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Phase transformation ß→α in sintered SiC involving feathers formation

Part 1 *Microstructure*

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The $\beta \rightarrow \alpha$ phase transformation has been studied in SiC sintered with addition of boron and carbon by optical microscopy, and scanning and transmission electron microscopy. In the late stage of densification and during subsequent anneals, α feathers develop at the expense of the β grains. They are constituted of two adjacent grains whose crystalline structures are related to one another by four symmetry operations. From the orientation relationship it is shown that the feathers can be describe as penetration twins.

1. Introduction

It is well established that SiC crystallizes under numerous crystallographic structures called polytypes. In general, the rhombohedral or hexagonal polytypes (α phase) are more stable than the cubic one (β phase). This is true in particular under temperatures ranging from 2000 to 2200° C and pressures of inert gas inferior or equal to one atmosphere [1]. Under such conditions, which are precisely those of sintering (and hot pressing), cubic SiC undergoes a phase transformation, $\beta \rightarrow \alpha$. The microstructure and therefore the mechanical properties of the material are widely influenced by this phase transformation. In series of materials, Heuer and co-workers [2] show that the $\beta \rightarrow \alpha$ transformation occurs by nucleation and growth of α plates. This mechanism is nevertheless not always involved. Another one has sometimes been observed by the above mentioned authors in SiC conventionally sintered with addition of boron and carbon. Instead of α plates, "feathers" constituted of two adjacent α grains develop at the expense of the cubic ones. This formation of feathers has recently been observed by Bressiani [3] in SiC hot pressed after adding B_4C or BN. In order to understand the $\beta \rightarrow \alpha$ phase transformation in SiC, it has to be established when and how feathers are formed. This article deals with the structural characterization of the feathers, and the phase transformation mechanism will be studied in a subsequent paper.

2. Experimental methods

2.1. Materials

Two kinds of materials have been studied:

(a) as-received SiC†: it has been obtained by sintering of submicron powder of β SiC at 2080° C, using boron and carbon (approximately 0.5% of each) as aids; the material possesses a density of 97% of the theoretical density;

(b) annealed SiC: part of the as-received SiC was annealed 1 h at 2150° C either under vacuum or argon atmosphere.

2.2. Experimental techniques

1. Characterization of the grain size. Samples have been mechanically polished to 1 μm smoothness with diamond paste and then chemically etched. Murakami's reagent (10 g NaOH + 10 g $K_3Fe(CN)_6$ + 100 cm^3 H_2O at ebullition) and a fused salt mixture (90 g KOH + 10 G KNO_3 at 480° C) have been used. The samples have been observed thanks to optical microscopy and scanning electron microscopy.

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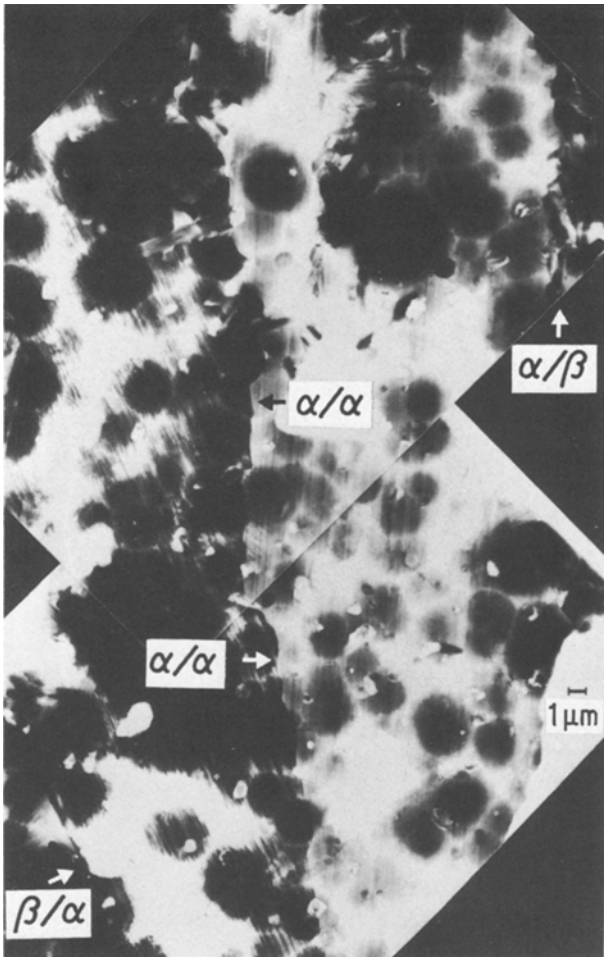


Figure 1 Bright field transmission micrograph of a feather observed in as-received SiC. It shows the faceted interface α/α, the precipitates included in the α phase, the interphase α/β (cf. arrows). The variation in the thickness of the sample is related to the necessary experimental procedure for the preparation of the specimens.

2. Characterization of the structure. The average amount of α phase has been evaluated by X-ray diffraction.

The volume fraction of the feathers has been estimated by measuring their surface fractions at different depths with a commercial image analyser. Their crystalline structure has been determined by means of transmission electron microscopy (TEM) at 200 keV. Due to the low density of the features in as-received SiC or to their tangling-up in annealed SiC, it was difficult to obtain both grains forming genuine feathers in the area transparent to the electron beam. Therefore, 2 mm thick specimens have been cut, polished and chemically etched. Using optical microscopy, the zone containing a feather was localized and the sample thinned by ion milling of the opposite side. Due to this necessary procedure, the thickness of the samples was even less uniform than usually observed in SiC (Fig. 1) and this has been a source of difficulties for the interpretation of TEM observations.

3. Results

3.1. Evidence of the phase transformation

The as-received SiC is composed of two types of grains (Fig. 2):

(i) More than 98% of β phase with an average grain size equal to a few microns (Figs. 2a and 3a). These grains contain stacking faults.

(ii) Less than 2% of feathers. They are formed of two α grains whose length can reach 100 μm. Each grain is composed of a stacking of plates parallel to the basal plane (Figs. 1, 3c). They contain a lot of small inclusions ($\phi \sim 0.5\,\mu$m) (Fig. 1) and some smaller α plates whose orientation differs from those of the grains (Fig. 3b).

Feathers formation occurs during sintering in the late stage of densification [1]. By subsequently annealing samples at a temperature of 2150° C

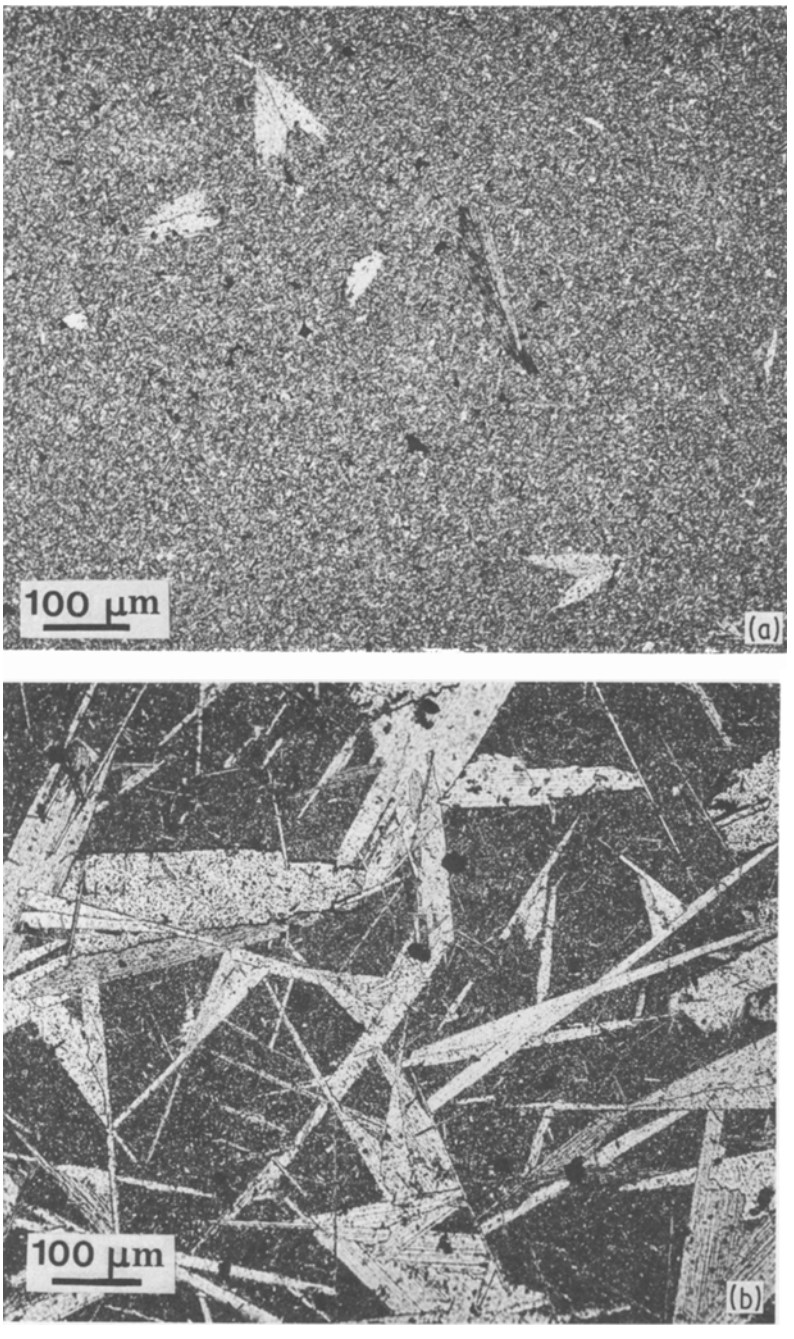
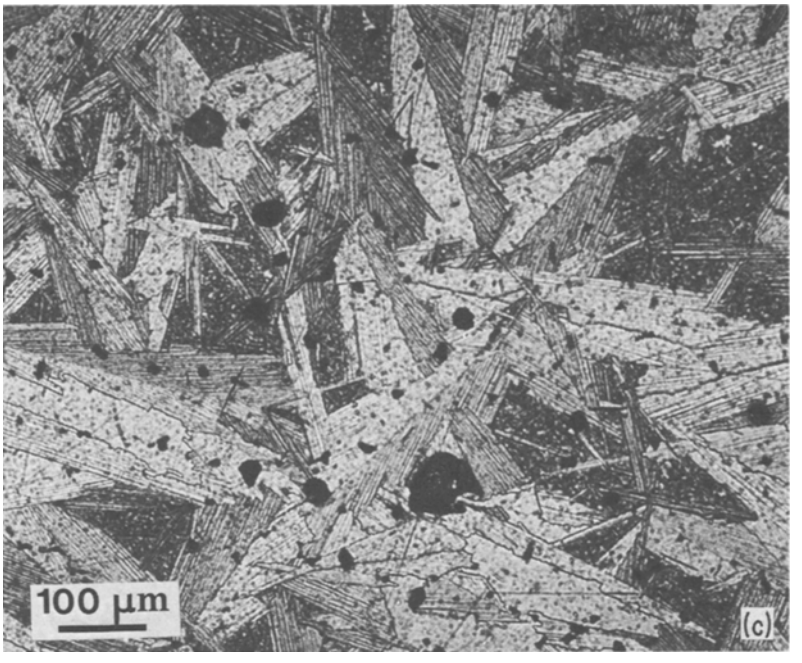


Figure 2 Optical micrographs of SiC sintered at 2080° C (a), annealed one hour at 2150° C under vacuum (b) or under argon atmosphere (c). The β phase is constituted by the small grains, the α phase by the feathers.

during one hour, the size and density of the feathers are increased (Figs. 2b and c). In the more heavily transformed material, the feathers may reach 200 or 300 μm (Fig. 2c); their growth has been limited by impingement. The kinetics of the transformation depends on the atmosphere during the anneal. The amount of feathers is about equal to 20% in SiC annealed under vacuum and to 80% in SiC annealed under argon atmosphere. This observation is in good agreement with results obtained by Stutz during a sintering study of SiC [4]. Comparison between the density of the feathers estimated by image analysis and the content of α SiC measured by X-ray diffraction shows that $\beta \rightarrow \alpha$ phase transformation generates mainly feathers formation.

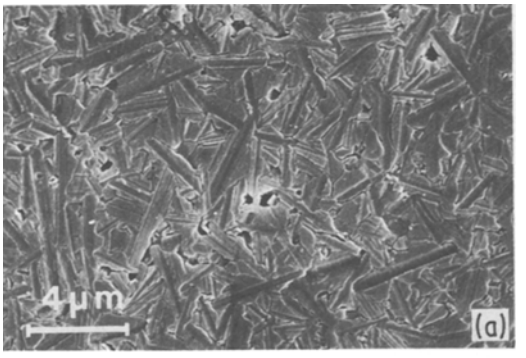
Figure 2 Continued.

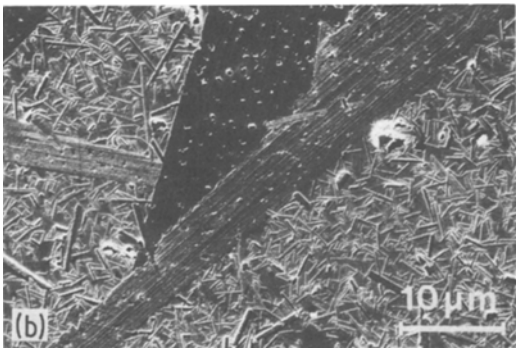


3.2. Crystalline structure of grains forming the feathers

Three feathers formed during the sintering and five feathers obtained during subsequent annealing under vacuum have been studied. Their crystalline structures have been determined from diffraction patterns. In all feathers, both grains are mainly constituted of the same polytype. These results confirm those found previously by Ogbuji *et al.* [2].

In seven of the feathers the crystalline structure of both grains is mainly 6H and in the other one 4H. Fig. 4 shows the stacking of 6H and 4H polytypes in a plane (1 1 $\bar{2}$ 0). As expressed by Ramsdell nomenclature [5], the structures 6H and 4H are hexagonal. Identical layers are stacked perpendicular to the hexagonal axis, the so-called *c*-axis. The periodicity of the stacking, here respectively 6 and 4, is characteristic of the





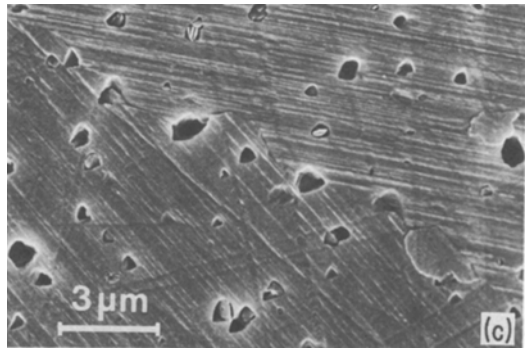


Figure 3 Scanning electron micrographs of annealed SiC etched by Murakami reagent and fused salt mixture: (a) cubic phase, (b) feather surrounded by β phase and some α plates, (c) detail of the interface α/α between the two grains forming a feather.

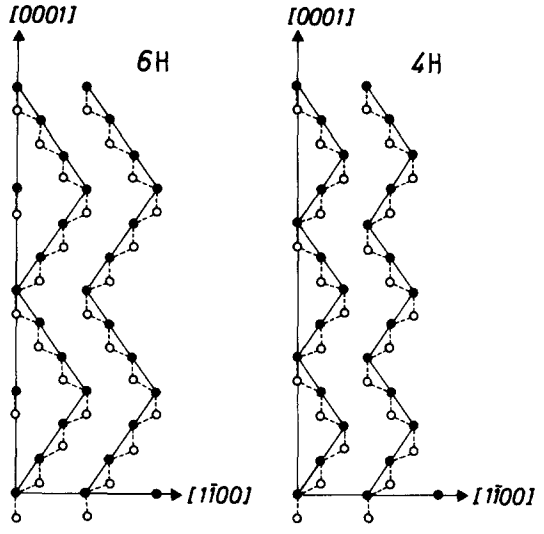


Figure 4 For 6H and 4H polytypes, packing of the silicon atoms (•) and carbon atoms (○) in (1 1 $\bar{2}$ 0).

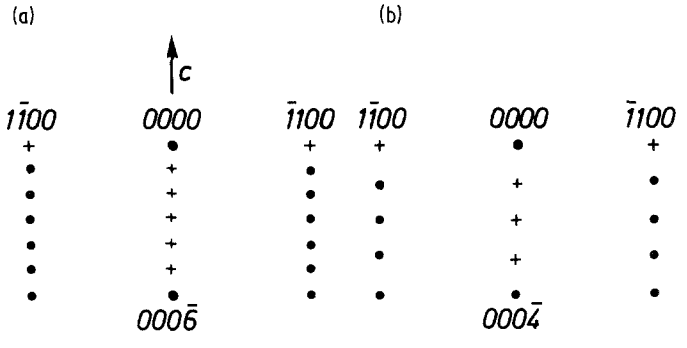
polytype. In what follows the {0 0 0 1} planes which defined the hexagonal cells, that is to say, every 6 or 4 layers perpendicular to the *c*-axis, are called basal planes. If the grains were formed of only one polytype, the [1 1 $\bar{2}$ 0] diffraction patterns would be identical to those represented graphically in Figs. 5a and b. Streaks observed along the *c*-axes indicate the presence of other polytypes, the percentage of these remaining small. In some areas, extra spots appear along the *c*-axes, as shown in Figs. 5d and f. In such areas, the grains are formed by the stacking perpendicularly to the *c*-axis of 6H and 4H layers, 6H being clearly predominant in Fig. 5d, and 4H in Fig. 5f.

3.3. Orientation relationship between the two branches of the feathers

In the eight feathers studied, the two grains have a [1 1 $\bar{2}$ 0] direction in common. This result has been found by Ogbuji *et al.* [2] in particular in a 15R feather. Therefore it seems to be independent of the structure of the predominant polytype.

The angle 2α between the axes C_1 and C_2 of the two grains has been measured using Kikuchi lines and the [1 1 $\bar{2}$ 0] diffraction pattern when possible (Figs. 6a and c). A value of $2\alpha = 64 \pm 0.3°$ has been obtained in the 4H feather. In 6H feathers, all the experimental measurements lie in the range $2\alpha = 41.3 \pm 0.5°$.

Fig. 6b represents the stereographic projection for the [*u v t w*) directions of grains 1 and 2



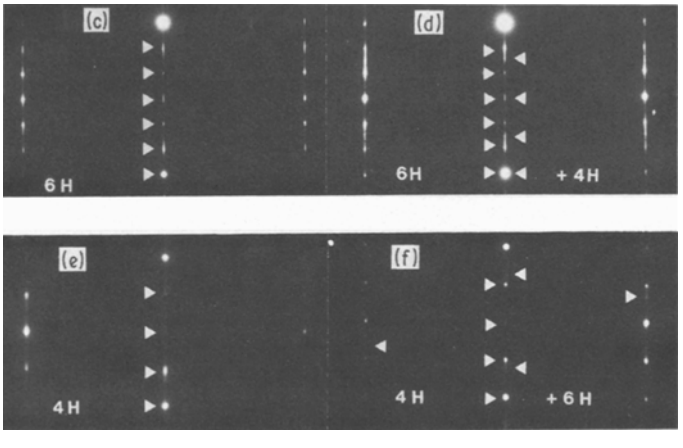


Figure 5 ⟨1 1 $\bar{2}$ 0⟩ electron diffraction patterns: (a) and (b) expected spots along the *C*-axes typical of 6H and 4H structures, (c) 6H phase containing stacking faults which induce streaks along the *C*-axis, (d) area of a 6H phase where 4H stacking faults are important enough to induce extra spots along the *C*-axis, (e) 4H phase with stacking faults, (f) area of 4H phase containing 6H stacking faults.

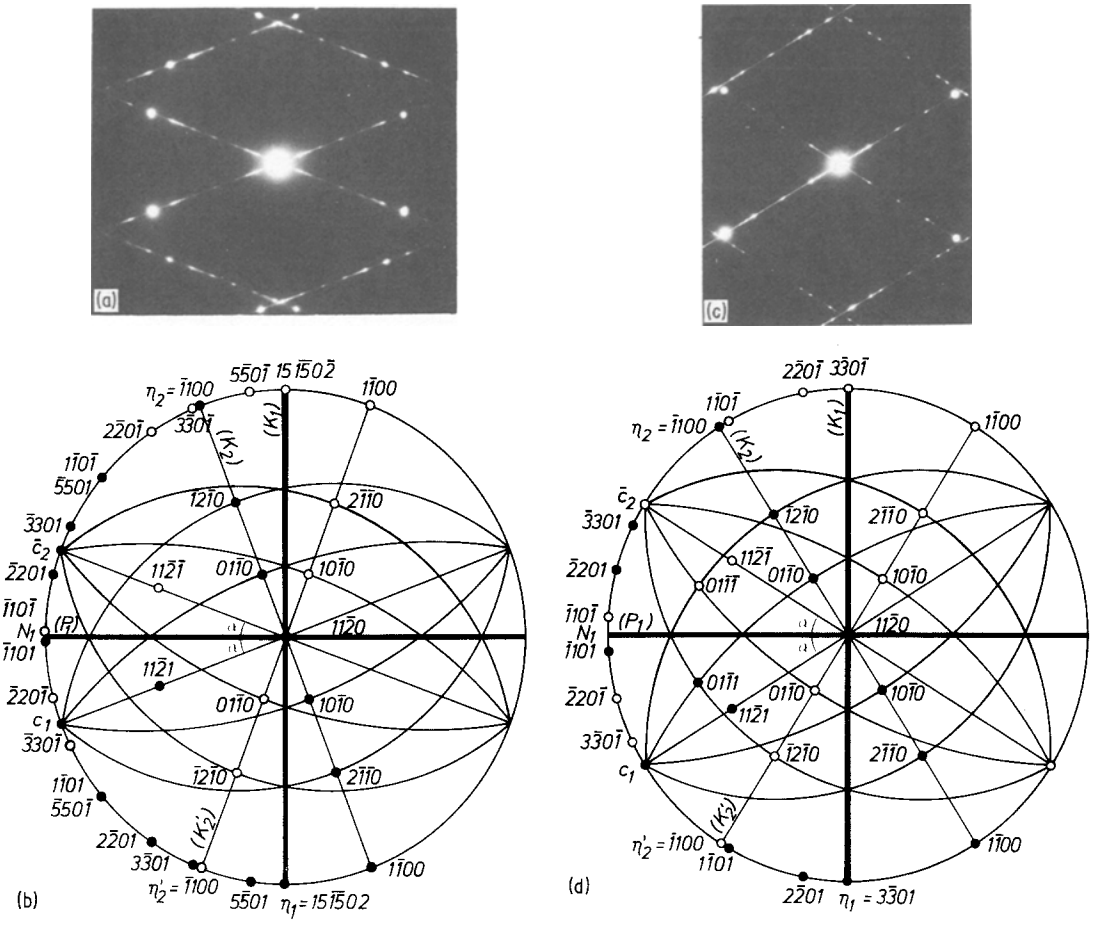


Figure 6 Orientation relationship between the two grains of the feathers: [1 1 $\bar{2}$ 0] diffraction patterns for 6H (a) and 4H (c) feathers. Stereographic projection of directions $[u\ v\ t\ w]_1$ (•) and $[u\ v\ t\ w]_2$ (○) for 6H (b) and 4H (d) feathers.

forming a 6H feather in their common (1 1 $\bar{2}$ 0) plane. It shows that crystal 1 can be deduced from crystal 2 by one of the following operations of symmetry:

(a) symmetry across the plane K_1,

(b) symmetry across the plane P_1,

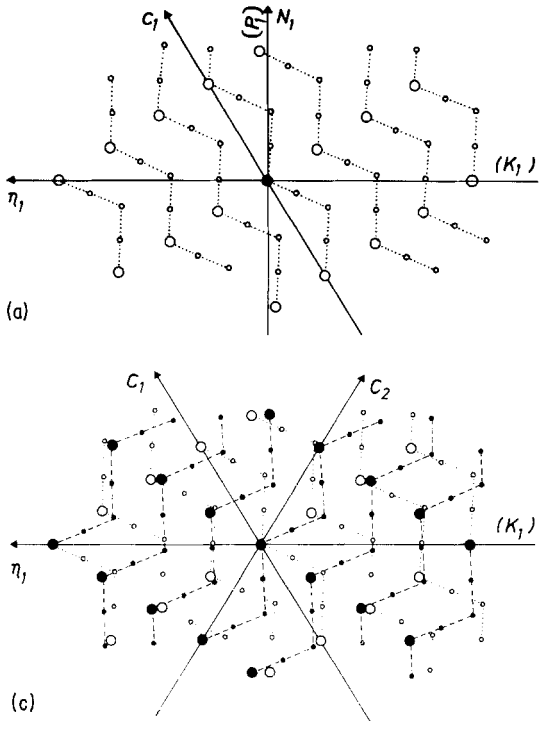
(c) rotation of Π about the axis η_1,

(d) rotation of Π about the axis N_1.

The three planes K_1, P_1 and (1 1 $\bar{2}$ 0) are perpendicular. K_1 and P_1 intersect along [1 1 $\bar{2}$ 0], K_1 and (1 1 $\bar{2}$ 0) along η_1, P_1 and (1 1 $\bar{2}$ 0) along N_1. Whereas $P_1 = (15\ \bar{15}\ 0\ 32)$ and $N_1 = [\bar{16}\ 16\ 0\ 15]$ have not low indices, $K_1 = (\bar{1}\ 1\ 0\ 15)$ and $\eta_1 = [15\ \bar{15}\ 0\ 2]$ may be considered as crystallographic plane and direction.

As shown in Fig. 6d, the same description can be made for the 4H feather. The difference between the 4H and 6H feathers lies in the indice of the symmetry planes and axes. But in the 4H feather, as in the 6H ones, $K_1 = (\bar{1}\ 1\ 0\ 6)$ and $\eta_1 = [3\ \bar{3}\ 0\ 1]$ have lower indices than $P_1 = (3\ \bar{3}\ 0\ 7)$ and $N_1 = [\bar{7}\ 7\ 0\ 6]$.

Let us now examine what these symmetry laws mean for the relative position of the atoms in the two crystals. The same conclusions can be obtained with 6H and 4H feathers. For the sake of clarity in the drawings, the case of a 4H feather is discussed. Fig. 7a represents the positions of silicon atoms (or carbon atoms) in the (1 1 $\bar{2}$ 0) plane for the grain 1. P_1 and K_1 are perpendicular to (1 1 $\bar{2}$ 0) and their traces in this plane are respectively N_1 and η_1. Fig. 7b represents the common (1 1 $\bar{2}$ 0) plane where the positions of atoms belonging to grains 1 and 2 are indicated. In this drawing, grain 2 is obtained starting from grain 1 by symmetry across P_1 or by rotation of Π about N_1. In such cases, P_1 and N_1 are elements of symmetry for all atomic positions. K_1 and η_1 are



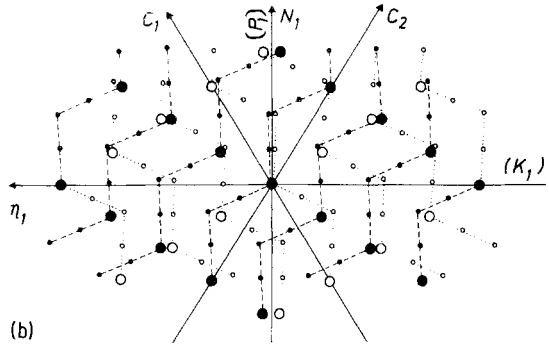


Figure 7 These figures show the packing of silicon atoms in the (1 1 $\bar{2}$ 0) plane for a 4H feather, taken that big dots or big circles represent atoms belonging to basal planes and small dots or small circles stand for all the other atoms and taken that circles correspond to grain 1 and dots to grain 2. Atoms of grain 1 (○) (a); atoms of grains 1 (○) and 2 (●) when the two crystals are related by symmetry across P_1 or rotation of Π about N_1 (b) or by symmetry across K_1 or rotation of Π about η_1 (c).

not, although they are symmetry elements for crystallographic planes and directions (cf. directions C_1 and C_2 on the drawing).

If the grain 2 is obtained by symmetry across K_1 or rotation of Π about η_1, the atoms occupy in the plane (1 1 $\bar{2}$ 0) the positions represented in Fig. 7c. In this case K_1 and η_1 are symmetry elements for all atomic positions whereas P_1 and N_1 are not.

As the carbon lattices can be deduced from those of the silicon by translation in the (1 1 $\bar{2}$ 0) plane (Fig. 4) the above descriptions are valid for them.

3.4. Interface between the two grains forming a feather

The interface is quite irregular in all twins studied by TEM or by scanning electron microscopy (Figs. 3 and 1). Its average orientation is not along any significant crystallographic plane. It is faceted in three dimensions. The orientations of the facets are under study. They seem to be different from the planes K_1 or P_1.

4. Discussion

4.1. Description of the feathers as twins

In all the feathers studied, the crystallographic structures of the two adjacent branches are similar and related according to symmetry rules, reflection across a plane or rotation of Π about one axis. In such a case, if the mirror plane or the rotation axis is a crystallographic plane or a crystallographic direction the two crystals are called twins. Therefore, the feathers may be said to be mirror twins, the twinning plane being K_1, or rotational twins, the twinning axis being η_1.

4.2. Description of the feathers as mechanical twins

From inspection of the atomic positions in the common (1 1 $\bar{2}$ 0) plane (Fig. 7), twin relationships can be found. $[\bar{1}\ 1\ 0\ 0]_2$ (grain 2) can be deduced from $[\bar{1}\ 1\ 0\ 0]_1$ (grain 1) by a shearing process parallel to K_1 in the η_1 direction. $[\bar{1}\ 1\ 0\ 0]$ and (0 0 0 1) are invariant in the transformation, as shown more clearly in Figs 8a and 9. This means that the grains in feathers can be said to be mechanical twins. The transformation laws in 4H and 6H feathers differ by the indices of K_1 and η_1, whereas the plane of shear $S = (1\ 1\ \bar{2}\ 0)$ as well as the invariant plane $K_2 = (0\ 0\ 0\ 1)$ and direction $\eta_2 = [\bar{1}\ 1\ 0\ 0]$ are the same.

The unit cell C based on the three vectors $[1\ 1\ \bar{2}\ 0]$, η_1 and η_2 is not a unit Bravais lattice. Therefore, only a superlattice is restored by the shearing process. More precisely, only the atoms located on the basal planes in grains 1 and 2 are deduced from each other by the shearing process. As the two grains have the same structure, atoms

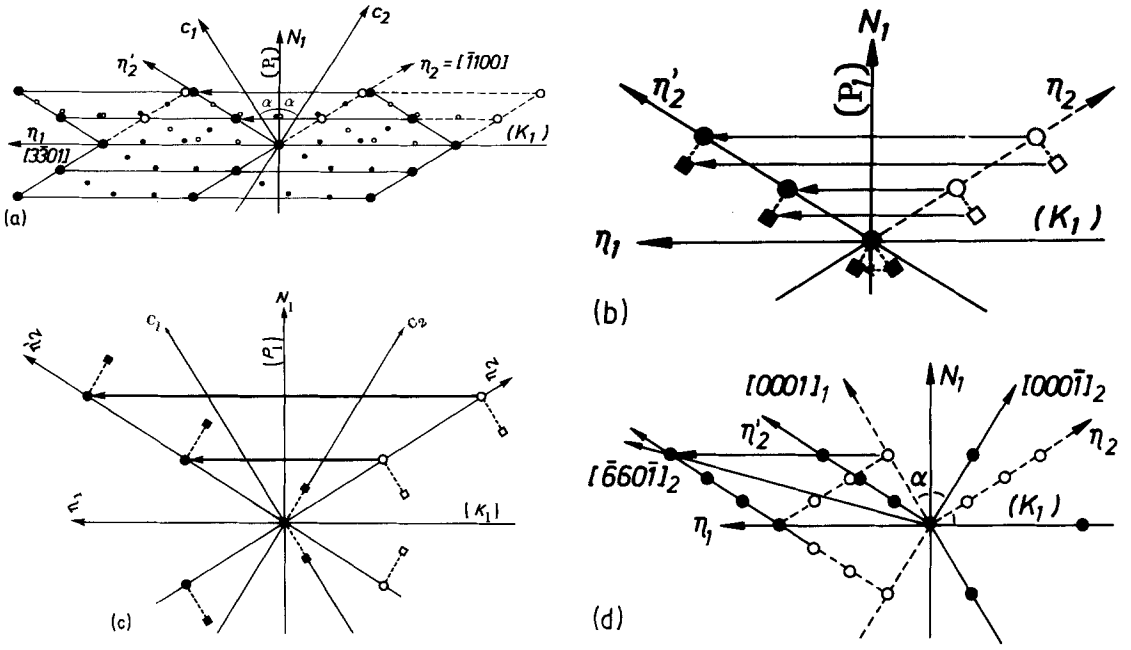


Figure 8 Twinning in a 4H feather – positions of the atoms in the $(1\,1\,\bar{2}\,0)$ plane. η_1 is the trace of K_1, η_2 of K_2 and N_1 of P_1 in the $(1\,1\,\bar{2}\,0)$ plane. (a) Big dots or big circles represent atoms belonging to the basal planes and small dots or small circles stand for all the other atoms. Filled circles are the positions of silicon atoms in grains 1 and 2. Open circles represent the starting positions of the silicon atoms of grain 2 before the operations of reflection in P_1 or rotation of Π about N_1. Arrows indicate the resulting shears. (b) Starting and final positions for silicon (○, ●) and carbon (□, ■) atoms when grain 2 is deduced from grain 1 by reflection in P_1 or rotation of Π about N_1. Arrows indicate the resulting shears. (c) As in b when grain 2 is deduced from grain 1 by reflection in K_1 or rotation of Π about η_1. (d) Transformation of $[0\,0\,0\,1]_1$ into $[\bar{6}\,6\,0\,\bar{1}]_2$ by shearing parallel to K_1 in the η_1 direction.

located inside the cell C, that is to say between the basal planes, undergo shuffles.

In the above description, only one kind of atom has been considered but both silicon and carbon lattices are related by the four independent operations of symmetry. For a 4H structure, the positions of silicon and carbon atoms in plane $(1\,1\,\bar{2}\,0)$ are represented in Figs. 8b or c when the basal planes of both lattices are related by these symmetries (for a 6H structure the result is similar). The positions of the atoms in Figs. 8b and c are equivalent for the diffraction of electrons but are not so as to relate the silicon and carbon lattices of the two grains by shearing: The same shearing parallel to K_1 in the η_1 direction can twin simultaneously the silicon and carbon sublattices in the case 8b but not in the case 8c. To describe the two grains as mechanical twins these lattices must be related by one of these two operations of symmetry:

(i) by rotation of Π about N_1; the twins are said to be of the first kind,

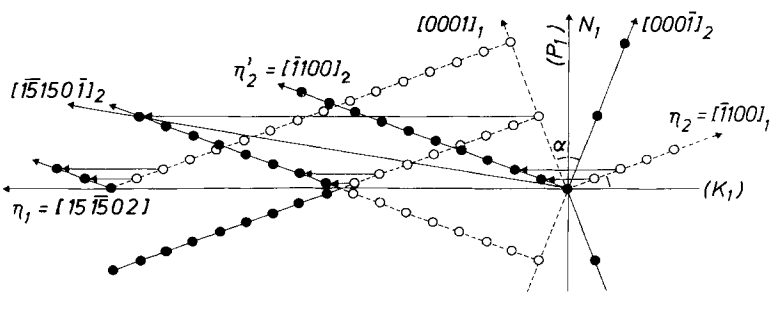


Figure 9 Twinning in a 6H feather. Positions of atoms in $(1\,1\,\bar{2}\,0)$. η_1 is the trace of K_1, η_2 of K_2 and N_1 of P_1 in $(1\,1\,\bar{2}\,0)$. Filled circles are the positions of silicon atoms in grain 1 or 2. Open circles represent the starting positions of silicon atoms when grain 2 is obtained from grain 1 by reflection in P_1. Arrows indicate the shear. $[0\,0\,0\,1]_1$ is transformed in $[\bar{1}5\,1\,5\,0\,\bar{1}]_2$ by shearing.

TABLE I Matrices of transformation relating the planes (M) and directions (Q) of the individuals forming a feather

Twins	Plane	Direction
First kind	$M_I = \begin{vmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ \bar{a} & a & \bar{1} \end{vmatrix}$	$Q_I = \begin{vmatrix} 0 & \bar{1} & \bar{a} \\ \bar{1} & 0 & a \\ 0 & 0 & \bar{1} \end{vmatrix}$
Second kind	$M_{II} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \bar{a} & a & \bar{1} \end{vmatrix}$	$Q_{II} = \begin{vmatrix} 1 & 0 & \bar{a} \\ 0 & 1 & a \\ 0 & 0 & \bar{1} \end{vmatrix}$

For 6H feathers $a = 15$.
For 4H feathers $a = 6$.

(ii) by symmetry across P_1; the twins are said to be of the second kind.

Using the twinning elements, the matrices of transformation (Cf. Table I) relating $(h_2\ k_2\ l_2)$ to $(h_1\ k_1\ l_1)$ or $[u_1\ v_1\ w_1]$ to $[u_2\ v_2\ w_2]$ have been derived [6, 7]. Using these matrices it is possible to show that in a 4H feather, $[0\,0\,1]_1$ and $(\bar{1}\,1\,4)_1$ are transformed, respectively, into $[\bar{6}\,6\,\bar{1}]_2$ and $(\bar{1}\,1\,8)_2$ (cf. Fig. 8d). In a 6H feather, $[0\,0\,1]_1$ and $(\bar{1}\,1\,4)_1$ are transformed into $[\bar{1}\bar{5}\,15\,\bar{1}]_2$ and $(\bar{1}\,1\,26)_2$ (cf. Fig. 9).

4.3. Validity of the description of feathers as mechanical twins

The laws for mechanical twinning given above permit the orientation relationships of the two individuals forming a feather to be described. These twins present, nevertheless, some peculiarities to be discussed.

Although crystallographic plane and direction, K_1 and η_1, possess high indices, particularly in 6H feathers. Some authors consider that in true twins K_1 and η_2 (type I) or η_1 and K_2 (type II) should have low indices. The notion of twins has been introduced by Friedel [8] to classify numerous experimental observations. Cahn [9] underlines that the most ambiguous part of the definition concerns the symmetry laws relating the two crystals. There is experimental evidence that twinning elements have low indices in highly symmetric structures. In hexagonal zirconium or titanium one of the twinning laws is defined by $K_1 = (1\,1\,\bar{2}\,2)$, $\eta_1 = [\bar{1}\,\bar{1}\,2\,3]$, $K_2 = (1\,1\,\bar{2}\,\bar{4})$, $\eta_2 = [\bar{2}\,\bar{2}\,4\,\bar{3}]$ [10]. The 4H and 6H structures of SiC are even more complex than the hexagonal compact one. Therefore, less simple twinning elements might be expected.

Considering twinning laws are found in SiC, it is interesting to bear in mind that each individual forming a feather is not a single crystal (Section 3). It is possible to show that the same shearing can twin the 6H grains and the 4H stacking faults inserted inside. In a 6H structure, the angle between $[0\,0\,0\,1]$ and η_1 is $\simeq 69.3°$. In a 4H structure, the angle between $[0\,0\,0\,1]$ and $[5\,\bar{5}\,0\,1]$ is $\simeq 69.4°$. Therefore, η_1 and K_1 are respectively parallel to $\langle 5\,\bar{5}\,0\,1\rangle$ and $\{\bar{1}\,1\,0\,10\}$ of the 4H layer. The 4H layer can be sheared parallel to K_1 in the η_1 direction. The mechanism of shear is similar to that represented in Fig. 8 with again $K_2 = (0\,0\,0\,1)$, $\eta_2 = [\bar{1}\,1\,0\,0]$ and $S = (1\,1\,\bar{2}\,0)$. Similarly, it is possible to demonstrate that the 4H grains and 6H stacking faults can be twinned using the same shearing elements. For the 6H layer, K_1 is parallel to $(\bar{1}\,1\,0\,9)$, η_1 to $[9\,\bar{9}\,0\,2]$ and the shearing mechanism is similar to that shown in Fig. 9. Therefore, the same operation of symmetry relates the 4H and 6H layers of each individual forming a feather. The twinning elements should be such that the stacking faults could be sheared as well as the main polytypes. It should be interesting to verify if the twinning laws observed when 6H is the main polytype are also obtained when 4H is the main one, and reciprocally.

Another peculiarity of these twins is the large fraction of atoms undergoing shuffle to restore the lattice after shearing. In fact, the feathers are formed by phase transformation and perhaps recrystallization. Transformation or growth twins which are generated by internal stresses are basically mechanical in nature [9]. The twinning laws allow the orientation relationship between the two individuals to be described, but not the co-operative movements of the atoms which occur during the twin formation.

The last characteristic of the feathers is the interface, which is crystallographically irregular and distinct from the twinning plane. The two individuals appear as if they had grown simultaneously but independently. Feathers are "penetration twins", which is the name given to growth or transformation twins when such an interface is observed.

5. Conclusion

The $\alpha \rightarrow \beta$ phase transformation involving the formation of feathers has been studied in SiC conventionally sintered with boron and carbon. It has been shown that feathers are penetration twins. The twinning laws have been established.

To understand the formation of the penetration twins two questions should be solved: the twin nucleation and the growth of the individuals. These mechanisms are under study.

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References

1. C. A. JOHNSON and S. PROCHAZKA, in "Ceramic Microstructure 76", edited by R. Fulreath and T. A. Pask (Westview Press, Berkeley, 1977).
2. (a) A. H. HEUER, G. A. FRYBURG, L. U. OGBUJI, T. E. MITCHELL and S. SHINOZAKI, *J. Amer. Ceram. Soc.* **61** (1978) 407; (b) T. E. MITCHELL, L. U. OGBUJI and A. H. HEUER, *ibid.* p. 412; (c) L. U. OGBUJI, T. E. MITCHELL and A. H. HEUER, *ibid.* **64** (1981) 91; (d) L. U. OGBUJI, T. E. MITCHELL, A. H. HEUER and S. SHINOZAKI, *ibid.* **64** (1981) 100.
3. E. BRESSIANI, Ph. thesis, Stuttgart Universität (1984).
4. D. STUTZ, to be published.
5. L. S. RAMSDELL, *Amer. Min.* **32**, (1947) 64.
6. O. MÜGGE, *Neues Jahrb. Mineral. Geol.* **11** (1889) 98.
7. B. A. BILBY and A. G. CROCKER, *Proc. Roy. Soc.* **A288** (1965) 240.
8. G. FRIEDEL, "Leçons de Cristallographie" (Paris, Berger-Levrault, 1926).
9. R. W. CAHN, *Adv. Phys.* **3** (1954) 363.
10. A. KELLY and G. W. GROVES, "Crystallography and Crystal Defects" (Longman Group Ltd, London, 1970) Chap. 10.

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