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Siliconated Pyrolytic Graphite

Part 2 *The State of Silicon Present in Siliconated Pyrolytic Graphite*

SEISHI YAJIMA, TOSHIO HIRAI
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan

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By X-ray diffraction, surface oxidation, X-ray microanalysis, electron diffraction, and electron microscopy, the state of silicon present in siliconated pyrolytic graphite has been examined on several samples prepared under a variety of conditions.

In the siliconated pyrolytic graphite prepared at the deposition temperatures below 1730° C, the greater part of the silicon occurs as β-SiC. It does not segregate in the cone boundaries but disperses uniformly. It exists as flake-like single crystals, whose size increases with decreasing temperature. The (111) plane of β-SiC is parallel to the (001) planes of graphite.

1. Introduction

A considerable amount of research has been concerned with lamellar compounds of pyrolytic graphite PG in which the dopant elements are inserted between the carbon layers [1]. The mode of accommodating foreign elements in PG-lamellar compounds is well understood; but there seem to have been very few investigations of PG-deposited compounds, which are prepared by pyrolysis of a mixture of hydrocarbon gas and the hydride or halide of a doping element. Katz and Gazzara [2] studied the influence of boron content on the fine microstructure of boronated pyrolytic graphite, and reported that boron substituted for carbon up to 0.5 wt %, above which it was present as B_4C.

We have prepared siliconated pyrolytic graphite PG(Si) by pyrolysing a mixture of propane gas and silicon tetrachloride vapour, and examined its surface characteristics, microstructure and density [3]. In the present experiments, we investigated the nature of the silicon present in PG(Si) prepared under various conditions, utilising X-ray diffraction, surface oxidation, X-ray microanalytical, electron diffraction, and electron microscopical techniques.

2. Experimental Procedures

The process used for preparing PG(Si) was fully described in the preceding paper [3]. The reactant was a mixture of propane and silicon tetrachloride vapour: the total gas pressure (P_{total}) was 10 or 50 torr: the partial pressure of silicon tetrachloride vapour (P_{SiCl_4}) was up to 13 torr, and the deposition temperature (T_{dep}) was 1440 to 2025° C.

The amount of silicon in the product was practically independent of P_{total} and P_{SiCl_4}, but markedly dependant on temperatures. The relation between silicon content and temperature is summarised in fig. 1.

1. *X-ray diffraction analysis:* X-ray measurements were made with a diffractometric unit or a Debye-Scherrer camera (11.46 cm diameter), using Ni-filtered CuKα radiation on the powdered samples (200 to 325 mesh).

2. *Surface oxidation:* it was supposed that the silicon and graphite matrix in PG(Si) would behave differently when oxidised. The parallel (c-plane) and the perpendicular (cross-section) planes (fig. 2) were polished by an ordinary metallographic technique, and oxidised at a temperature of 1000° C for 1 to 40 h in 20 torr of

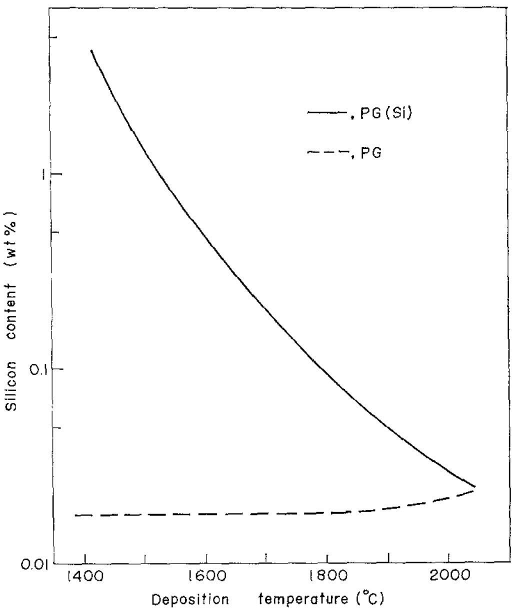


Figure 1 The relation between silicon content and deposition temperature.

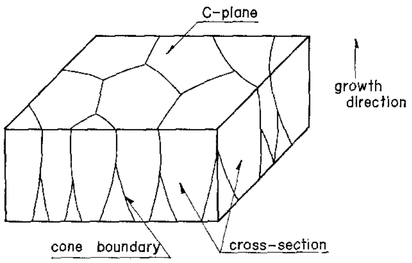


Figure 2 Cone boundaries in the specimen for a surface oxidation experiment and an X-ray microanalysis.

oxygen. After oxidation the surfaces were observed by optical microscopy.

3. *X-ray microanalysis:* the *c*-plane and the cross-section (fig. 2) of three kinds of PG(Si) were observed by an X-ray microanalyser. The preparation conditions and silicon content of these samples are given in table I. Special attention was given to checking for segregation of silicon in the cone boundaries. The measurements were made under the following conditions: SiKα (7.126 Å); accelerating voltage = 30 kV; sample current = 0.038 μA; analysing crystal, 4 in. ADP.

4. *Electron microscopic observation and electron diffraction analysis:* the powdered samples were observed by transmission electron microscopy and selected area diffraction.

TABLE I Samples for an X-ray microanalysis.

Sample	Deposition temp. ° C	P_{total} torr	P_{SiCl_4} torr	Si content wt %
A	2025	50	6	0.018
B	1830	50	6	1.0
C	1440	50	13	3.8

3. Results and Discussion

3.1. X-ray Diffraction Analysis

Figs. 3a and 3b show typical powder patterns of two kinds of PG(Si) samples; One (a) (Si = 1.0 wt %) was prepared at T_{dep} = 1535° C, P_{total} = 50 torr and P_{SiCl_4} = 6 torr: the other (b) (Si = 0.035 wt %) at T_{dep} = 1925° C, P_{total} = 50 torr and P_{SiCl_4} = 13 torr. "G" indicates the reflections of graphite. Samples containing large amounts of silicon give additional reflections (see fig. 3a).

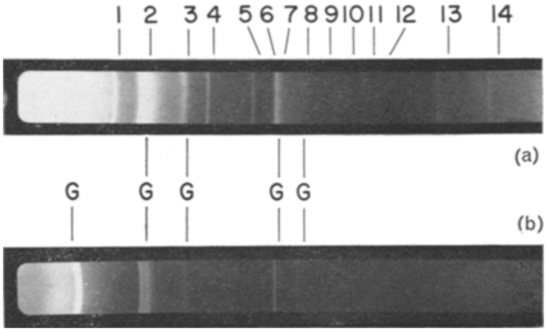


Figure 3 X-ray diffraction patterns. (a) Si = 1.0 wt%; T_{dep} =1535° C; P_{total} = 50 torr; P_{SiCl_4} = 6 torr. (b) Si= 0.035 wt%; T_{dep} = 1925° C; P_{total} = 50 torr; P_{SiCl_4} = 13 torr. G, reflections of graphite.

The powder diffraction data from fig. 3a are listed in table II, together with the diffraction data of graphite [4] and β-SiC [5]. The pattern other than "G" is indexed according to β-SiC (cubic, ZnS-type). This shows that, in PG(Si) formed at low and medium temperatures (below about 1700° C), silicon is present as β-SiC. The lattice parameter obtained for β-SiC in this experiment is 4.358 Å, which corresponds well with the value reported previously [5]. Moreover, additional weak reflections are observed in PG(Si) prepared in the medium temperature range (1600 to 1700° C). These seem to be due to stacking faults in β-SiC, or the coexistence of α-SiC. No β-SiC reflections are

TABLE II X-ray data for the sample shown in fig. 3a.

Serial no of. line	d_{obs}	I_{obs}	β-SiC [5] d	I	index	Graphite [4] d	I	index
1	2.506	S	2.51	100	(111)		[100	(002)]
2	2.123	VS	2.17	20	(200)	2.13	2	(100)
3	1.703	VS				1.682	8	(004)
4	1.536	S	1.54	63	(220)			
5	1.309	S	1.31	50	(311)			
6	1.256	W	1.26	5	(222)			
7	1.223	S				1.232	6	(110)
8	1.133	M				1.155	6	(112)
9	1.119	W				1.12	2	(006)
10	1.090	W	1.09	6	(400)			
11	0.999	M	1.00	18	(331)			
12	0.9735	W	0.97	6	(420)			
13	0.8879	M	0.89	13	(422)			
14	0.8382	M	0.84	10	(333) (511)			

observed in the PG(Si) prepared at high temperatures, near 2000° C.

Fig. 4 shows the (111) reflection line of β-SiC in PG(Si) containing 3.8 wt % Si prepared at $T_{dep} = 1440°$ C, $P_{total} = 50$ torr and $P_{SiCl_4} = 13$ torr, which was obtained from the diffractometer. From the half-width of the line in fig. 4, the crystallite size of β-SiC in the [111] direction is calculated to be about 200 Å. This value will be discussed in conjunction with results of electron microscopic observation and electron diffraction analysis in a later section.

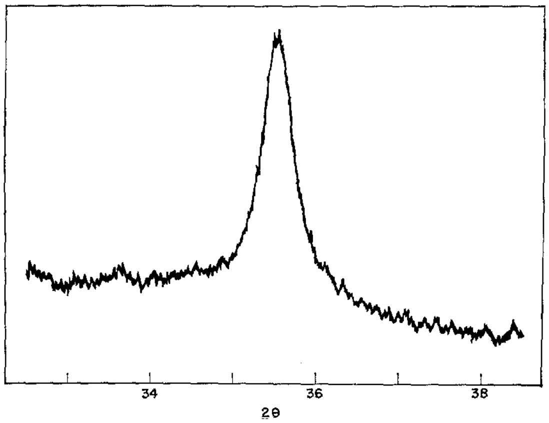


Figure 4 Typical (111) reflection line of β-SiC.

3.2. Surface Oxidation

The X-ray diffraction analysis indicates clearly that silicon in PG(Si) forms β-SiC at low and medium temperatures, but does not make clear the state of dispersion or segregation of β-SiC in a specimen. An oxidation study of SiC at 900 to 1200° C showed the formation of amorphous silica [6]. If β-SiC segregates in the cone boundaries, its segregation can be detected by optical microscopic observation of the oxidised surface.

The oxidised surfaces parallel to the deposition surface (*c*-plane) of PG(Si) containing large amounts of silicon show an interference colour, which becomes more conspicuous with increasing oxidation time. The surfaces of PG(Si) containing small amounts of silicon remain unchanged after oxidation. On the other hand, the oxidised *cross-section* surfaces give *no* interference colour.

Figs. 5 to 8 show the change in the surface (*c*-plane) with oxidation for the sample (Si = 1.1 wt %) prepared at $T_{dep} = 1535°$ C, $P_{total} = 50$ torr and $P_{SiCl_4} = 13$ torr. The surface before oxidation is shown in fig. 5. Figs. 6a and b indicate the surface oxidised for 11 h. The cone boundaries are dark and there seem to be cracks in fig. 6a, but not in 6b. The darkness in the cone boundaries is due to the differences in oxidation behaviour. The surfaces oxidised for 19 h are shown in figs. 7a and b. The cone boundaries widen with increasing oxidation time. Figs. 8a and b show the surface oxidised for 40 h. Each oxidised surface gives beautiful interference colours, which seem to result from the formation of a transparent film on the surface.

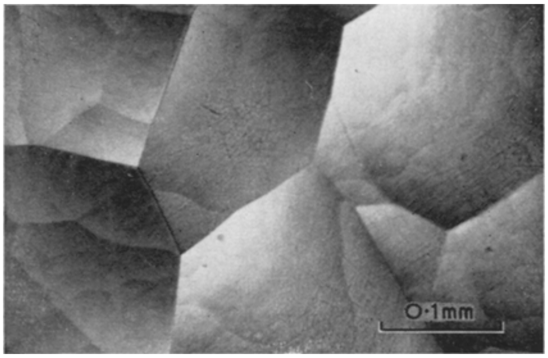
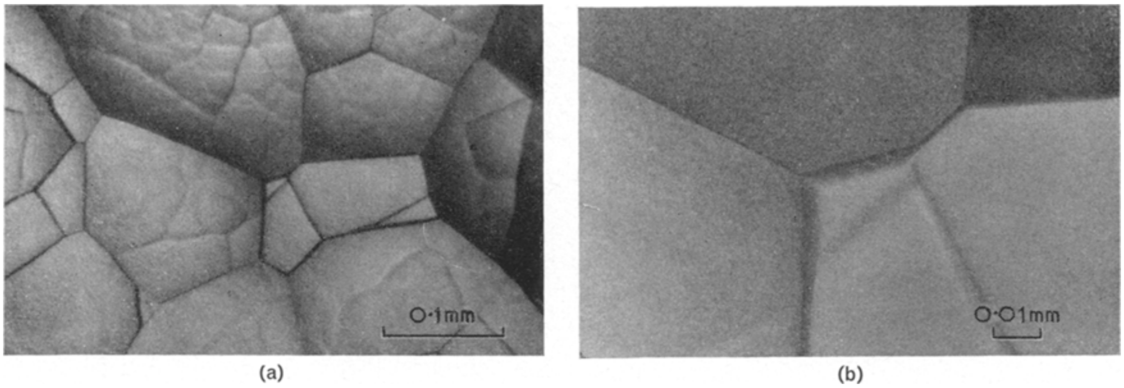


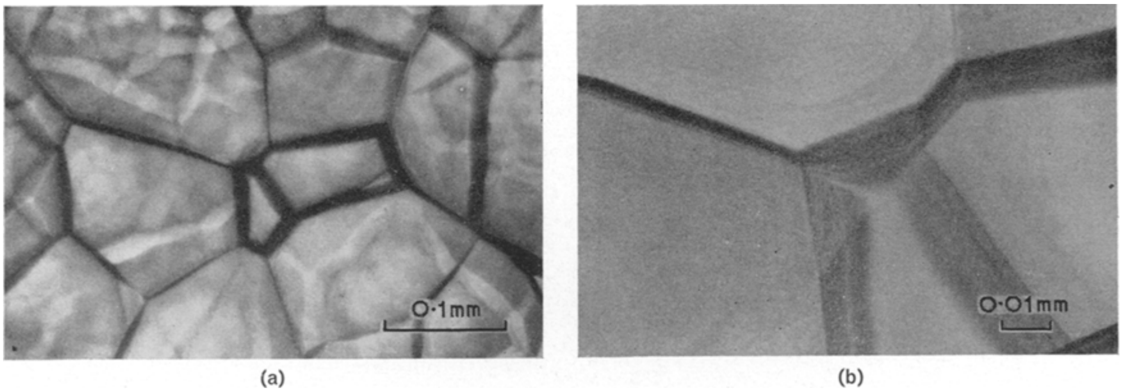
Figure 5 The surface before oxidation.

Fig. 9 shows, schematically, the change in the surface as a result of oxidation, or of subsequent hydrofluoric acid treatment. The oxidation of graphite proceeds at the edge of the hexagonal carbon network. As shown in fig. 9a, the inclination angle of the carbon network to the flattened surface at cone boundaries is larger than within the cones. Therefore, a rapid oxidation occurs and a thick film of SiO_2 forms at the



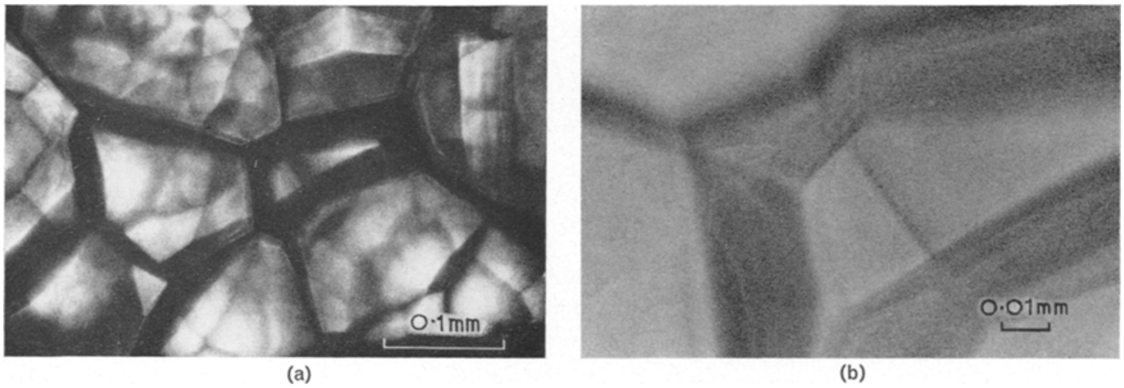
(a) (b)

Figure 6 The surface oxidised for 11 h.



(a) (b)

Figure 7 The surface oxidised for 19 h.



(a) (b)

Figure 8 The surface oxidised for 40 h.

cone boundaries. Thus the oxidised surface assumes interference colours because of the lack of uniformity in the thickness of the SiO_2 film. When the specimen, covered with a thick film of SiO_2 produced by prolonged oxidation, is dipped into hydrofluoric acid, the SiO_2 dissolves and the flat oxidised surface becomes pebble-like, as shown in fig. 9c. The lack of interference colours on the *cross-section* surface is caused by its *uniform* oxidation.

From these observations, it is concluded that SiC does not segregate in PG(Si).

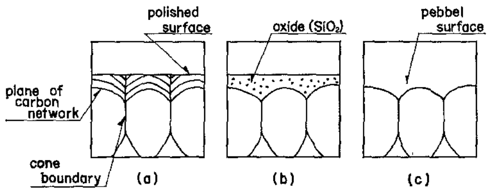


Figure 9 Change in the surface with oxidation and hydrofluoric acid treatment: (a) before oxidation; (b) after oxidation; (c) after HF-treatment.

3.3. X-ray Microanalysis

As described above the results of surface oxidation indicate that SiC does not segregate in the cone boundaries. To confirm this, an X-ray microanalysis was carried out on the c-plane and the cross-section surface.

Fig. 10 shows the results obtained for the samples (A, B, C) listed in table II: the positions of the cone boundaries are marked by arrows. No changes in silicon content are observed at the cone boundaries in either the c-plane or the cross-section. The counts from the c-plane were the same as those from the cross-section. From the counting rate, the amounts of silicon in each sample were calculated using the following equation:

$$C_{\mathrm{Si}} = (N_{\mathrm{Si}} - N_{\mathrm{B}})/(N_{(\mathrm{Si})} - N_{(\mathrm{B})}),$$

where C_{Si} = amount of silicon in PG(Si), N_{Si} = counts of silicon in PG(Si), N_{B} = counts of background of PG(Si), $N_{(\mathrm{Si})}$ = standard counts of silicon, $N_{(\mathrm{B})}$ = standard counts of background.

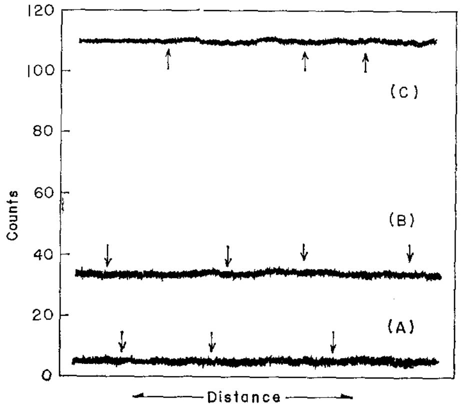


Figure 10 The results of an X-ray microanalysis for three kinds of samples. (A) 0.018 wt % Si; (B) 1.0 wt % Si; (C) 3.8 wt % Si; ↓, the positions of the cone boundaries.

The amounts of silicon thus calculated are as follows: A = 0.034 wt % (0.018 wt %), B = 0.97 wt % (1.0 wt %) and C = 3.73 wt % (3.8 wt %). The values obtained in the preceding paper [3] are shown in parentheses.

The results of the X-ray microanalysis show that SiC does not segregate in the cone boundaries, but disperses uniformly.

3.4. Electron Microscopic Observation and Electron Diffraction Analysis

The results of the X-ray diffraction analysis show that silicon in PG(Si), prepared in the temperature range of 1400 to 1700° C, forms β-SiC, and that the crystallite size of β-SiC in the [1 1 1] direction is about 200 Å for the sample (Si = 3.8 wt %) prepared at $T_{\mathrm{dep}} = 1440°$ C, $P_{\mathrm{total}} = 50$ torr and $P_{\mathrm{SiCl_4}} = 13$ torr. Moreover, the results of the surface oxidation experiment and the X-ray microanalysis indicate that SiC does not segregate in the cone boundaries and disperses throughout a specimen. To determine the morphology and the state of dispersion of SiC, the powdered samples were observed by electron microscopy and electron diffraction.

Figs. 11a, b, and c show the results obtained on the same sample (Si = 3.8 wt %). It is observed that flakes are dispersed in the graphite matrix. A typical selected area diffraction pattern of a flake is shown in fig. 11c. The weak rings and the spots indicate the graphite matrix and β-SiC, respectively. This result shows that the flake is a single crystal of β-SiC. The diameters of the flakes shown in figs. 11a and b are about 2000 Å. Moreover, the intensity of the transmitted electron beam indicates that the flakes are fairly thin. The indices of the spots, and the direction of the flake axes relative to the incident beam will be described below.

Fig. 12 shows the result for a sample containing 1.1 wt % Si ($T_{\mathrm{dep}} = 1535°$ C, $P_{\mathrm{total}} = 50$ torr, $P_{\mathrm{SiCl_4}} = 13$ torr). The size of β-SiC decreases as the silicon concentration is lowered. However, the diffraction spots are also observed for this sample. This shows that the β-SiC is monocrystalline, regardless of the amount of silicon.

As shown in figs. 13a and b, which were obtained from a sample containing 0.021 wt % Si ($T_{\mathrm{dep}} = 2025°$ C, $P_{\mathrm{total}} = 50$ torr, $P_{\mathrm{SiCl_4}} = 13$ torr), the flakes of β-SiC are not observed and the diffraction pattern shows only the rings for graphite.

The typical diffraction pattern obtained from various samples is shown in fig. 14, in which the

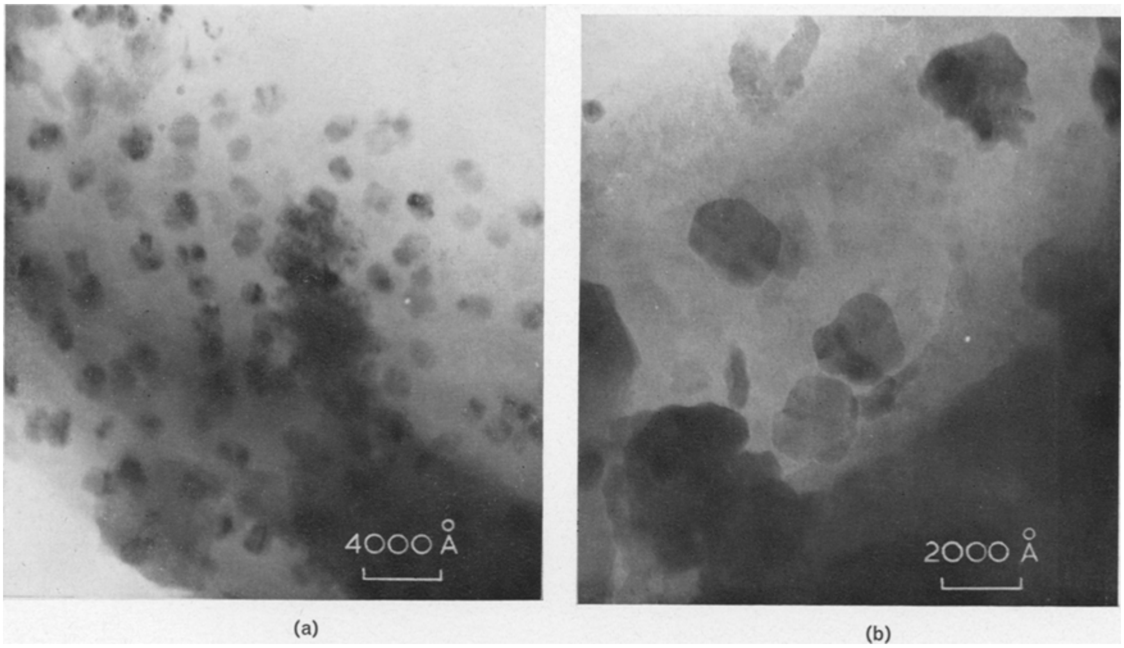


Figure 11 Electron micrographs and electron diffraction pattern of the sample containing 3.8 wt% Si (T_{dep} = 1440° C; P_{total} = 50 torr; P_{SiCl_4} = 13 torr). (a) DM×16 500; (b) DM × 32 900; (c) electron diffraction pattern obtained from a second-phase particle.

rings from graphite and the spots from β-SiC are indexed. The rings of the (001) planes of graphite are not obtained, which shows that these planes are perpendicular to the incident beam. The diffraction pattern in fig. 14 has a sixfold rotation symmetry and the spots correspond to the {1 1 1}, {3 1 1} and {3 3 1} reflections, so that the incident beam is parallel to the [1 1 1] direction of the β-SiC crystal. Thus, a (1 1 1) plane of β-SiC is parallel to the (001) planes of graphite, as shown in fig. 15.

Powdered samples of PG show a considerable degree of preferred orientation when mounted in a sample holder, and only the (001) reflection lines appear strongly. Since β-SiC exists in PG(Si) as shown in fig. 15, it orients with the crystallite of graphite. Thus the 200 Å crystallite size of β-SiC, obtained from the line width of the (1 1 1) reflection line shown in fig. 4, corresponds to the thickness in the direction of the *c*-axis shown in fig. 15.

For a face-centred cubic lattice the {2 2 0} and {4 2 2} spots ought to appear generally, but in fact the {1 1 1}, {3 1 1} and {3 3 1} spots are clearly observed in this experiment. These results indicate that the reciprocal lattice points are streaked out parallel to the direction of the incident beam i.e. the [1 1 1] direction. The following possible reasons for the streaking are considered: (a) the sample thickness is as small as 20 to 30 Å; (b) stacking faults exist in the samples. Since the thickness is about 200 Å

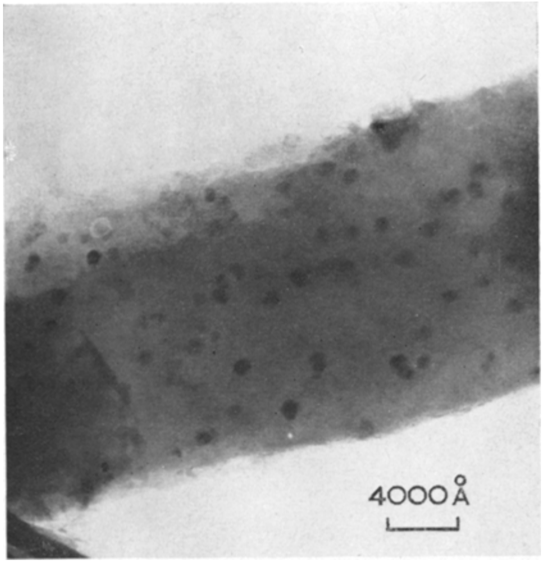


Figure 12 Electron micrograph of the sample containing 1.1 wt % Si ($T_{\mathrm{dep}} = 1535°$ C; $P_{\mathrm{total}} = 50$ torr; $P_{\mathrm{SiCl_4}} = 13$ torr).

the first reason may be neglected. On the other hand, it is well known that many structures differing in the stacking types exist in SiC crystals, and that they transform mutually.

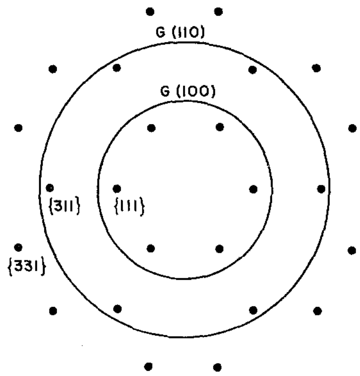


Figure 14 Typical electron diffraction pattern of PG(Si) containing a large amount of silicon: G reflection rings of graphite; ● reflection spots of β-SiC.

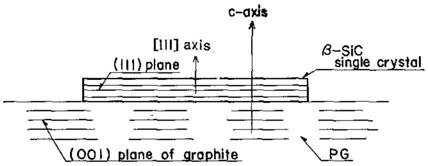
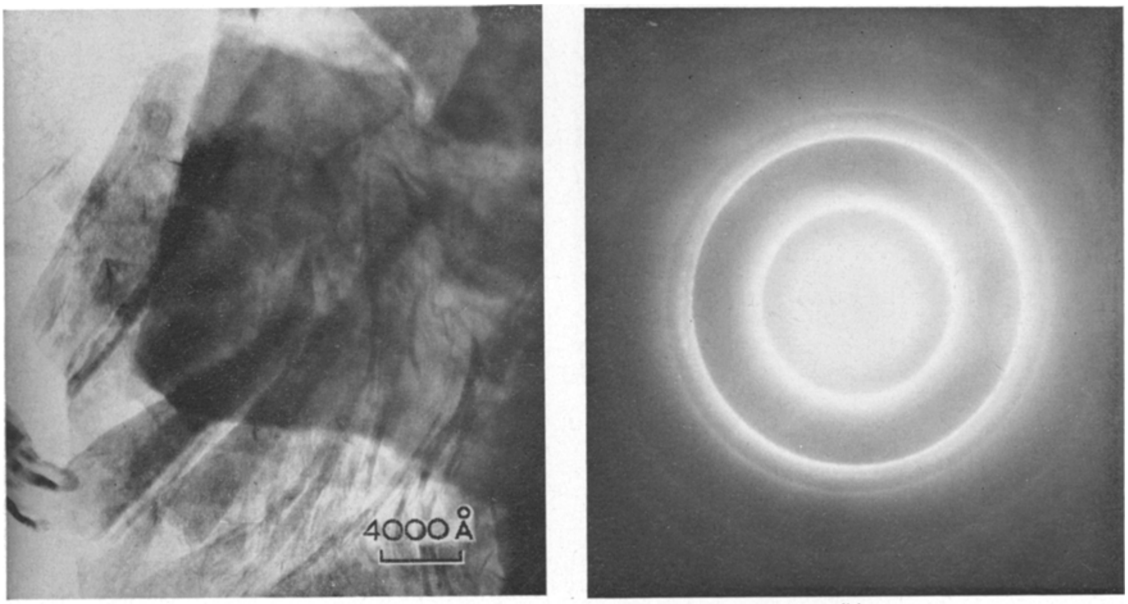


Figure 15 Mutual arrangement of graphite matrix and β-SiC single crystal.



(a) (b)

Figure 13 Electron micrograph (a) and electron diffraction pattern (b) of the sample containing 0.021 wt % Si ($T_{\mathrm{dep}} = 2025°$ C; $P_{\mathrm{total}} = 50$ torr; $P_{\mathrm{SiCl_4}} = 13$ torr).

Moreover, the reflection lines of α-SiC seem to be observed with the diffraction pattern of β-SiC in this experiment. These facts show that many stacking faults are included in the crystal of β-SiC obtained here. Thus, we conclude that the appearance of the {1 1 1}, {3 1 1} and {3 3 1} spots follows from reason (b).

4. Summary

1. In PG(Si) containing a large amount of silicon the greater part of the silicon forms β-SiC.
2. The β-SiC is present as flake-like single crystals, whose size decreases with increasing temperature. Silicon seems to form α-SiC in PG(Si) containing a small amount of silicon, prepared at the high temperatures near about 2000° C.
3. The lattice parameter of β-SiC in PG(Si), obtained in this experiment, is 4.358 Å.
4. The results of the surface oxidation experiment and the X-ray microanalysis show that SiC does not segregate in the cone boundaries and disperses uniformly in PG(Si).
5. A (1 1 1) plane of β-SiC is parallel to the (001) planes of graphite.
6. The crystallite size of β-SiC is about 200 Å (thick) by about 2000 Å (diameter), when prepared at $T_{\mathrm{dep}} = 1440°$ C, $P_{\mathrm{total}} = 50$ torr and $P_{\mathrm{SiCl_4}} = 13$ torr.

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References

1. A. R. UBBELOHDE and F. A. LEWIS, "Graphite and its Crystal Compounds" (Oxford University Press, 1960).
2. R. N. KATZ and C. P. GAZZARA, *J. Materials Sci.* **3** (1968) 61.
3. S. YAJIMA and T. HIRAI, *ibid* **4** (1969) 416.
4. M. H. READ, ASTM Card, 12-212.
5. H. THIBAULT, ASTM Card, 1-1119.
6. P. J. JORGENSEN, M. E. WADSWORTH, and I. B. CULTER, "Silicon Carbide", edited by J. R. O'Connor and J. Smiltens (Pergamon Press, Oxford, 1960) p. 241.