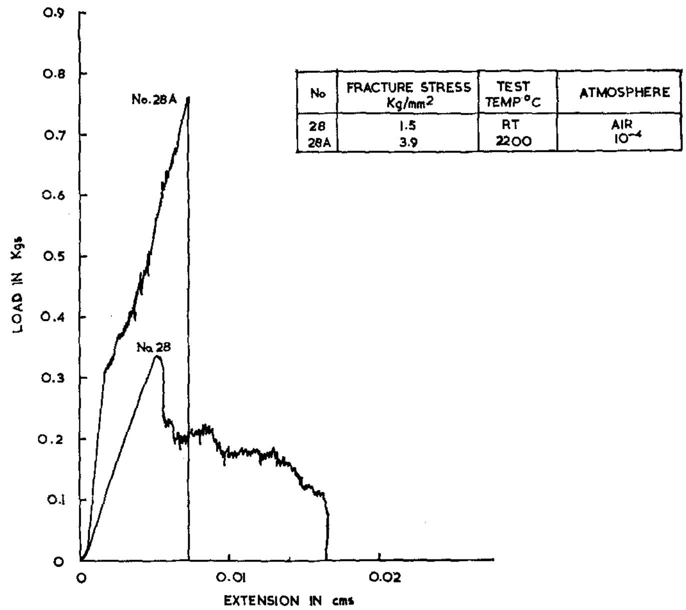
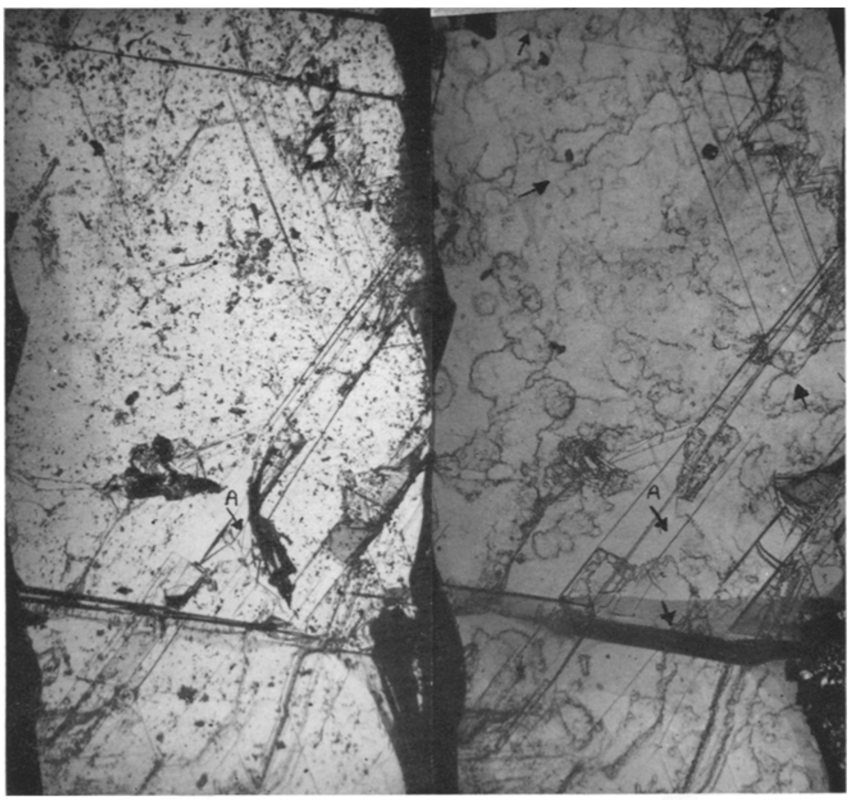
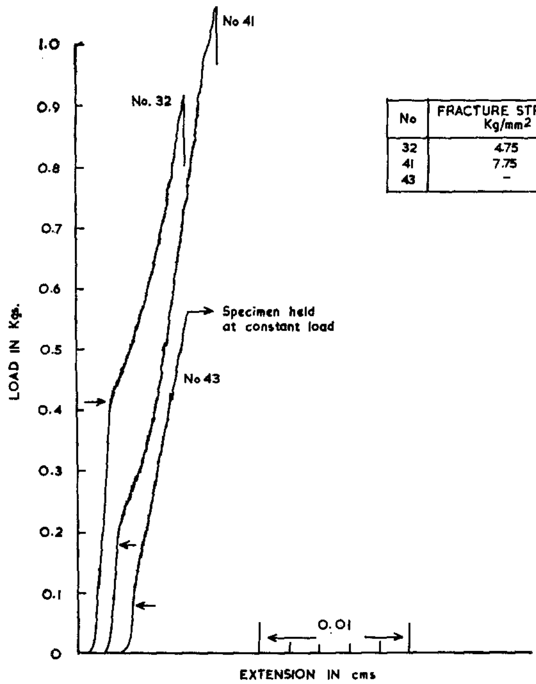


Figure 8 Variation of fracture strength and shape of tensile curve with temperature for identical specimens.



(a) (b)

Figure 9 Single crystal loaded in tension, (a) before deformation; (b) after deformation at 2350° C. Note elimination of some twins. Position of original twins shown by arrows (× 34).

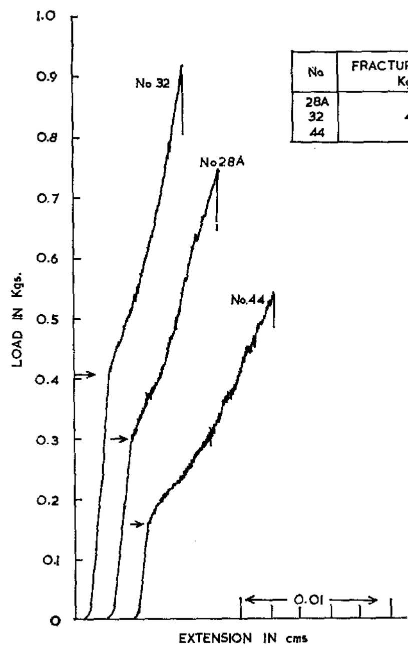


No	FRACTURE STRESS Kg/mm^2	TEST TEMP°C	ATMOSPHERE	ORIENTATION OF TWINS
32	4.75	2200	vac. 10^{-4} mm	8°
41	7.75	2350	vac. 10^{-4} mm	8°
43	-	2400	vac 10^{-4} mm	8°

Figure 10 Variation of fracture strength and yield stress as a function of temperature for a given orientation of the twin trace.

axis. The slopes of the jerky part of the curves are similar after the initial stages of plastic extension.

Tensile tests, at a constant temperature of 2200° C (fig. 11), show a decrease in the yield stress as the twin trace moves towards the normal to the tensile axis. There is also a corresponding decrease in the slope of the jerky load/elongation



No	FRACTURE STRESS Kg/mm^2	TEST TEMP. °C	ATMOSPHERE	ORIENTATION OF TWINS
28A	3.9	2200	vac. 10^{-4}mm	4°
32	4.75	2200	vac. 10^{-4}mm	8°
44	2.6	2200	vac. 10^{-4}mm	1°

Figure 11 Variation of fracture strength and yield stress as a function of orientation of the twin trace at 2200° C

curve. Plastic extension is observed to increase for those specimens with twin traces closer to the tensile axis normal.

Fracture at temperatures in excess of 2200° C occurs in an irregular manner, sometimes at an angle to the basal plane or along a jogged contour, but never in the interleaved type fracture as observed in tests between 20 and 2000° C. Delamination is very pronounced in this temperature range, concomitant with twin motion, and on fracture some of these delaminated regions open up into large cleavage cracks (fig. 12).

In order to evaluate the effect of time at stress, the specimen was loaded in the normal way to a given level of stress and the drive mechanism switched off. After the initial relaxation of the testing rig the load remained fairly constant. Under such conditions of loading the twin and tilt boundaries can be almost entirely eliminated. Fig. 13a shows the surface of a specimen prior to deformation and fig. 13b the same surface after $1\frac{1}{2}$ h loading. The extension as measured between twins is approximately 2%. The dark tilted regions in fig. 13b are tilts across the whole specimen, being larger at the front edge than at the rear. In the case of the left-hand tilt, the axis of tilt is aligned along the original $<10\bar{1}0>$ type direction and for the right-hand tilt the axis is also $<10\bar{1}0>$ but of the reverse rotation. Examination of sections of the crystal shown in fig. 13b by electron microscopy indicated a complete absence of tilt boundaries and large areas free from basal dislocations.

4. Discussion

The highest value recorded for the tensile strength of graphite whiskers is 2000 kg/mm² [3]. Figs. 2 and 7 show that the tensile strength for bulk single crystals varies between only 1 and 8 kg/mm² over the temperature range 20 to 2400° C.

4.1. Twins and Fracture

Experimental observation has shown that the striations on the basal planes (fig. 1) can be classified into simple tilts of two types; twins having a single definite tilt angle and habit plane, or tilts exhibiting variable tilt angles and habit plane. Tilts did not seem to be connected with the fracture process. The most noticeable feature of fractured tensile specimens is the relationship of the fracture to the original twin traces (fig. 4). All crystals tested in tension fractured at twin traces. For crystals tested in such a way that the free edges were tension free, fracture occurred along twin traces oriented at an angle to the tensile axis. This general conclusion, that twins are responsible for the low tensile strength of graphite single crystals, was confirmed when twin-free crystals were shown to exhibit fracture strengths as high as 100 kg/mm². Furthermore, as fracture stress is not affected by the testing atmosphere, it can be concluded that fracture is independent of the basal plane surface. From the constant pull-out stress of 11 g/mm² it can be argued that fracture occurs simultaneously across the whole specimen at the fracture stress and that subsequent pull-out (delamination) of the interleaved areas results in a jerky motion. In some specimens this extension amounts to 20% whereas the maximum extension which could result from annihilation of twins is 8%.

4.2. Twins Boundary Stability

The formal description of the twin boundary is

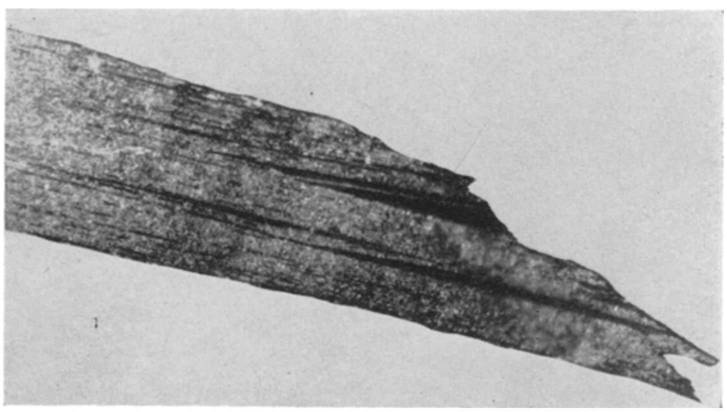
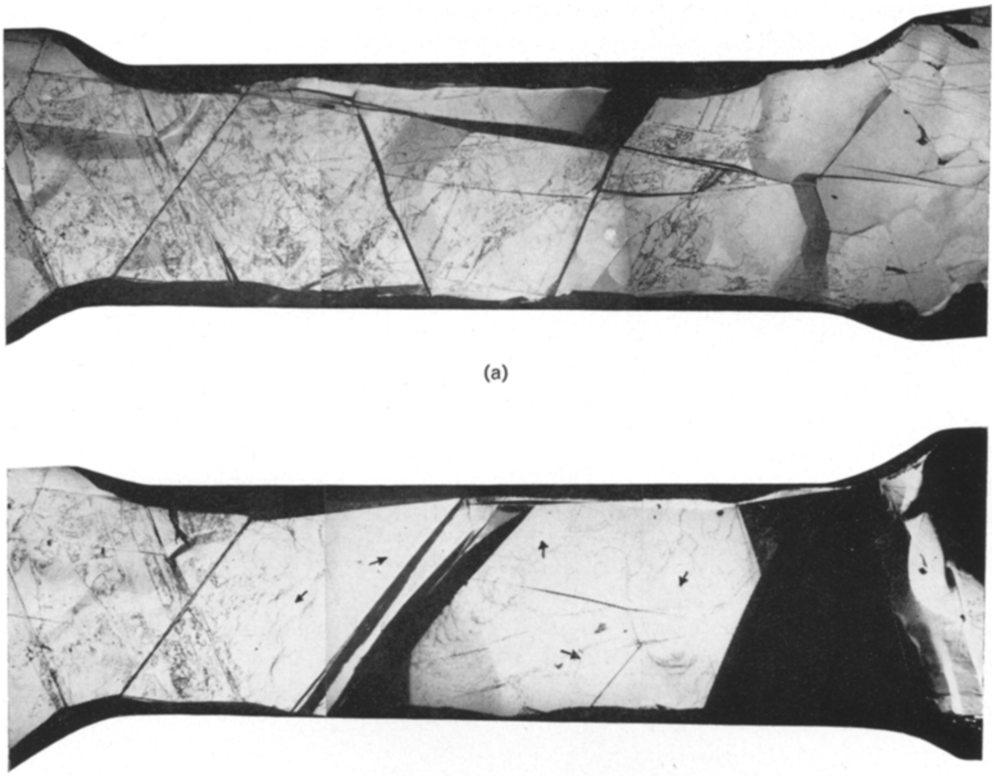


Figure 12 Fracture of single crystal after deformation at 2400° C (× 53).



(a)

(b)

Figure 13 (a) Natural single crystal undeformed showing twin traces. (b) Surface of same crystal after tensile deformation at 2400° C. Position of original twins are indicated by arrows. (× 11).

given by Freise and Kelly [1]. In terms of dislocations, the 20° 48′ twin boundary is composed of one partial dislocation on each layer plane with an associated minimum energy configuration. The angle of tilt is large so that the individual dislocations may have no significance. The stress required to pull out an edge dislocation from a symmetrical tilt boundary [15, 16] of dislocation spacing h is approximately

$$\sigma_{x,\,y} = \tau_0\, \mathbf{b}/h \qquad (1)$$

where τ_0 can be written in terms of the anisotropic elastic constant for shear on the basal plane, i.e. $C_{44} = (0.39 \pm 0.04) \times 10^{11}$ dynes/cm^2 [17], and **b** is the magnitude of the Burger's vector for a partial dislocation on every layer plane.

For the tilt boundary of 20° this stress is approximately 300 kg/mm^2, which is $\approx 20\%$ of the whisker strength for graphite. Such a boundary will be exceedingly "narrow" and behave as if it has a large Peierls-Nabarro stress to move it. It is thus not expected that dislocations will be driven out of the boundary.

4.3. Crack Initiation

Owing to the configuration and consequent immobility of the twin boundary it is expected that the presence of twins will result in stress concentrations. Considering a twin boundary as a notch which is atomically sharp, the crack length required to give a stress concentration of the order of 1000 : 1 is greater than the specimen width. Thus the low tensile strength of graphite crystals cannot be explained wholly in this way.

Alternatively the boundary could act as a wall for dislocation pile-ups. If the twins are considered as lying normal to the tensile axis and the specimen has a fracture strength of 1 kg/mm^2, then the resolved shear stress on the twinned basal layer planes is 320 g/mm^2 which is far in excess of the critical resolved stress for basal slip (50 g/mm^2). Thus basal dislocations will glide towards a twin boundary. The glide of such dislocations in twinned crystals would be expected to change the elastic modulus S_{11} observed in tensile tests. (Other experiments have confirmed such a modulus variation from 7.5×10^{11}

dynes/cm^2 [11] for twinned crystals to 8×10^{12} dynes/cm^2 [3] for graphite whiskers.) Two possible results follow: (*a*) formation of a cleavage crack along the basal plane; (*b*) formation of a crack along the twin plane.

(*a*) A dislocation pile-up could result in cracking and delamination along the basal plane [18]. Such dislocation movement and subsequent delamination has not been observed in tensile tests at temperatures below 2000° C, although delamination was observed at temperatures above 2000° C.

(*b*) As the twinning plane is a strong barrier for the blocking of dislocations, a pile-up of a group of dislocations will produce a very localised and large concentration of the applied stress.

Near to the head of a piled-up group, the shear stress exerted in its glide plane is given by

$$\sigma_1 \approx \frac{2L\sigma_S{}^2}{\mathrm{Gb}} \qquad (2)$$

where L = the pile-up length, G the shear modulus and σ_S the shear stress on the glide plane. Using the values of the elastic shear modulus for graphite [17]

$$\mathrm{G} = (0.39 \pm 0.04) \times 10^{11} \text{ dynes/cm}^2 \qquad (3)$$

If $L = 0.02$ mm and $\sigma_S = 3.5 \times 10^7$ dynes/cm^2, then the concentrated stress at the head of the pile-up is approximately 5×10^9 dynes/cm^2 or 50 kg/mm^2. This value gives a stress concentration of 50 : 1 which alone is insufficient to reduce the strength from that of whiskers to those observed.

According to these ideas, graphite single crystals under a tensile load will exhibit a linear stress/strain curve (fig. 3) with a modulus lower than that for graphite whiskers because of dislocation movement in the twinned regions. Stress concentrations resulting in part from twin notches and in part from dislocation pile-ups at the twin boundary will cause fracture along a twin interface, as shown in fig. 4. Such a fracture will increase immediately the stress on other layer packets containing twins, resulting in almost simultaneous fracture. The tail of the stress/strain curve has been shown to result from the pulling out of the interleaved layers between fractures at twin boundaries.

Below 2000° C, graphite crystals have a roughly constant fracture strength. However, at temperatures of 2200° C and above, there is a marked increase in the strength, which is dependent both on the test temperature and the angle between the twin trace and the tensile axis (fig. 7). Although the fracture strength can be increased four to five times by such treatment, it is still considerably below the 2000 kg/mm^2 recorded for graphite whiskers [3] at room temperature. Figs. 9 and 14 show that the increase in fracture strength is accompanied by twin annihilation, fracture occurring near the grips for specimen temperatures of approximately 2200° C and in the grip shoulders for specimen temperatures of approximately 2400° C. Fracture in these areas is always along a twin trace. This is understandable since the grip shoulders are at a lower temperature (100 to 300° C) than the gauge length, provided the deformation at high temperature increases the strength (Figs. 11, 12).

The change in length on the elimination of a twin is given by

$$\Delta = t(\sec\theta - 1) \qquad (4)$$

where t is the thickness of the twin and θ the angle between the basal plane in the twin and matrix. For a crystal containing one complete twin lamella across its thickness, the maximum extension is 8%. This is much more than the total extension observed in the specimens of figs. 12 and 13, and it is concluded that a considerable part of the observed extension could be due to elimination of twins. In a real crystal consisting of a number of layer packets, each with a given twin density, the total extension will be variable.

The tilts produced during deformation (fig. 13) are accommodation kinks introduced as a result of either grip restraint or non-axiality of loading [19]. They are formed by compression along the basal plane.

5. Conclusions

(*a*) Graphite with a modulus of $\approx 10^{13}$ dynes/cm^2 and a fracture strength in excess of 2000 kg/mm^2 is inherently weak when twins are present in the structure. The strength is reduced by 1000 : 1.

(*b*) A twin boundary is difficult to move, with the result that twin boundary motion is not observed at low temperatures. Moreover, dislocation penetration is unlikely and dislocation pile-up can occur at the boundary.

(*c*) Dislocation glide within the twinned region can account for the low modulus determined in twinned single crystals.

(*d*) It has been concluded that the mechanism for the low fracture strength of single crystal graphite results from stress concentrations at the twin boundaries. Dislocation pile-ups cause a stress concentration of 50 : 1 and a further stress concentration arises from the twin notch. Fracture occurs along the twin boundary in the layer packet with a resulting stress increase and simultaneous fracture in other layer packets.

(*e*) Tensile deformation of graphite single crystals, at temperatures above 2200° C, results in an increase in the fracture strength over values recorded at all lower temperatures. This increase is accompanied by the movement and annihilation of twin boundaries, and hence the complete elimination of these could lead to single crystals of high strength. There is some evidence of a decrease in yield stress at higher temperatures.

Acknowledgements

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