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Optical and Interferometric Studies on the Cleavages of Graphite and their Etch Patterns

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Single crystals of natural graphite have been cleaved and the cleavage faces have been studied by using multiple-beam interferometry. The cleavages have been etched in the melts of oxidizing agents. The cleavage faces and their etch patterns have been studied by multiple beam interferometry. The interferometric study has revealed that the etch attack is twofold, one producing the general dissolution and the other revealing the sites of the dislocations. The etch pattern consists of flat and point-bottomed hexagonal pits, which are asymmetric. Correspondence has been established in the etch patterns produced on the matched cleavage faces. Correspondence is also established in the etch patterns produced on the two sides of a thin flake. It is observed that prolonged etching produces holes at the sites of some of the pits. The formation of the holes has been discussed.

Introduction

Optical studies on the isolated cleavage faces of single crystals of natural graphite and their etch patterns have been made by a number of investigators, particularly Freise & Kelly (1961), Hughes & Thomas (1962), Hughes, Williams & Thomas (1962) & Thomas, Hughes & Williams (1963). It seems that the earlier investigators did not study the topography of natural graphite cleavages. Their etching experiments were carried out in gases, possibly because graphite being soft and brittle is very difficult to handle. In the present work, the authors have tried to examine the cleavage faces of natural graphite crystals and their etch patterns, using multiple beam interferometry (Tolansky, 1948). The investigation has also been extended to matched cleavage faces and their etch patterns. The present study has revealed striking information regarding graphite.

Experimental

The work described in this paper was done on natural graphite single crystals obtained from Dr J. M. Thomas of the University College of North Wales, Bangor, Wales and from Dr Shanker of the Atomic Energy Establishment, Trombay, India. The crystals being soft and brittle were usually small pieces, from which we selected crystals of suitable size for our work. Many of the crystals were hardly one to two mm across. The selected crystals were carefully cleaved with a very sharp razor blade and the freshly cleaved faces thus obtained were first mounted on glass flats and examined after the deposition of thin silver films on them. It was not necessary to clean the freshly cleaved faces before depositing silver. For the etching work the crystals already mounted for the optical studies were removed from the flat very carefully by placing them in benzene, which dissolved the polyvinyl acetate and thus detached the crystal from the flat. It may be mentioned that all these operations required very careful handling; otherwise either the crystals broke into small pieces or the surface patterns to be studied were obliterated.

Etching was carried out by heating the crystals in melts of oxidizing agents such as sodium or potassium nitrate at temperatures between 400 °C and 500 °C for the required periods. They were then removed carefully from the melt and cleaned, and the usual procedure was followed for examination. It may be mentioned that it was very difficult to get perfectly matched cleavages as material was easily lost owing to the brittle nature of the crystal. However, the authors, by extremely careful handling, have succeeded not only in getting matched cleavages but also in retaining their matching nature even after handling them in two or three different operations.

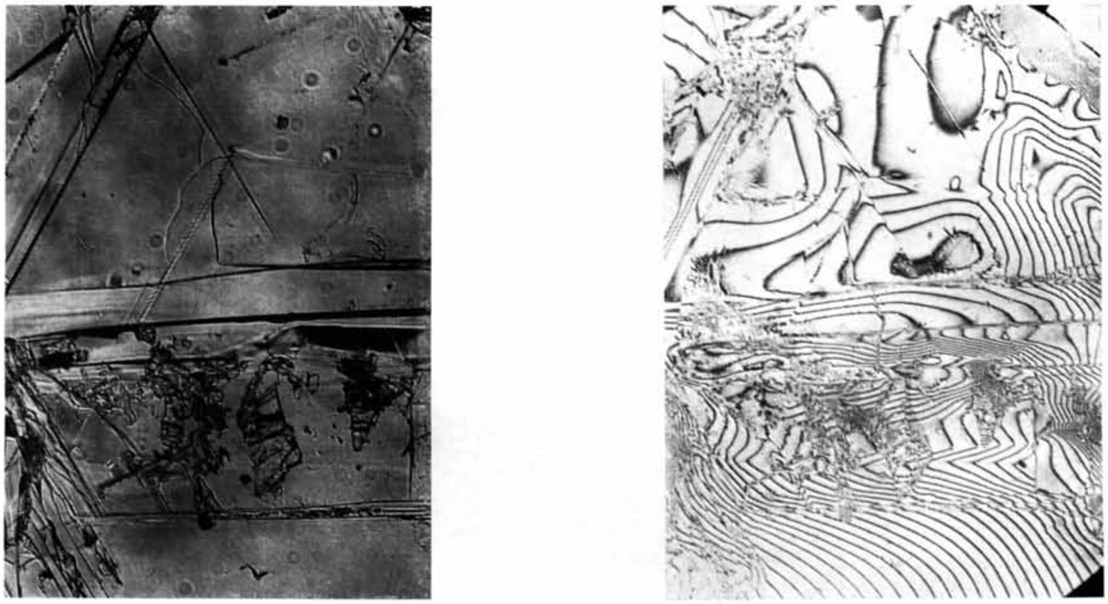
Observations

Fig. 1(*a*) represents a cleavage face of graphite in which the cleavage lines as well as the twin lines are clearly seen; the twin lines run in the $\langle 10\bar{1}0\rangle$ directions. The cleavage pattern is altogether different compared with the cleavage patterns as described by Zappfe & Worden (1949). The 'river' pattern usually observed on crystals cleaved by a gentle blow is completely missing. The cleavage pattern resembles more or less that of mica. Fig. 1(*b*) is a multiple beam interferogram, taken with the 5461 Å line of mercury, revealing the topography of the cleavage face of Fig. 1(*a*). Attention is drawn to the following:

(i) The complicated nature of the fringes indicates that the surface is very uneven.

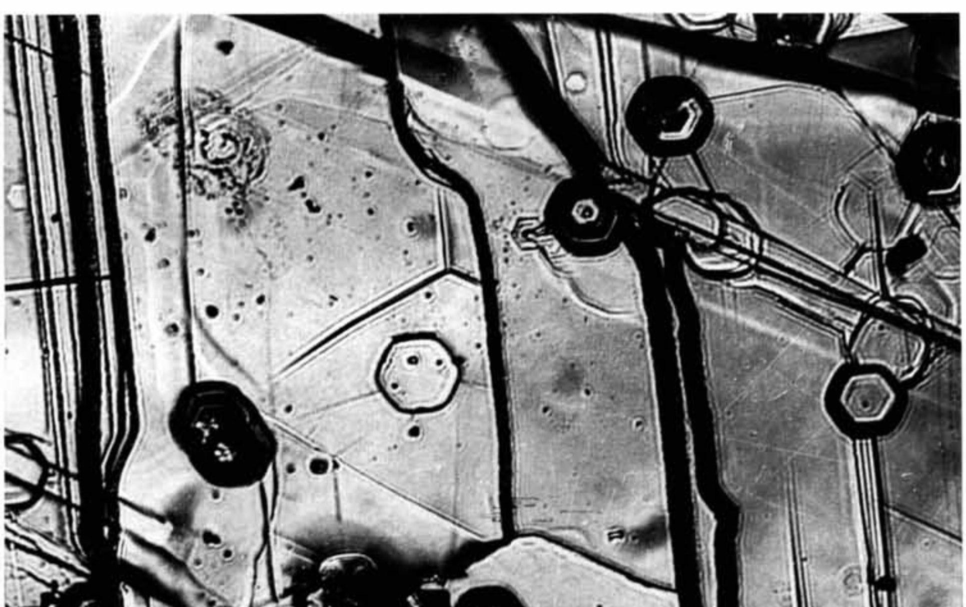
(ii) The surface contains hills and dales as in the case of mica.

(iii) Like mica the cleavage lines represent discontinuities in level.



(a) (b)

Fig. 1. (a) (0001) cleavage of graphite (× 140). (b) Multiple beam interferogram on (a) (× 140).



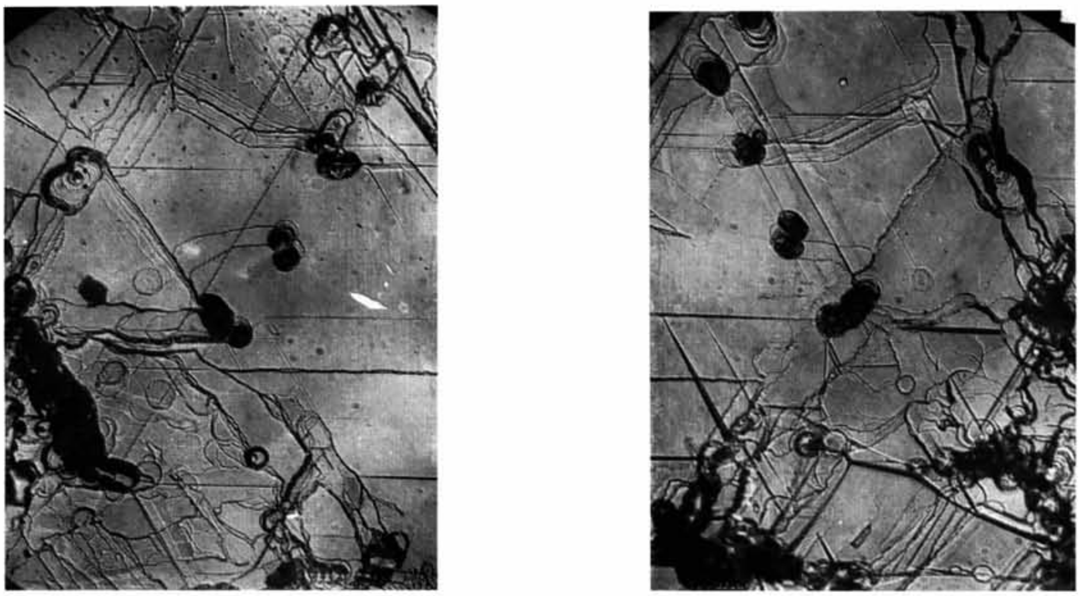
(a)

Fig. 2. Etch pattern on a graphite cleavage (× 480).

(a)

(b)

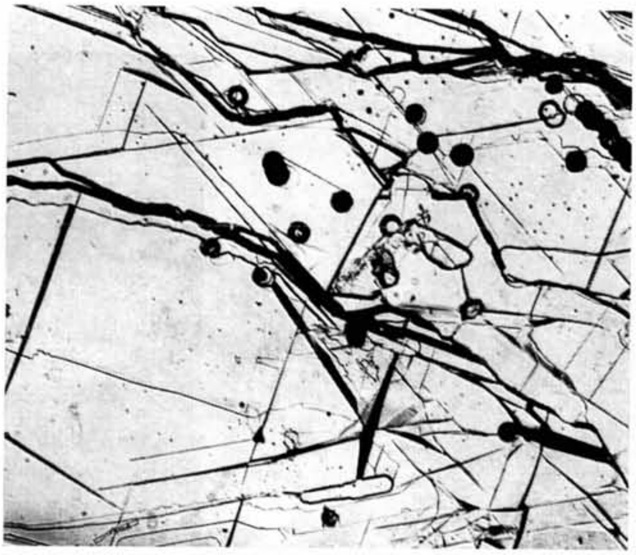
Fig. 3. (*a*) Etch pattern on another graphite cleavage (× 140). (*b*) Multiple beam interferogram on (*a*) (× 140).



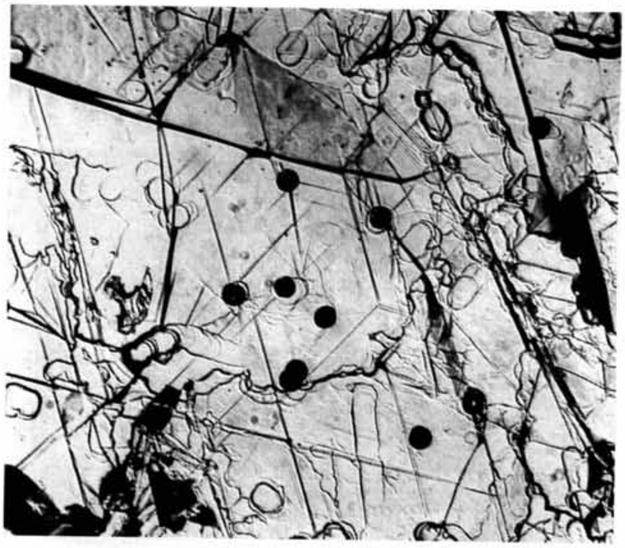
(*a*) (*b*)

Fig. 4. Etch patterns on matched cleavages of graphite (× 140).

Fig. 5. Multiple light profile running across the two pits of Fig. 4(*a*) (× 880).

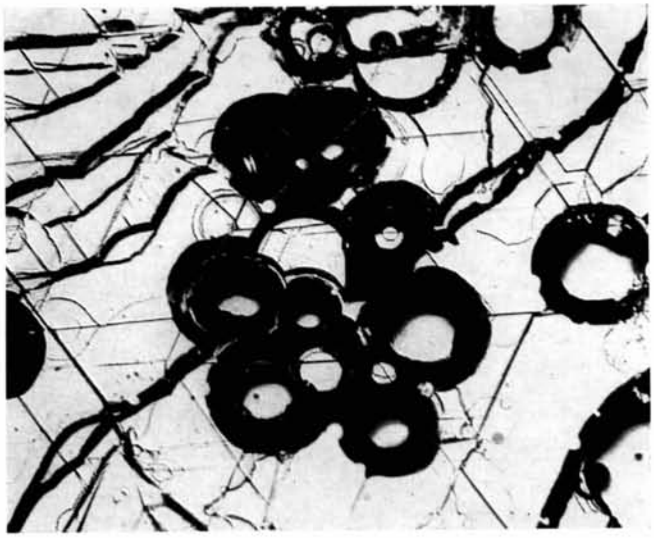


(a)

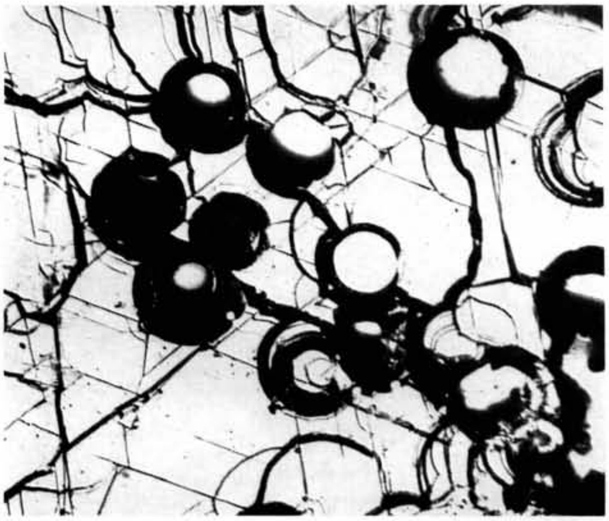


(b)

Fig. 6. Etch patterns on the two sides of a thin graphite flake (× 140).



(a)



(b)

Fig. 7. Etch patterns on the same regions of Fig. 6(*a*) and (*b*) respectively after further etching (× 140).

(iv) There exist areas between cleavage lines which are optically uniform.

(v) The fringes while crossing some twin lines sometimes indicate clear vertical steps.

Fig. 2 shows the typical etch pattern which is produced on a cleavage face of graphite by heating it in a potassium nitrate melt at 500 °C for two hours. Attention is drawn to the following features:

(1) The pits, as reported by Hughes & Thomas (1962), are hexagonal but they are perpendicular even though the etching temperature is 500 °C. According to Thomas, Hughes & Williams (1963), when etching is carried out in pure oxygen at a temperature below 800 °C the pits are always parallel.

(2) The pits are shallow as well as deep and point bottomed.

(3) The point bottoms of the point bottomed pits are not quite central, but they are asymmetric.

(4) The thick black lines running vertically downwards, which are the cleavage lines, appear to have been attacked by the etchant.

(5) Micropits and the stratigraphical pattern as reported by Patel & Tolansky (1957) on diamond are completely absent. The density of the pits has been calculated in many such samples and it is about 10^4 cm^{-2}.

Fig. 3(*a*) shows an etch pattern produced on another cleavage face by etching in a sodium peroxide melt at 360 °C for twenty minutes. Fig. 3(*b*) is a multiple beam interferogram, taken with the 5461 Å line of mercury, taken on the region of Fig. 3(*a*). The interferogram reveals that the etch pattern consists of shallow as well as deep pits. It further reveals that the dark looking pit of Fig. 3(*a*) is about 6 microns deep. The lower part of the interferogram reveals that the fringes in this region have some structure which indicates that the surface might have undergone a general dissolution, though the usual micropitting bringing about the general dissolution is not observed.

Fig. 4(*a*) and (*b*) shows the etch patterns on two matched cleavage faces etched simultaneously at 360 °C for half an hour. The etch patterns on both the faces consist, as usual, of some black looking deeper pits and some flat bottomed shallow pits. There is one to one correspondence in the position and numbering of black looking pits, but no such correspondence exists in the case of flat bottomed shallow pits.

Fig. 5 is a magnification of the region of the black pits of Fig. 4(*a*) in which a multiple light profile is running across the pits revealing the depths of the pits. The calculations made from the light profile show that the pit on the right hand side is 7 microns deep.

During the etching experiments on thin flakes of graphite it was observed that at a few places the etching was so rapid that holes were formed instead of pits. In order to investigate (*a*) how far the dislocation lines, whose terminations on the cleavage faces become the sites of preferential attack, penetrate into the body of the crystal and (*b*) why the holes are formed only at a few isolated sites of the pits, a thin flake of graphite, 0·3 mm thick, was etched in a sodium peroxide melt. The etch patterns produced on both sides of the cleavage flake were optically examined. Thus Fig. 6(*a*) and (*b*) represents the etch patterns on the two sides of the thin flake. A careful study reveals that there is quite a considerable amount of correlation in the number and position of the etch pits on the two sides. The same cleavage flake was further etched, for 50 minutes more at 360 °C, till some holes were formed at some places. The etch patterns on the two sides were again recorded. Thus Fig. 7(*a*) and (*b*) shows the photomicrographs of the same regions of Fig. 6(*a*) and (*b*) respectively produced after further etching.

If the position of the holes in Fig. 7(*a*) and (*b*) is carefully compared with the position of the etch pits in Fig. 6(*a*) and (*b*) respectively, it is clearly revealed that the holes are formed only at the positions of those pits of Fig. 6(*a*) and (*b*) which had correlation on the two sides. The explanation of the formation of the holes is now clear. It may be conjectured, as reported by Patel & Ramanathan (1962) in the case of mica, that dislocation lines exist in the body of the graphite. When the crystal is cleaved these dislocation lines are cut by the cleavages leaving their terminations on the cleavage faces. Some of the dislocation lines might terminate on the two faces of a thin graphite flake. When such flakes are etched, pits will be produced at the sites of the termination of dislocation lines, thus producing the correlation in the etch pits on the two sides. Wherever there is correlation the etch attack at these places starts from both the sides, thus producing the holes earlier at these sites, as observed, in comparison with other places.

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