$\beta \rightarrow \alpha$ Phase transformation in sintered SiC involving feather formation

Part 2 *Microstructure of hot-pressed SiC*

M. LANCIN, F. ANXIONNAZ
L.P.M. - C.N.R.S. Bellevue, 1, Place Aristide Briand, 92195 Meudon Cedex, France
J. THIBAULT-DESSEAUX
L.P.S. - C.E.N. Grenoble, 34041 Grenoble Cedex, France
D. STUTZ, P. GRIEL
Pulvermetallurgisches Laboratorium, Institute für Werkstoffurssenschaften, Max Planck Institut für Metallforschung, 7000 Stuttgart 80, FRG

The beta–alpha phase transformation has been studied in hot pressed boron doped SiC (HP SiC). The microstructure has been characterized using optical microscopy, scanning and transmission electron microscopy. The influence of the sintering times and temperatures on the crystalline structure of the materials has been checked. The phase transformation which occurs during the sintering involves the formation of feathers. These feathers, constituted by two adjacent alphas grains, can be described as mechanical twins. Three different twinning laws have been observed. To check the influence of the external pressure on the feathers formation, the previous study in pressureless boron doped SiC (PS SiC) has been completed by a new investigation. The results obtained in both PS and HP boron doped SiC show that the external pressure has no influence on the microstructure of the feathers.

1. Introduction

$\beta \rightarrow \alpha$ phase transformation occurs in SiC during the sintering process or subsequent anneals [1]. It involves the formation of α plates or α "feathers" which are constituted of two adjacent α grains. Both mechanisms have been observed and studied in boron-doped pressureless-sintered SiC (PS SiC) [2–5]. α plates have been characterized in boron-doped hot-pressed SiC [HP SiC] by Heuer and co-workers [2–4], but the authors did not identify feathers in their material. Features, looking like feathers, have been observed by Almeido-Bressiani in boron-doped HP SiC [6].

The aim of this work was to verify if the $\beta \rightarrow \alpha$ transformation in boron-doped HP SiC may involve the formation of feathers and in such a case, to investigate the influence of the pressure on their microstructure. It forms part of a more extended investigation of the $\beta \rightarrow \alpha$ phase transformation in boron-doped SiC.

2. Experimental procedure

2.1. Material preparation

The hot-pressing process was used to obtain fully densified materials ($\varrho > 0.95\,\varrho_{th}$). Sintering times and temperatures from 2060 to 2200° C were chosen to determine their influence on the crystalline structure of the materials.

β-SiC powder, containing ~1.5% free carbon [7] was mixed with 0.5% additional boron in *n*-hexane. It was dried at 70° C, sieved and filled in a graphite die, and sintered under 12.6 MPa in a flowing argon atmosphere. The heating rate was 70° C min^{-1}, with an ageing of 30 min at 1350° C performed in order to redistribute the additives and to evaporate oxygen gas species. The sintering times and temperatures are given in Table I as well as the density of the materials.

2.2. Experimental methods

The Grain boundaries were revealed by etching mechanically polished samples with Murakami reagent or fused salt mixture. The grain shape and size were determined using optical microscopy, scanning electron microscopy and an image analyser.

A polytype analysis of the α-phase was performed using $\langle 1\,1\,\bar{2}\,0\rangle$ electron diffraction patterns: the spots and the streaks observed along the *c*-axis are characteristic of the polytypes and of the stacking faults [8]. Figs 1 and 2 show the stacking of the more common polytypes and the corresponding $\langle 1\,1\,\bar{2}\,0\rangle$ diffraction patterns, respectively. High-resolution microscopy (200 KeV) was used to image the $\{1\,1\,\bar{2}\,0\}$ planes and therefore the stacking of the polytypes in the *c*-direction.

TABLE I Characteristics of the HP SiC. *T*, sintering temperature; *t*, sintering time, ϱ, density; $\varrho_{th} = 3.21\,g\,cm^{-3}$

	Material				
	1	2	3	4	5
T(° C)	2060	2060	2150	2150	2200
t(min)	10	30	30	60	60
ϱ($g\,cm^{-3}$)	3, 13	3, 18	3, 17	3, 18	3, 18
Phase (± 10% wt %)	77	84	85	87	94

0022–2461/87 $03.00 + .12

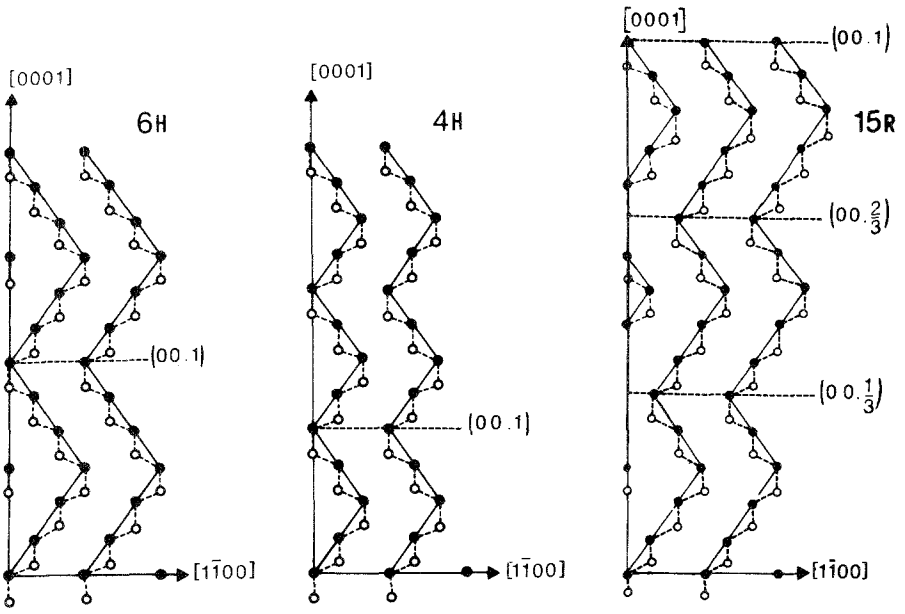

Figure 1 Stacking of (●) silicon and (○) carbon atoms in $\{1\,1\,\bar{2}\,0\}$ planes of the more common polytypes. The inter-reticular spacing between $\{0\,0\,0\,1\}$ planes is equal to 0.251 nm. The unit cell parameters are $a = 0.395$ nm and $c = 1.5$ nm (6H), $c = 1$ nm (4H) and $c = 3.77$ nm (15R).

The orientation relationships between grains were determined using diffraction patterns, kikuchi diagrams and the computer method developed by Karakostas *et al.* [9].

3. Results

3.1. Polytypes analysis

Figs 3 and 4 show typical micrographs obtained by optical microscopy or scanning electron microscopy. The materials are constituted of large (diameter $\simeq 200$ to 300 μm) and of small (diameter $\simeq 1$ to 3 μm) grains. The percentage of each depends on the time and temperature of the sintering process. Electron diffraction showed that the α-phase corresponds to the large grains and the β-phase to the small ones. The amount of $\beta \rightarrow \alpha$ phase transformation, evaluated from an image analysis, is given in Table I. These observations show that materials 2, 3 and 4 are characterized by similar grain size and crystalline structure; they also possess the same density. Therefore, SiC2 has been taken as representative of SiC3 and 4 for a more detailed polytype analysis.

The α grains consist of a complex stacking of polytypes, only 3 to 20% of each grain being transparent to the electron beam. To obtain reliable information on the crystalline structure of the materials, it appeared necessary to observe a large number of grains: 63, 52 and 31 α grains were analysed in SiC 1, 2 and 5, respectively, and the results obtained in the three materials are comparable.

In the area analysed three different diffraction patterns were observed:

1. Despite some streaks, the diffraction pattern exhibits spots characteristic of one polytype. This predominant polytype was either 15R or 6H, except in one grain.

2. The diffraction pattern shows spots characteristic of both 15R and 6H polytypes. The crystal consists essentially of 15R and 6H layers, the percentage of the two polytypes being of the same order of magnitude as shown in Fig. 2d.

3. No further characteristic spots are seen along the c-axis. On the other hand, the streaks attest the complex stacking of the polytypes (Fig. 2e) and the corresponding grains possess no dominant crystalline structure.

Table II summarizes the results, giving the different crystalline structures which were predominant in the area observable by TEM and the corresponding number of grains. It shows that the 15R structure is the most favoured during the $\beta \rightarrow \alpha$ phase transformation, whatever the sintering conditions.

To observe in detail the stacking faults in the materials, HREM images of different grains were obtained (Fig. 5): they represent $\{1\,1\,\bar{2}\,0\}$ planes. The $\{0\,0\,0\,1\}$ planes were perpendicular to the images. In Fig. 5c, it is possible to see that the white dots correspond to tunnels in the structure. Slight misalignment of the samples in Figs 5a and b has not permitted this interpretation. HREM observations show that the α grains possess very irregular crystalline structures as illustrated in Fig. 5a. This represents a grain which exhibits a 15R diffraction pattern, containing numerous faults. As shown in Figs 5a, b and c, the more

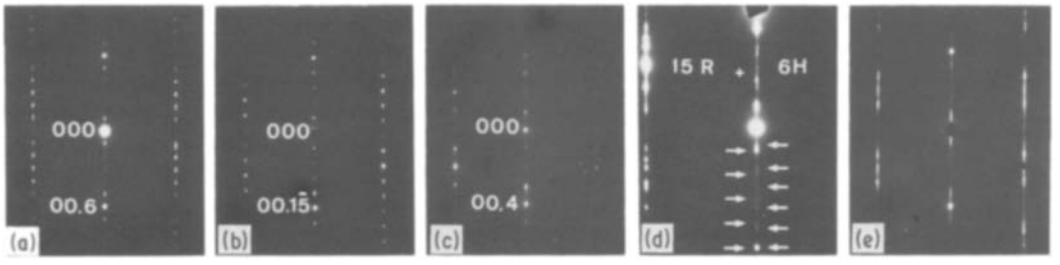

Figure 2 $\langle 1\,1\,\bar{2}\,0 \rangle$ diffraction patterns characteristic of (a) 6H, (b) 15R, (c) 4H, (d) 6H + 15R, (e) complex stacking of polytypes.

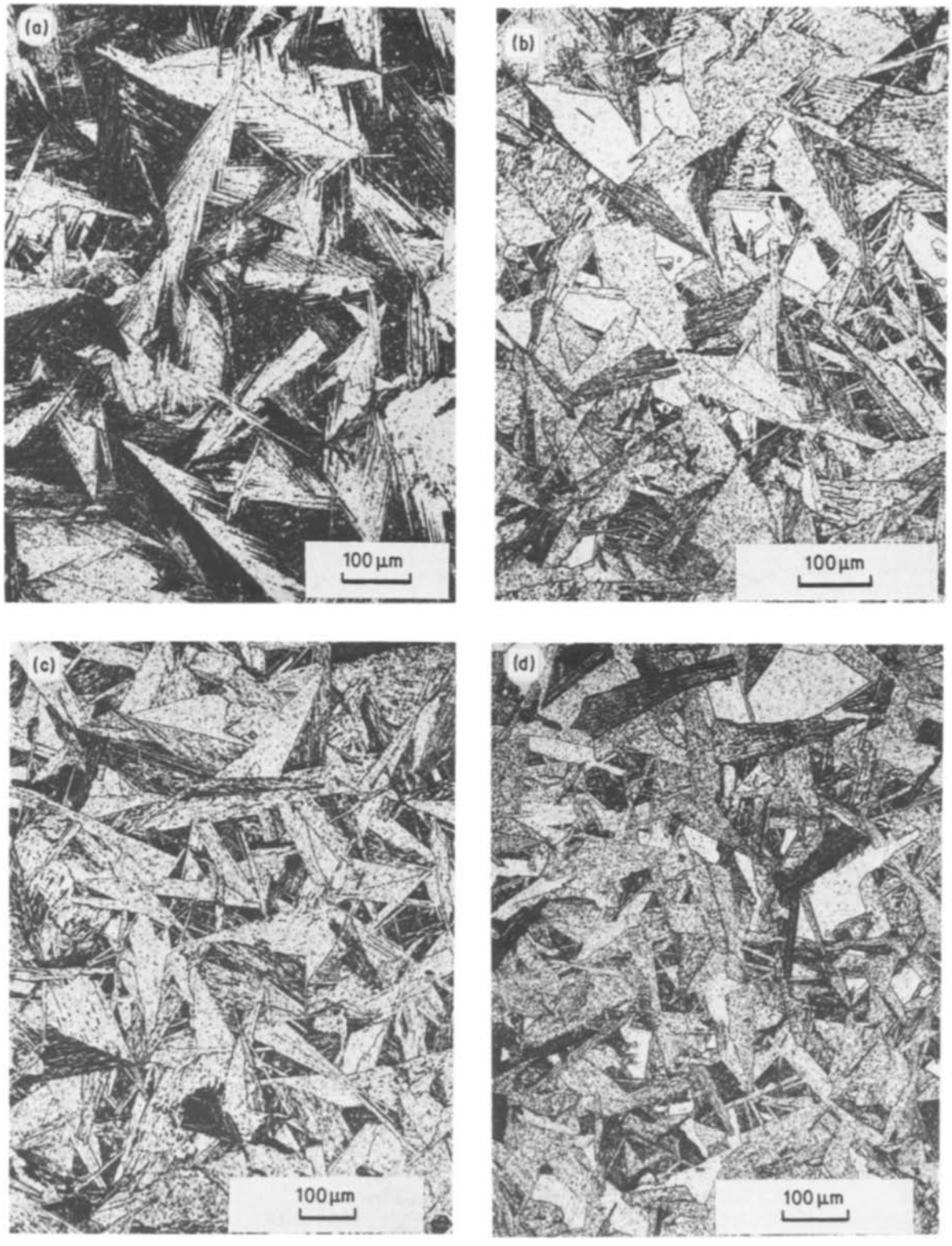

Figure 3 Optical micrographs of SiC etched using Murakami reagent. Large grains correspond to the α-phase, small ones to the β-phase. The materials were sintered: (a) $t = 10$ min, $T = 2060°$ C; (b) $t = 30$ min, $T = 2060°$ C; (c) $t = 30$ min, $T = 2150°$ C; (d) $t = 60$ min, $T = 2150°$ C; (e) $t = 60$ min, $T = 2200°$ C.

TABLE II Crystalline structure and the corresponding number of α-grains in HP SiC

	Number of grains studied	Number of grains of the following structures				
		15R	6H	4H	15R + 6H	Complex structure
SiC 1	63	34	16		6	7
SiC 2	52	40	3	1	4	4
SiC 5	31	24	5			2
Total	146	98	24	1	10	13

TABLE III Different crystalline structures and orientation relationships observed in pairs and corresponding number of pairs. Pairs consist of two α grains, 1 and 2.

Angle between the *c*-axis of grains 1 and 2	Number of pairs with the crystalline structures			
	15R–15R	6H–6H	Complex structure	Total
$2\alpha = 41.4°$	17	9	5	31
$2\alpha = 65.5°$	17			17

Figure 3 Continued

commonly observed stackings are 15R, 6H and 4H. Initially 15R and then 6H stackings are favoured. Except in one grain, 4H layers are not sufficiently extended to produce typical diffraction patterns.

In SiC 1 to 5, the α grains always contain numerous inclusions (Fig. 6). Such inclusions were also observed in conventionally sintered boron-doped SiC [5]. Their chemical composition will be given in Part 3.

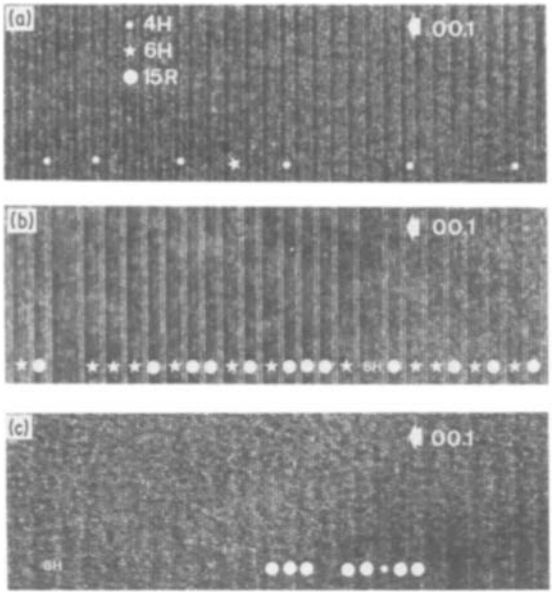

Figure 5 High resolution images of (a) 15R, (b) 15R + 6H and (c) 6H grains. They represent $\{1\,1\,\bar{2}\,0\}$ planes. The white dots in (c) correspond to the tunnels in the structure. Traces of $\{0\,0\,0\,1\}$ planes, which are perpendicular to the images, are arrowed.

3.2. Orientation relationships between α grains

Of the 146 grains studied, 96 formed pairs related with mutual orientation: they shared a $(1\,1\,\bar{2}\,0)$ plane; in the common plane their c-axes formed an angle $2\alpha = 41.4° \pm 0.3°$ or $2\alpha = 65.5° \pm 0.5°$ as shown in $[1\,1\,\bar{2}\,0]$ diffraction patterns. 15R pairs are seen in Fig. 7 and 6H pairs in Fig. 6a of Lancin [5]. There was no simple or reproducible orientation relationship between pairs and the surrounding α grains. Because

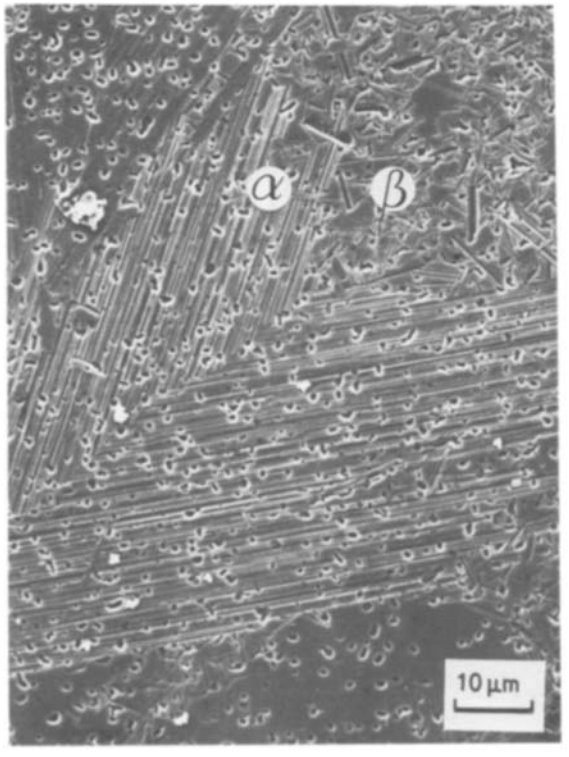

Figure 4 Scanning electron micrographs of SiC 2 etched using a fused salt mixture. Large grains correspond to the α-phase, small ones to the β-phase. The stacking faults in the α-phase and in the β-phase are revealed.

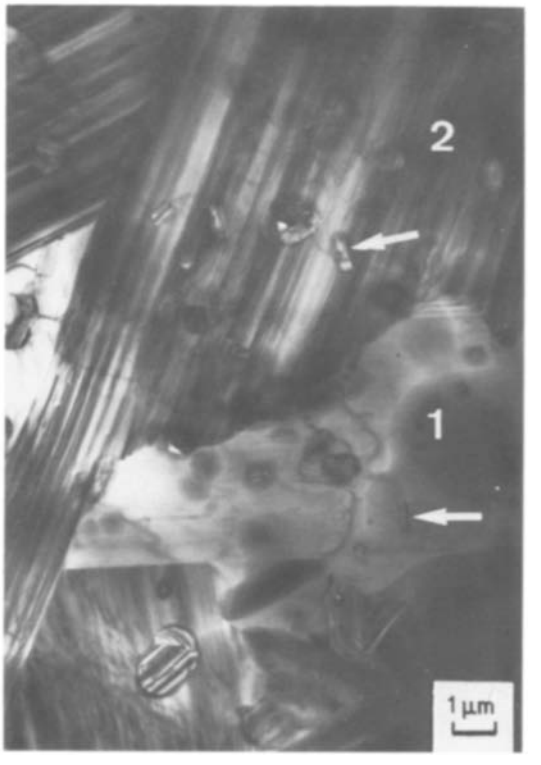

Figure 6 Bright-field transmission micrograph of SiC 1 showing the inclusions observed in the α grains: two are arrowed. Grains 1 and 2 form a pair.

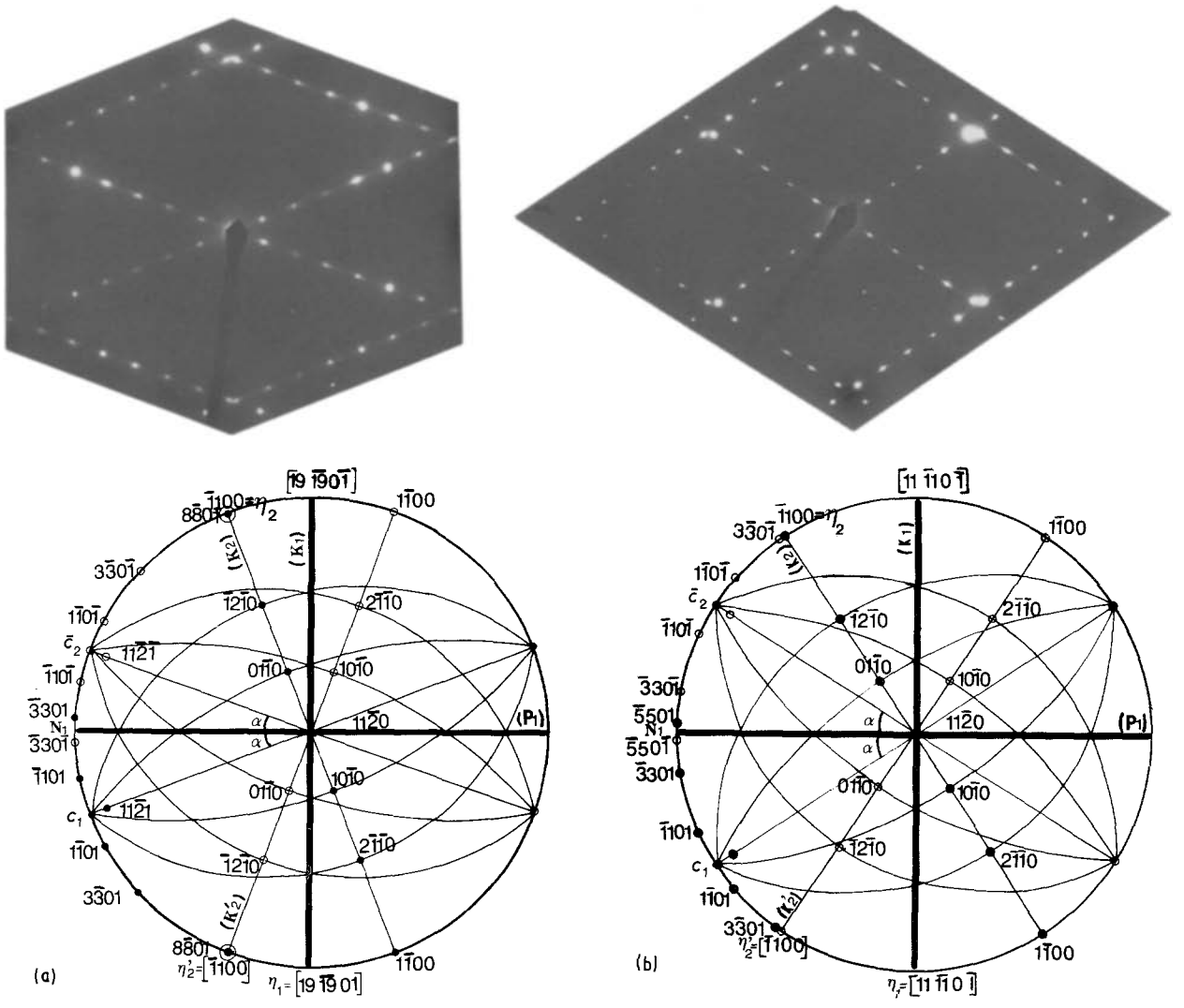

Figure 7 Orientation relationships between α grains 1 and 2 forming pairs. (a) 15R pairs, $2\alpha = 41.4°$, (b) 15R pairs $2\alpha = 65.5°$. The picture shows the [1 1 $\bar{2}$ 0] diffraction patterns and the stereographic projections in the common (1 1 $\bar{2}$ 0) plane of the directions of the grains 1 (●) and 2 (○).

of the large grain size, it could not be proved whether or not unpaired grains formed pairs with grains not located in the area observable by TEM.

The pairs are classified according angle α and the predominant polytypes constituting their grains (grains 1 and 2) in Table III. In most of the pairs, both grains exhibit the same predominant crystalline structure. Considering these predominant structures, the stereographic projections of grains 1 and 2 in their common (1 1 $\bar{2}$ 0) plane have been drawn and are shown in Fig. 7 for 15R pairs and in Fig. 6a of Lancin [5] for 6H pairs. In the three possible configurations, crystal 1 can be obtained from crystal 2 by symmetry across K or P_1, or rotation of π about η_1 or N_1. The only difference between the pairs lies in the indices of the elements of symmetry.

3.3. Microstructure of boron-doped pressureless-sintered SiC

To compare the $\beta \rightarrow \alpha$ phase transformation in PS and HP boron-doped SiC, extensive characterization was necessary in both materials. Part 1 of this study [5] has been completed by a new investigation of PS SiC.

To investigate the phase transformation in PS SiC, processing was carried out in order to obtain different amounts of α-phase. The time and temperature of the pressureless sintering were chosen to minimize the phase transformation [1]. As a result, the material contained only 2% α-phase. Subsequent anneals were then applied to induce phase transformation and 20 or 80% α-phase was reached [5].

The new investigation confirms and completes the study in Part 1 of the microstructure of PS SiC containing 2, 20 or 80% α-phase (referred to as PS 2, PS 20 and PS 80): (i) α grains consist essentially of 6H or of 15R polytypes (Table IV); (ii) in PS 2 and PS 20, α grains are less heavily faulted than in PS 80; (iii) α grains form pairs of "feathers" – in PS 2 and PS 20, SEM and TEM show that most, if not all, the α grains constitute feathers. It is likely that PS 80 results from

TABLE IV Crystalline structure and the corresponding number of α-grains in PS SiC

Material	Number of grains studied	Number of grains of the following structures				
		15R	6H	4H	15R + 6H	Complex structure
PS 2	16	2	12	2		
PS 20	12		10			2
PS 80	30	18	7		3	2
Total	58	20	29	2	3	4

TABLE V PS SiC: Different crystalline structures and orientation relationships observed in pairs and corresponding number of pairs. Pairs consist of two α grains, 1 and 2.

Angle between the c-axis of grains 1 and 2	Material	Number of pairs with the crystalline structures				
		15R–15R	6H–6H	4H–4H	Complex structure	Total
$2\alpha = 41.4°$	PS 2	1	5			
	PS 20		5			21
	PS 80	6	2		2	
$2\alpha = 65.5°$	PS 80	2				2
$2\alpha = 64°$	PS 2			1		1

the same transformation mechanism; (iv) the microstructure of the α feathers is given in Table V. 6H [5] and 15R [2–4] feathers characterized by $2\alpha = 41.4°$ were identified as before. In PS 80, 15R feathers with $2\alpha = 65.5°$ were also found; (v) 6H feathers were most commonly observed in partly transformed materials (PS 2 and PS 20).

4. Discussion

Large α grains develop during sintering or subsequent annealing of boron-doped SiC when the temperature of the $\beta \rightarrow \alpha$ phase transformation is exceeded. This transformation occurs in both PS and HP SiC. The α grains always contain numerous stacking faults. Nevertheless, they are less heavily faulted when formed during the early stage of phase transformation (PS 2).

A comparison between HP and PS SiC shows a predominance of 6H polytype in PS 2 and PS 20 and of 15R polytype in PS 80 and HP SiC. 6H polytype develops preferentially during the first stage of the phase transformation; the phase then preferentially consists of 15R polytypes formed either by nucleation or 6H to 15R transformation. The stacking faults which develop in the α-phase to release the internal stresses favour 15R stacking and very complex structures.

Pairs are formed during the $\beta \rightarrow \alpha$ phase transformation in HP SiC. They possess the same microstructural characteristics as the "feathers" previously found in PS SiC [2–5]. Therefore, phase transformation involves even so incompletely, the formation of feathers in both HP and PS boron-doped SiC; the external pressure has no influence on the microstructure of the feathers. The formation of 6H feathers is favoured during the early stage of the phase transformation. Then 15R feathers with $2\alpha = 41.4°$ are the most frequently formed.

In Part 1 [5] it was shown that 6H feathers, with an angle 2α equal to 41.4°, could be described as twins. The elements of symmetry are:

$\eta_1 = [15\bar{1}502]$ the twinning direction

$K_1 = (\bar{1}1015)$ the twinning plane

$\eta_2 = [\bar{1}100]$ the invariant direction

$K_2 = (0001)$ the invariant plane

$N_1 = [\bar{1}6160\,15]$

$P_1 = (15\bar{1}532)$

$S = (11\bar{2}0)$ the shear plane

By the same reasoning, 15R feathers can also be described as twins and the elements of symmetry are: when $2\alpha = 41.4°$

$$\eta_1 = [19\bar{1}901]$$
$$K_1 = (\bar{1}1038)$$
$$\eta_2 = [\bar{1}100]$$
$$K_2 = (0001)$$
$$N_1 = [\bar{8}803]$$
$$P_1 = (3\bar{3}016)$$
$$S = (11\bar{2}0)$$

when $2\alpha = 65.5°$

$$\eta_1 = [11\bar{1}\bar{1}01]$$
$$K_1 = (\bar{1}1022)$$
$$\eta_2 = [\bar{1}100]$$
$$K_2 = (0001)$$
$$N_1 = [\bar{9}902]$$
$$P_1 = (1\bar{1}09)$$
$$S = (11\bar{2}0)$$

As emphasized by Cahn [10], twins formed to release strains during phase transformation are mechanical in character. It was shown in Part 1 that feathers could be described as mechanical twins if the two lattices are related by one of the two following operations of symmetry: (a) rotation of π about N_1 (twins of the first kind); (b) symmetry across P_1 (twins of the second kind). Because of the high indices of P_1, the first description is to be preferred. In addition, it is normal to describe twins by a two-fold axis. The shearing mechanisms resulting in 15R feathers with $2\alpha = 41.4°$ or $2\alpha = 65.5°$ are illustrated Fig. 8.

Owing to the large number of stacking faults, the 15R, 6H and 4H layers must be sheared using the same shearing elements. Such a condition is satisfied when $2\alpha = 41.4°$ (in 4H layers, η_1, and K_1 are, respectively, parallel to $[5\bar{5}01]$ and $(\bar{1}1010)$, cf. Part 1). The condition is also satisfied for 15R and 6H polytypes when $2\alpha = 65.5°$. In a 6H layer, η_1 and K_1 are, respectively, parallel to $[9\bar{9}02]$ and $(\bar{1}109)$. For a 4H layer, no relatively simple twinning elements are found for $2\alpha = 65.5°$ but simple twinning laws exist when $2\alpha = 64°$ (cf. Part 1, $\eta_1 = [3\bar{3}01]$ and $K_1 = (\bar{1}106)$). Small deviations from the twinning angle are generally

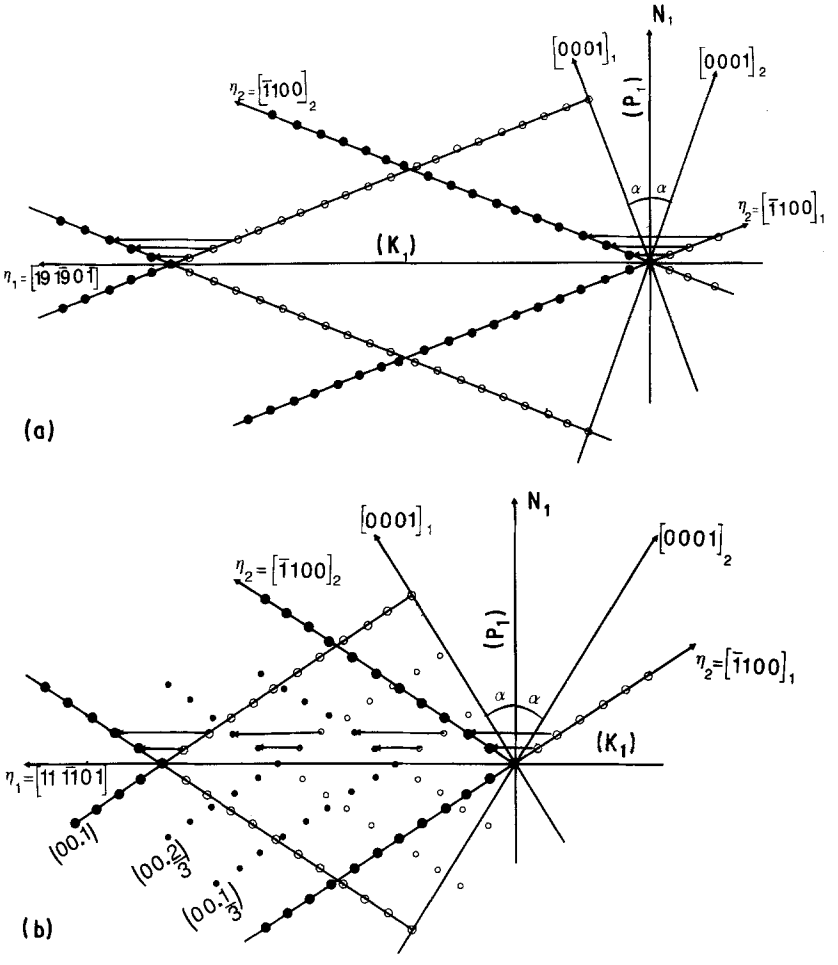

Figure 8 Twinning in 15R feathers when (a) $2\alpha = 41.4°$ and (b) $2\alpha = 65.5°$. The position of the silicon atoms in the $(1\,1\,\bar{2}\,0)$ are shown. (●) Positions of the atoms in grain 1 and 2, (○) the starting positions of the atoms when grain 2 is obtained by rotation of π about N_1. Arrows indicate the resulting shear. η_1 and N_1 are the traces of K_1 and P_1 in $(1\,1\,\bar{2}\,0)$.

accommodated by dislocations at the twin boundaries. Because of the small extent of the 4H layers (a few nanometres), HREM studies must be performed to verify this hypothesis.

The twins formed during the $\beta \rightarrow \alpha$ phase transformation in PS and HP boron-doped SiC are characterized by twinning elements of high indices and very high indices of coincidence. This peculiarity may be due to the complex stacking of polytypes in α grains. This point will be discussed further in Part 3 where the grain-boundary studies performed on PS and HP SiC will be described.

5. Conclusion

The $\beta \rightarrow \alpha$ phase transformation was studied in both pressed and pressureless conventionally sintered boron-doped SiC. During sintering under pressure, phase transformation occurs, at least partly, by formation of feathers. These feathers exhibit the same characteristics as those observed in PS SiC and can be described as twins. Their peculiar twinning laws should be related to the complex crystalline structure of α-SiC.

Acknowledgements

M. Lancin wishes to thank Dr Rühle for helpful discussions, and the Max-Planck Institüt for a maintenance grant in MPI für Metallforschung, Stuttgart.

References

1. C. A. JOHNSON and S. PROCHASZKA, in "Ceramic microstructure 76", edited by R. Fulreth and J. A. Pask (Westview, Berkeley, 1977) p. 366.
2. A. H. HEUER, G. A. FRYBURG, L. U. OGBUJI, T. E. MITCHELL and S. SHINOZAKI, *J. Amer. Ceram. Soc.* **61** (1978) 407.
3. L. U. OGBUJI, T. E. MITCHELL and A. H. HEUER, *ibid.* **64** (1981) 91.
4. L. U. OGBUJI, T. E. MITCHELL, A. H. HEUER and S. SHINOZAKI, *ibid.* **64** (1981) 100.
5. M. LANCIN, *J. Mater. Sci.* **19** (1984) 4077.
6. A. H. de ALMEIDO-BRESSIANI, Dr Thesis, University of Stuttgart (RFA) (1984).
7. D. H. STUTZ, S. PROCHASZKA and J. LORENZ, *J. Amer. Ceram. Soc.* **6** (1985) 68.
8. J. P. GAUTHIER, Thèse d'Etat, Faculté des Sciences, Lyon, France (1978).
9. T. H. KARAKOSTAS, G. NOUET, G. L. BLERIS, S. HAGEGE and P. DELAVIGNETTE, *Phys. Status Solidi (a)* **50** (1978) 703.
10. R. W. CAHN, *Adv. Phys.* **3** (1954) 363.

Received 6 May
and accepted 23 July 1986