Microstructural Studies of Fluidized-Bed $\beta$-Silicon Carbide

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The fluidized-bed vapour phase deposition of $\beta$-SiC on nuclear fuel granules can produce polygonal crystals. The examination of these and their etch figures by scanning electron microscopy indicates an internal structure composed of {111} planar sheets. The disposition of these sheets is discussed with the aid of three-dimensional models. It is concluded that a maximum of four sheet orientations can occur. From these, six families of sheet pairs can be made by appropriate combinations; these are labelled according to the [110] directions of the spines created by their intersections. The sheets produce traces on the external crystal faces, and the various possible juxtapositions of these traces are discussed.

1. Introduction

The fluidized-bed vapour phase deposition of $\beta$ silicon carbide has been developed in connexion with SiC-coated nuclear fuel particles (Ford, Hibbert, Ingleby & Walker, 1968). Extensive experimental work has established the optimum conditions for obtaining high-density pure $\beta$-SiC (Ford, Walker & Ferguson, 1972).

Previous structural studies of pyrolytic $\beta$-SiC have concentrated upon ceramographic polished sections (Cochran & Knipping, 1968; Gyamarti & Hoven, 1970; Walker, 1967) but these can be misleading (Walker, 1972). Moreover, conventional X-ray methods of determining orientation are inappropriate for small polycrystalline spherical particles (1 mm diameter).

Using a hydrogen/methyltrichlorosilane gas mixture at 1500°C, and maintaining other parameters constant, the microstructure of SiC varies with the coating rate (Walker, 1967, 1972). Fast coating rates produce irregular crystals on the surface, while at slow rates these crystals approximate to regular polyhedra.

The latter type of crystal is considered here, and the microstructural implications of etch figures and scanning electron microscopy are discussed.

2. Experimental

2.1. Deposition of SiC

A mixture of methyltrichlorosilane vapour and hydrogen was led into a 38 mm diameter fluidized bed containing 14 ml of 0.5 mm diameter spherical uranium monocarbide particles, at 1500°C. The SiC deposition rate was $\sim 40$ g h$^{-1}$.

Experimental evidence shows that deposition occurs by a vapour–liquid–solid mechanism, so that a liquid silicon film is maintained on the growing crystal (Ford, Walker & Ferguson, 1972).

2.2. Sample preparation

Coated particles were etched in molten NaOH at 500°C for $\sim 20$ min. The alkaline residue was removed by washing in hot water and in hot concentrated nitric acid. Coated particles were examined in a Cambridge Stereoscan (SEM) Type IIa in a secondary emission mode, with 20 kV acceleration voltage.

3. Basic considerations

$\beta$-SiC belongs to the non-centrosymmetric cubic space group $F43m$ which favours the tetrahedral habit and in which the frequency of occurrence of the crystal faces is predicted to occur in the descending order: {111}, {100}, {110}, {113} (Donnay & Harker, 1937).

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Fig. 1. Doubly truncated tetrahedron crystal displaying {111}, {111}, {100}.

Fig. 2. Truncated octahedron crystal displaying {111}, {111}, {100}.

Fig. 3. Truncated polygonal $\beta$-SiC crystal displaying {111}, {111}, {100}, {113}.
Moreover, the non-centrosymmetric nature of the crystal produces so-called 'positive' and 'negative' tetrahedra, (Phillips, 1963) so that an ideal crystal would be a doubly truncated tetrahedron with \{111\}, \{\bar{1}\bar{1}\} and \{100\} faces (Fig. 1). The \{111\} and \{\bar{1}\bar{1}\} faces are each populated by one sort of atom, i.e. Si or C respectively.

\[\text{Fig. 4. External surface of slow-coated } \beta\text{-SiC (} \times 700).\]

\[\text{Fig. 5. Polygonal SiC crystal (etched). Same coat as Fig. 4 (} \times 2200).\]

\[\text{Fig. 6. Slow-coated SiC crystal (etched) displaying } \{111\}, \{1\bar{1}\}, \{100\} \text{ and } \{113\} (\times 1830).\]

This crystal habit occurs for many mineralogical specimens of the \emph{F43m} group, e.g. sphalerite, ZnS (Becke, 1883), which exhibits size differences between the \{111\} and \{\bar{1}\bar{1}\} faces. These sizes are more nearly equal in \(\beta\)-SiC however, owing, it is suggested, to the increased covalency of the bonding relative to ZnS. In the extreme case, equally sized \{111\} and \{\bar{1}\bar{1}\} faces make the \{100\} face square, to give a truncated octahedron (Fig. 2) – a shape generally associated with the more symmetrical \(m\,\text{m}\,\text{m}\) class. However, the inherent \(4\,\text{m}\,\text{m}\) symmetry of \(\beta\)-SiC can be recognised from the presence of \{113\} but not \{1\bar{1}3\} faces, as well as the different chemical nature of the \{111\} and \{\bar{1}\bar{1}\} faces (Fig. 3) (Thibault, 1944; Wolff, 1967). These authors noted the absence of \{110\} faces on \(\beta\)-SiC crystals.

Etching also reveals the non-centrosymmetry of \(\beta\)-SiC. The \{111\} faces give threefold symmetrical etch pits as expected, but the \{1\bar{1}1\} faces suffer unpredictable nondescript surface attack (Faust, 1962).

\[\text{4. Results and discussion}\]

An area of pyrolytic \(\beta\)-SiC crystals is shown in Fig. 4. Identification of the side faces is difficult because they are masked by adjacent crystals, and so one must study selected crystals.

The etched crystal in Fig. 5 displays triangular etch-pit symmetry and so, conventionally for SiC it will be referred to here as a \{111\} face. Since it etches readily, it plausibly consists of Si atoms, and such faces will be referred to here as 'Si faces'. On these faces, etch pits are arranged either singly or run together into grooves.
The grooves lie in the \langle 110 \rangle directions, but their disposition does not markedly display threefold symmetry — i.e., two directions are usually more prominent than the third, as is discussed below.

Related to the top surface grooves in Fig. 5 are ridges on the adjacent \{111\} carbon 'C' side face. A trellis-like pattern is formed by these ridges which lie in the \langle 101 \rangle and \langle 011 \rangle directions. The \langle 110 \rangle ridge is missing, however.

In Fig. 5 the ridges are interspersed with minute, ill-defined detail, but in general these trellises lie on a smooth dark background (Fig. 6). In the latter crystal, the \{113\} faces are present (see Fig. 7). Their appearance is rare on β-SiC prepared in a fluidized bed, and they usually occur as vicinal faces. By analogy with \{111\} above, the \{113\} faces in Fig. 6 are also composed of Si atoms. Concurrent with the grooves of the \{113\} vicinal faces are ridges on the \{111\} C face (see Fig. 7). In this particular crystal, the ridges are in the \langle 011 \rangle and \langle 101 \rangle, but not the \langle 110 \rangle direction (Fig. 7b).

In general, it is difficult to relate \{100\} etch figures to those on \{111\} because these faces etch at very different rates. Nevertheless, in Fig. 8, which shows them both, the \{100\} etch figures are grooves lying parallel to the \{100\} face edges (Fig. 9), although similarly oriented separate oblong pits can occur (Walker, 1972). The grooves on \{100\} and \{111\} have respectively two and threefold symmetries, and display different textural appearances. Thus the etched \{111\} faces are generally pock-marked between shallow grooves, while the smooth \{100\} faces are crossed by deep, straight grooves (Fig. 8). The \{100\} faces display, as expected, two mutually perpendicular sets of etched grooves (Fig. 8), one set being deeper than the other. It is likely that set 'a' (Fig. 8b) is the trace of \{111\} Si atom planes upon \{100\}, while set 'b' refers similarly to C atom planes.

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Fig. 7. (a) Labelled faces of crystal shown in Fig. 6. (b) Idealized diagram of the \{111\} C face of the crystal shown in (a). The face edges are labelled according to general type, but \{ \} brackets are omitted to assist clarity.

Fig. 8. Etch figures on a SiC crystal. (a) Full crystal (x 3800); (b) \{100\} face (x 15000).
The concurrence of \{111\} grooves with \{1\overline{1}\} ridges, as in Fig. 5, indicates the presence in the SiC crystal of intersecting planar sheets, which may be fine sets of polysynthetic twins on \{111\}. The geometrical behaviour of these sheets will now be discussed in terms of three-dimensional models (cf. Knippenberg, 1963).

Consider the disposition of such sheets within a truncated tetrahedron/octahedron crystal. This is best described by considering the 'spine' created at the intersection of the sheets. These spines point along the six \{1\overline{1}0\} directions, i.e. Fig. 10(a) \langle1\overline{1}0\rangle and \langle1\overline{1}0\rangle; Fig. 10(b) \langle10\overline{1}\rangle and \langle1\overline{1}0\rangle; Fig. 10(c) \langle011\rangle and \langle0\overline{1}1\rangle. Such spines are often seen in fracture sections (Ford, Walker & Ferguson, 1972; Walker, 1972).

The spines of the sheets when they impinge on the etched crystal faces (i.e. grooves and ridges) are significant. With only two internal sheets, the following traces are possible on adjacent \{111\} and \{1\overline{1}1\} faces: two silicon traces (2Si) associated with 1C (Figs. 10(a), (b), (c), 11(b), (c)); 1Si with 2C (Fig. 11(a), (b), (c)); 2Si with 2C (Figs. 10(a), (b), 11(b), (c)). Also 1Si and 1C is possible [Fig. 11(b), (c)], although here the two traces are parallel, and not adjacent, consequently each is associated with a different internal sheet.

When the two-sheet structure is viewed from an aspect perpendicular to a \{100\} face, i.e. along \{1\overline{1}0\}, six different sheet orientations are once again possible. In Fig. 11(a) the sheets produce one trace on each Si face, and these traces occur as two parallel lines tilting leftwards on either side of the square \{100\} face; a complementary pair tilts rightwards. In Fig. 11(b) the traces are on adjacent C and Si faces, and are oriented, with respect to the square \{100\} face, in a V-shape, its vertex pointing leftwards. A complementary one points to the right. In Fig. 11(c) is a similar structure, but the orientation is a vertical V while a complementary inverted V can also be constructed. V-shapes occur only in connexion with faces having two traces.

Similar comments apply for three internal sheets. In Fig. 12(a), 2 Si traces are associated with 2 C on the adjacent faces, whilst in Fig. 12(b), 3 Si and 2 C are associated. Clearly 2 Si and 3 C are similarly associated as in Fig. 12(a). In no case will only one trace appear on any face, nor will 3 Si and 3 C be seen adjacently.
When there are four internal sheets (Fig. 13), three traces occur on every adjacent face. This is the maximum possible number of different internal sheets; any further ones must be coplanar with the four illustrated. Thus the appearance of the traces is helpful in assessing the orientation of the crystals which comprise pyrolytic SiC. It is clear that the crystal in Fig. 5 cannot be described in terms of the models shown in Figs. 10 and 11, which rest on a (100) plane, but it is directly comparable with Fig. 12(b). Thus the top Si face etch grooves display threefold symmetry whilst the front C face ridges are twofold, and a three-sheet system exists within the crystal. (This applies to Figs. 6 and 7 also.) The crystal has therefore grown with (111) perpendicular to the substrate, as might have been anticipated for \(\beta\)-SiC since \(\{111\}\) is the close-packed plane.

Comparison of Figs. 5, 10(a) and 12(b) suggests initially that the C face surface traces of the sheets in Fig. 7 are orientated in the 'wrong' direction. However, this is because the observed surface traces will vary according to how the sheets intersect (Fig. 14). In Fig. 14(a) the crossover occurs at the \(\{111\}/\{11\}\) edge as in Fig. 10(a). The two internal sheets in the model are therefore regular hexagons, crossing on their centre lines and producing an inverted V trace on the C face. In Fig. 14(b) the crossover is on the \(\{11\}\) face, thus the sheets are irregular hexagons (the (100) sides being shorter than the \(\{111\}\) sides). The crossover position is to one side of their centre lines, and the trace on the C face is X-shaped – i.e. a combined V and inverted V. These remarks apply equally to the Si face.

In practice, V, inverted V and X traces may all be seen on a crystal face in varying degrees of importance. In Fig. 6 an inverted V predominates. In addition to ridges on the C faces, small rounded islands are seen, with no recognizable orientation (Fig. 6). The cause of these is thought to be due to the ends of internal spines impinging on the C faces.

It should be noted that although the sheets give \(\{110\}\) traces [e.g. on the Si face in Figs. 10(a) and 14(a), the traces are \(\langle11\rangle\) (right-hand side) and \(\langle11\rangle\) (left)], the actual growth direction of the sheets themselves are \(\langle112\rangle\) and \(\langle112\rangle\) respectively (Fig. 14).

In the present paper, consideration has been given only to SiC crystals possessing a simple polygonal appearance. Many fluid-bed crystals are externally twinned while others are grossly columnar, with dendritic skeletons, but as their examination involves sectioning of the SiC coated particles, they are discussed elsewhere (Walker, to be published).

5. Conclusions

SiC deposition in a fluidized bed at slow rates produces polygonal crystals. The identity of the faces of these crystals can be deduced by scanning electron microscopy after consideration of the faces theoretically predicted to be present.

The \{111\} faces and the \{11\} faces can be distinguished. The former give threefold etch pits and grooves and are described as Si faces, while the latter give ridges and are described as C faces. On the other hand, \{100\} faces give twofold pits or grooves, and \{113\} vicinal faces are sometimes seen. The disposition of the facial grooves and ridges is consistent with an internal structure of interpenetrating sheets. The sheets grow in \(\langle11\rangle\) directions and meet in spines, orientated in the \(\langle11\rangle\) directions, of which there are six families. A maximum of four different sheets is possible in a crystal; further sheets must lie parallel to those already present. The internal complexity of a given crystal varies with the number of sheets present and this affects the external etched appearance.

In a particular instance considered in detail, the \(\beta\)-SiC crystal has grown with \(\langle111\rangle\) parallel to the coating (radial) direction.

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