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Defects in Silicon Carbide

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Defects in various forms of SiC, both single crystal and polycrystalline, have been examined using transmission electron microscopy. Dislocations were not as common as stacking faults, which were observed in all materials examined. The mechanism of formation of stacking faults is discussed and two types of both intrinsic and extrinsic faults are shown possible. The stacking-fault energy of SiC was measured to be 1.9 ergs/cm^2 by the extended node method.

1. Introduction
Silicon carbide is of interest in several fields of science and technology due to a combination of useful properties. All forms of the material are extremely hard ($H_V \simeq 2600$), chemically stable and have a low neutron absorption cross section, making it attractive for use in nuclear reactor cores. In the form of single crystals the material is a high temperature semiconductor. Certain of the above properties are dependent on the microstructure and hence on any defects present. It has been the subject of several crystallographic investigations due to the numerous complex polytypic structures [1, 2], and to the symmetry and clarity of growth spirals present on the surface of selected single crystals [2, 3]. Similarly, defects in the form of stacking faults [4] and dislocations [3, 5-7] have been observed by etching low index surface planes of SiC. The etchants and techniques employed have been summarised by Jennings [8].

Direct observation of defects in SiC single crystals have been made by decoration of dislocations with a copper precipitate [9], by X-ray topography [10], by transmission electron microscopy of fracture chips [11, 12] and thin foils prepared chemically or by ion sputtering [13, 14]. Such observations have been limited either by the experimental method or the material, and it is the purpose of this paper to describe further observations made mainly on hot-pressed silicon carbide.

2. Experimental Techniques
Fine powders (<1 to 30 μm) of silicon carbide were vacuum hot-pressed in a graphite mould to pressures in excess of 400 kg/cm^2 and temperatures greater than 2500 K. By this means blocks of theoretical density polycrystalline SiC 2.5 $\times$ 0.6 cm square could be manufactured. A more detailed account of the equipment and processes involved is given elsewhere [15].

Discs 3 mm in diameter were trepanned ultrasonically from the larger block and diamond ground to a thickness of 0.012 cm. Further thinning was accomplished by means of a commercially available argon ion bombardment apparatus. A description of similar equipment and the variables involved in the thinning process is available [16]. Using the methods described, areas of thin foil suitable for transmission electron microscopy (TEM) could be reproduced with a satisfactory success rate. In addition to the hot-pressed material thin foils were made from commercially produced self bonded SiC, and from different purity α single crystals. Examination of the foils was carried out in a Phillips EM 300 at 100 kV in a specimen stage having a $\pm$ 6° tilt along one axis.

3. Results and Discussion
3.1. Dislocations
The most striking feature in all foils examined using TEM was the scarcity of dislocations. However, defects were nearly always present in the foils in the form of stacking faults and on occasions, twins. Several specimens were prepared from basally oriented α single crystals and a single dislocation observed on only one occasion. Etch pit studies on α SiC single crystals have been confined mainly to examination of defects intersecting the basal plane. Combined with the low dislocation density of

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the single crystals (10^2 to 10^5 cm^{-2}) and the fact that the projection of the dislocations on to the basal plane, as would be the case with a basal foil, is small, then the result is not entirely unexpected.

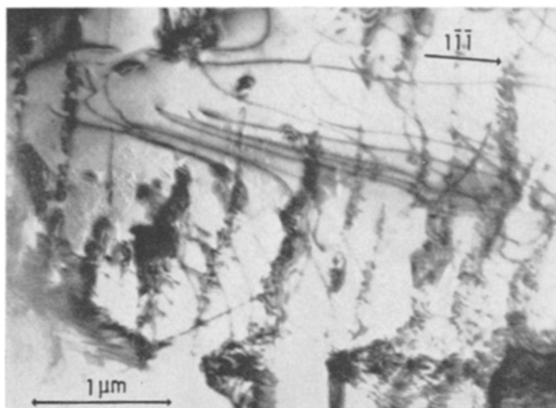

Figure 1 A grown-in network of dislocations in a fracture chip of SiC. The chip was taken from the fracture surface of a self-bonded SiC.

Examination of fracture chips of SiC using TEM [11, 12] revealed the presence of artificially introduced dislocations. In a very few instances, grown-in dislocations were observed in this type of specimen. A net of grown-in dislocations is shown in fig. 1, the array probably being part of a sub-boundary. Because of the non-uniform thickness and the small area of the fracture chips, extensive investigation is not possible. The irregular dark bands in the micrograph are due to variations in thickness of the foil caused by branching of the fracture path. Also of interest in the micrograph are the dislocation nodes, which appear to be extended, indicative of the relatively low stacking-fault energy of silicon carbide.

Dislocations introduced by movement of a crack front during fracture have been discussed earlier [11, 12]. However, it is doubtful whether such configurations can be considered typical or even similar to dislocations that might be present in unfractured material. For this reason hot-pressed SiC thin foils were prepared. Since manufacture of the hot-pressed silicon carbide involved temperatures in excess of 2500 K and pressures up to 420 kg/cm^2, dislocations present could be considered to be "fresh" and because of the high temperatures involved, to be in a stable configuration.

Although manufacture of the hot-pressed material involved extreme temperatures and pressures, dislocations were still uncommon in the foils. Evidence obtained during deformation studies of polycrystalline SiC [17, 18] indicated that grain-boundary diffusion procesess were rate controlling at temperatures up to 2450 K and pressures of 30000 psi. Together with the TEM observations this would suggest that generation and movement of dislocations in silicon carbide is difficult even under the extreme experimental conditions employed in the present study.

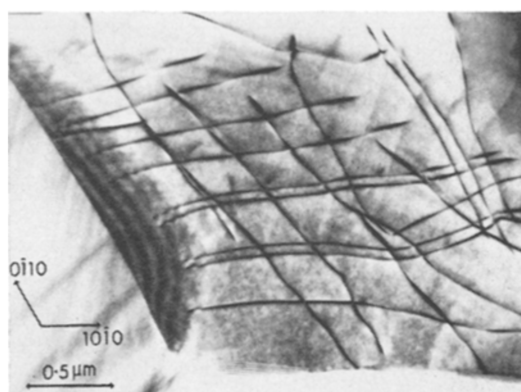

Figure 2 A network of dislocations lying in the basal plane of a grain of hot-pressed SiC.

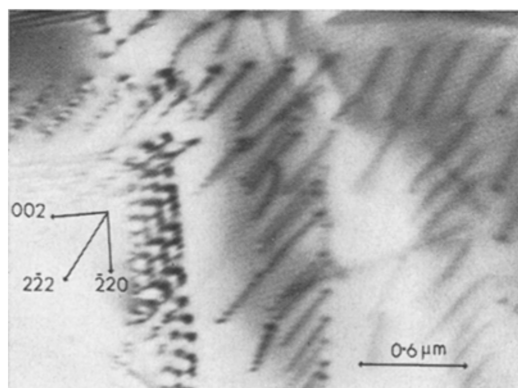

Figure 3 Simple arrays of dislocations forming a sub-boundary in a grain of hot-pressed SiC.

A network of dislocations in the basal plane is shown in fig. 2, the dislocations lying along $<10\bar{1}0>$ being anchored at a grain boundary. This type of dislocation would not normally

be visible on etched material although isolated dislocations have been reported [13]. Simple sub-boundary arrays of dislocations are shown in fig. 3. It is noticeable that the dislocations in both fig. 2 and fig. 3 lie along primary crystallographic directions, indicative of the high Peierls stress in SiC. In fig. 3, the sub-boundaries lie along primary directions, as is commonly observed in etch pit studies [3, 5]. The micrograph fig. 3, is indexed using cubic notation, although the hexagonal system could equally well be applied, since it is extremely difficult to distinguish between polytypes from electron diffraction patterns. Attempts have been made [19], and have been successful for simple polytypes in the form of basally oriented crystals.

The absence of dislocations in most of the foil is at first sight a puzzling feature. However, the nature of bonding between the silicon and carbon atoms is such that the bonds may be regarded as being stiff, strong, brittle and spatially directed [20]. Furthermore, in the sphalerite structure, the formation of all but one type of dislocation requires the presence of "dangling bonds" at the dislocation core[21]. Any movment of dislocations requires the breaking of bonds. Thus, the generation and movement of dislocations would be expected to be difficult, as is generally observed to be the case [17, 18] except in unusual circumstances [11, 12].

3.2. Stacking Faults

Stacking faults in the sphalerite and diamond cubic structures are closely related to those in the simpler fcc lattice, and have been discussed in some detail [20, 21] from a theoretical viewpoint.

In the fcc lattice the position in space of the close packed {111} planes can be represented by the series ABC ABC . . . . In the diamond cubic (a), or sphalerite lattice (b), pairs of like (a) and unlike (b) atoms in the [111] direction follow the same pattern as the single atoms in the fcc structure. Thus we have the sequence:

$$A\alpha B\beta C\gamma \; A\alpha B\beta C\gamma$$

where A and α represent the first layers of different atoms. Stacking faults can then be generated by removing or introducing a close packed layer. Thus we have:

$$A\alpha B\beta C\gamma \;\vdots\; B\beta C\gamma \;\vdots\; A\alpha \quad \text{intrinsic}$$
$$A\alpha B\beta C\gamma \;\vdots\; B\beta \;\vdots\; A\alpha B\beta C\gamma \quad \text{extrinsic}$$

The faults are shown in figs. 4 and 5, when the faulted structures with the bonds intact are indicated by the full lines. As can be readily seen, such a structure is heavily strained. The strain introduced by the stacking fault can be accommodated by a suitable movement of atoms to a position where the bonds are unstrained, as is indicated by the dotted lines in the diagrams (figs. 4 and 5).

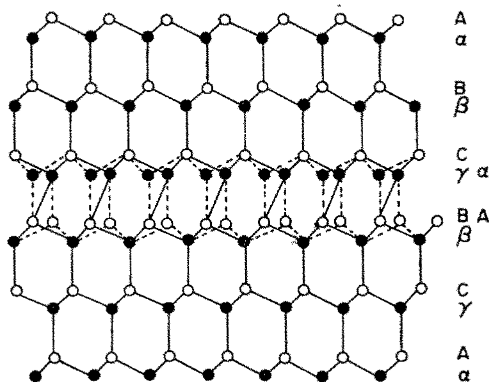

Figure 4 Projection of a {110} plane of β-SiC showing an intrinsic stacking fault in the {111} planes. The dotted lines show the two possible movements of the atoms and bonds to form an unstrained structure.

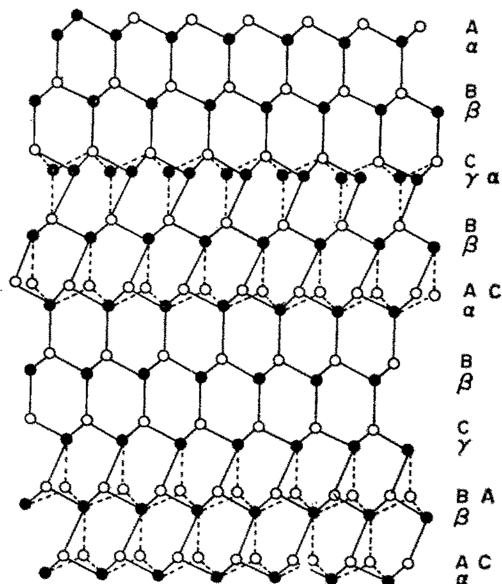

Figure 5 Projection of a {110} plane of β-SiC showing an extrinsic stacking fault. For the extrinsic fault two readjustments of the atoms and bonds are required to produce an unstrained structure.

The rearrangements of the stacking sequence for the region containing the faults is now:
Intrinsic
(i) $A\alpha B\beta C\gamma/\alpha B\beta C\gamma A\alpha$
(ii) $A\alpha B\beta C\gamma A/\beta C\gamma A\alpha$

Extrinsic
(i) $A\alpha B\beta C/\alpha B\beta C/\alpha B\beta C\gamma$
(ii) $A\alpha B\beta C\gamma A/\beta C/\alpha B\beta C\gamma$

The lines in the alphabetic sequence represent the position of a stacking fault violation. It is apparent from the diagrams that whereas only one shear movement is required to form an intrinsic fault, two are necessary for an extrinsic fault. In addition the constraint can be accommodated by two different stacking fault sequences in each case. For the intrinsic stacking fault, the bonds may become relaxed by movement of the γ sites to the α sites or secondly by B to A. Similar operations can be applied to the extrinsic fault with the exception that two operations are necessary to form the fault. The necessary rearrangement can be brought about by movement of Shockley partial dislocations, the process having been discussed for the case of the diamond lattice by Hornstra [20].

In the present investigations stacking faults were present in nearly all materials examined, the exception being a semiconductor grade single crystal. Stacking faults present in the hot-pressed SiC carbide are shown in figs. 6 and 7, illustrating the appearance of the most common faults. In fig. 6, a regular series of stacking faults can be seen traversing the grain. Such faults traversing a whole grain were extremely common. However, in this particular case, an unusual feature of the faults was their equal spacing, 750Å apart. All other faults traversing a grain were situated in a random fashion from each other. Also present in the material were many faults which terminated within the grain (fig. 7), the terminal position of the fault being the location of a partial dislocation.

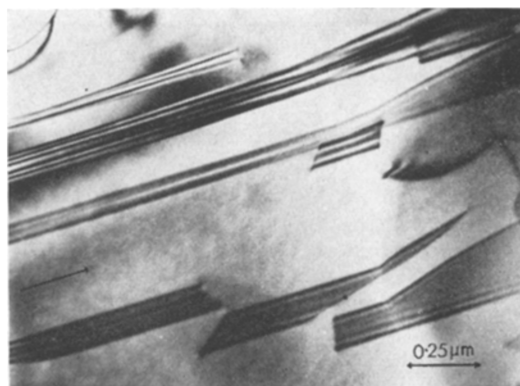

Figure 7 Stacking faults in hot-pressed SiC terminating within a grain.

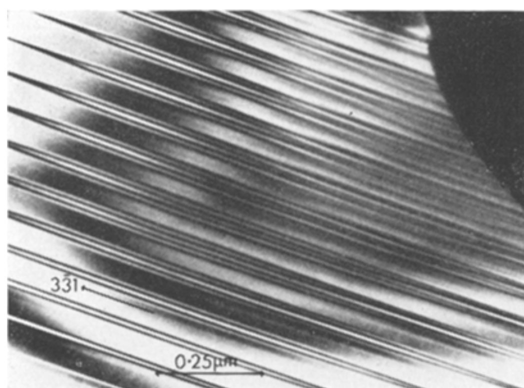

Figure 6 Regularly spaced stacking faults in hot-pressed SiC.

Growth faults have been analysed in some detail in whiskers of β SiC by Van Torne [22], who considered them to be microtwins on {111} planes, the microtwins consisting of a minimum of five {111} layers of silicon-carbon atoms. For this case there is a somewhat different configuration of the stacking sequence. Generation of stacking faults was shown to have occurred during the fracture process [12] together with the corresponding partial dislocations. In the present case, because of the history of the materials it is not possible to distinguish between the "stress-induced" stacking fault or the "grown-in" fault.

3.3. Stacking Fault Energy

The abundance of stacking faults and the numerous polytypes [2] known to exist in silicon carbide indicate an extremely low value of the stacking-fault energy [1]. An early attempt at measuring the stacking-fault energy of single crystal SiC gave a value of 4 ergs/cm^2. However, the method used, that of equating the energy of an area of stacking fault produced by elastic separation of the two partial dislocations is inaccurate, especially in the case of a material such as SiC having a high Peierls force, and requiring breaking of bonds for dislocation movement. In the present work such a

technique could have yielded values of stacking fault energy over a range of two orders of magnitude.

Griffiths [23], in a study of polytypism of SiC suggested that the stacking-fault energy was temperature dependent and since certain polytypes were preferentially nucleated over specific temperature ranges, this would suggest the stacking fault energy to be dependent on structure. Measurements gave a value of the stacking-fault energy for $6H$ material as 9 ergs/cm^2 whereas a β (cubic) single crystal gave a value of 13 ergs/cm^2.

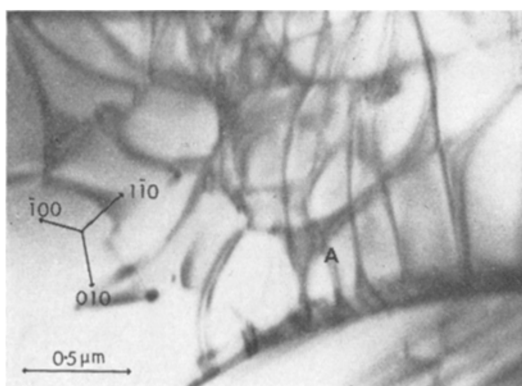

Figure 8 Extended dislocation nodes in hot-pressed SiC, with the stacking fault in contrast.

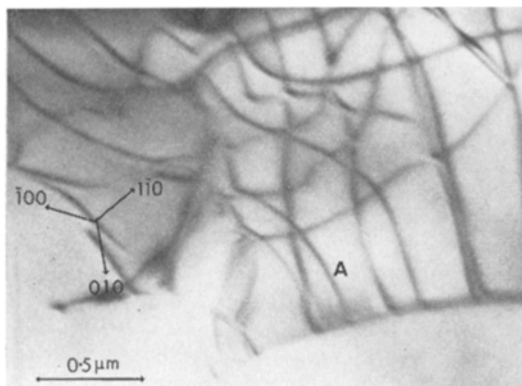

Figure 9 Same area as fig. 8 with the partial dislocations bounding the stacking faults in contrast.

Dissociated tri-point dislocation nodes were occasionally observed in the present investigation. Typical nodes are shown in fig. 8 with the stacking faults in contrast. Certain of the corresponding partial dislocations bounding the stacking fault are shown in fig. 9. Values of the stacking-fault energy computed from measurements of dislocation node widths of hot-pressed SiC gave a mean value of 1.9 ergs/cm^2 with a standard deviation 0.25 erg/cm^2 for ten measurements. Although this value is considerably lower then previously reported, the results are not necessarily inconsistent, since stacking-fault energy values are known to be extremely sensitive to material purity [24].

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References

1. A. R. VERMA and P. KRISHNA, "Polymorphism and Polytypism in crystals" (J. Wiley and Sons, New York, 1966).
2. P. T. B. SHAFFER, *Acta Cryst.* **B25** (1969) 477.
3. S. AMELYNCKX and G. STRUMANE, "Silicon Carbide" (Pergamon Press Ltd, New York, 1960) p. 162.
4. W. K. LEIBMANN, *J. Electrochem. Soc.* **111** (1964) 885.
5. S. AMELYNCKX and G. STRUMANE, *J. Appl. Phys.* **31** (1960) 1359.
6. F. HORN, *Phil. Mag.* **43** (1952) 1210.
7. I. N. FRANSEVITCH and V. A. KRAVETS, "Silicon Carbide" (Consultants Bureau, New York, 1970), p. 13.
8. V. J. JENNINGS, *Mat. Res. Bull.* **4** (1969) S 199.
9. E. A. TRICKETT and L. B. GRIFFITHS, *J. Appl. Phys.* **35** (1964) 3618.
10. R. W. BARTLETT and G. W. MARTIN, *ibid* **39** (1968), 2324.
11. R. STEVENS, *J. Mater. Sci.* **5** (1970) 474.
12. *Idem, ibid* **6** (1971) 324.
13. T. GABOR and R. STICKLER, *Nature* **199** (1963) 1054.
14. C. M. DRUM, *Phys. Stat. Sol.* **9** (1965) 635.
15. Y. BALLOFFET, E. PHILLIPS, and F. HUGHES, Atomic Energy of Canada Ltd, AECL 3673 March 1971.
16. D. J. BARBER, *J. Mater. Sci.* **5** (1970) 1.
17. P. L. FARNSWORTH and R. L. COBLE, *J. Amer. Ceram. Soc.* **49** (1966) 264.
18. T. L. FRANCIS and R. L. COBLE, *ibid* **51** (1968) 115.
19. D. L. GIBBON, Proceedings of the Electron Microscopy Society of N. America, 1970.
20. J. HORNSTRA, *J. Phys. Chem. Solids* **5** (1958) 129.
21. D. B. HOLT, *ibid* **23** (1962) 1353.
22. L. I. VAN TORNE, *J. Appl. Phys.* **37** (1966) 1849.
23. L. B. GRIFFITHS, *J. Phys. Chem. Solids* **27** (1966) 25.
24. A. W. RUFF JUN, *Metall. Trans.* **1** (1970) 2391.

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