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Phase Transformations and Grain Growth in Silicon Carbide Powders

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SUMMARY

The phase transformations, grain growth and habit changes occurring during annealing of different cubic silicon carbide powders have been studied in a semi-closed silicon carbide–carbon system. Variations in the process parameters—time, temperature, gas atmosphere and impurity content—have been investigated. It has been shown that the time parameter is an important factor that has to be taken into consideration when comparing the results of different experiments. Both the rate of transformation and of grain growth changed dramatically under different process conditions. The presence of certain impurities (aluminium, boron, nitrogen) was found to be the most important factor affecting the phase transformation and polytype distribution as well as the grain growth and resulting particle forms. These impurities stabilize certain modifications and enhance or slow down the grain growth in specific crystallographic directions. They also enhance or lower the rate of transformation. The rates of transformation and grain growth were found to be dependent on the dimension of the specific surface area of the powder. This shows that the rate-controlling step involves surface processes. The observed influences of the individual parameters on the phase transformation and grain growth have been found to act in a cumulative way when occurring simultaneously.

1. INTRODUCTION

Silicon carbide can be found in many different crystallographic modifications. These differ from each other only in their stacking order in the

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[0001] direction. There are four most common silicon carbide polytypes. The only cubic polytype, 3C, is mainly obtained when silicon carbide is synthesized below 2000 °C, the 6H and 4H hexagonal and 15R rhombohedral modifications being usually produced above 2000 °C. Many investigations on polytype formation and transformation have been performed, but the relevant mechanisms are still not fully understood.

In a fairly recent and extensive review[1] of polytypic transformation in silicon carbide the results of many investigations were collected, discussed and compared. Jepps and Page[1] tried to establish a coherent view of the possible mechanics and kinetics of such transformations. Their most important conclusions can be briefly summarized as follows:

— A number of different transformation mechanisms can occur, often in parallel, and these account for the wide range of transformation kinetics observed. The results from single crystal experiments suggest a solid-state mechanism, whilst the transformation kinetics of powdered and compact specimens are more consistent with a vapour or a surface fast transport mechanism. However, it appears that this latter mechanism requires either a pre-existing nucleus of the new polytype to be present, or this nucleus to be formed by solid-state transformation.

— Most measured values for the activation energies of the transformation in powdered samples approximate to the sublimation energy. This is interpreted as indicating that the obtained activation energies are associated with the growth rather than the nucleation stage of transformation.

— The fast material transport responsible for the observed high transformation rates in polycrystalline specimens also results in grain growth and recrystallisation.

— The important role of impurities in the transformation was pointed out. These seem to influence behaviour at all levels: they can possibly stabilize particular structures; they can provide liquid films for rapid transport during transformation. Evidence is given that electronically p-type materials (e.g. boron and aluminium) stabilize layers in hexagonal environments, while n-type materials (e.g. nitrogen and phosphorus) tend to stabilize layers in cubic environments.

— A relatively large number of observations of transformations have been described, but only a few studies have tried to make any form of detailed analysis of reaction kinetics.

Despite the many known facts it is still not possible in the case of real systems to predict the properties of silicon carbide powders. The simultaneous effects of a variation of the process parameters, such as temperature, time, gas atmosphere, impurity content and starting material, on the phase transformation, grain growth and sintering of the powder are not well known. Also the interactions of various influences (e.g. the influence of impurities on transformation kinetics) are almost unknown.

This investigation tries to obtain more data on the interactions of the various factors found to influence silicon carbide powders. It attempts to answer the question of whether from each β-silicon carbide powder a desired α-silicon carbide powder can be obtained simply by varying the process parameters, or whether the properties of the starting material determine the properties of the resulting powder.

2. EXPERIMENTAL

2.1. Starting materials

Five different manufactured types of β-silicon carbide powder were used as starting materials. Table 1 gives details of these materials and Table 2 summarizes the properties most important to this investigation. The powders differ either in their particle size or in their content of various impurities.

TABLE 1
Starting Materials

Trade name	*Manufacturer*	*Material code*
B 10	H. C. Starck, FRG	HB
A 10	H. C. Starck, FRG	HA
Betarundum ultrafine	Ibiden, Japan	BU
Betarundum standard	Ibiden, Japan	BS
'Experimental' powder	Philips, The Netherlands	PB
'Experimental' powder	Lonza, Switzerland	LB

2.2. Techniques

The experimental arrangement allowed rapid heating of a silicon carbide powder sample ($\simeq 20$ g) in a graphite crucible to the required annealing temperature. The crucible was closed with a lid, but was not gas tight. The crucible was heated with a high frequency generator. The time taken to heat the sample to 2000 °C was less than 3 min. The annealing temperature was varied between 1700 and 2400 °C and was measured with an optical

TABLE 2
Properties of the Starting Materials

Powder code	$S/m^2\,g^{-1}$	$r/\mu m$	*Impurity elements/wt %*				
			Al	*B*	*Fe*	*O*	*N*
HB (β)	14·2	0·7	0·15	0·01	0·02	0·4	0·01
BU (β)	18·7	0·29	0·03	nd	0·03	0·06	0·03
BS (β)	12·2	0·33	0·04	nd	0·03	na	na
PB (β)	0·006	1000	0·03	0·01	0·03	na	na
LB (β)	5·8	1·7	0·79	0·01	0·36	na	na
HA (α)	15·0	0·6	0·02	0·01	0·01	0·4	na

S = specific surface area.
r = mean particle size.
nd = not detected.
na = not analysed.

pyrometer. The time of annealing was varied between 0 and 240 min. After annealing the crucible was quickly removed from the heating zone to a fast-cooling zone. The static gas atmosphere could be argon, nitrogen or carbon monoxide up to 1 atm, or 'vacuum' (0·001 atm). The starting powders were partly doped with aluminium, aluminium oxide, boron, iron oxide, silicon dioxide, or carbon, or a mixture of these.

2.3. Analyses

After annealing, the polytype distribution was measured by X-ray diffraction (automatic diffractometer, Scintag/Seifert) and calculated according to the method of Ruska *et al.*[2] Scanning electron microscope (SEM) pictures of the powder were used to observe the grain growth and resulting habit change. The particle sizes were determined indirectly by calculation from measured values of the specific surface area. The specific surface area was measured by krypton adsorption and calculated with the help of the BET[3] equation.

Spectrochemical analysis (spark emission) was used to establish the impurity content of the powders.

3. RESULTS

A 'standard experiment' was performed initially to serve as a reference. The particle form, modification, rate of transformation and of grain growth, resulting from the variation of various parameters in the subsequent experiments, have been compared with the properties of the powder obtained in the standard experiment.

Most of the experiments were performed with the powders BU and HB; the other powders were only available in smaller quantities and therefore were used only for special experiments (e.g. powder PB, with an extremely small specific surface area, was used in experiments for establishing the influence of the specific surface area on transformation).

3.1. Standard experiment

The standard experiment was performed with a minimum number of factors affecting the resulting product specifications. The factors related to the manufacturing conditions (e.g. 'history' of the sample) could not be eliminated. The related parameters will be discussed when comparing the behaviour of different β-silicon carbide powders with almost identical specifications.

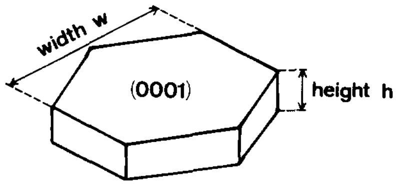


Fig. 1. Form of SiC-grains after annealing of powder BU, standard experiment.

Starting from very pure and fine-grained cubic silicon carbide (BU) the annealing was performed in an argon atmosphere which can be assumed inert. The powder showed the following behaviour (Fig. 1, Table 3):

- The transformation started at about 2000 °C and the resulting powder was predominantly of the 6H type.
- A large grain growth occurred during annealing. Big hexagonal platelets were formed; practically no sintering was observed.

3.2. The influence of the variation of time and temperature

The same powder (BU) as in the standard experiment was used for the following experiments. However, here the time of annealing was varied from 1 to 240 min and the temperature from 1700 to 2400 °C. Figure 2 shows the results for the transformation of 3C. The transformation at low temperature is very slow, so that in the investigated period of time the transformation did not proceed to completion.

TABLE 3
Example: Powder BU Before and After Annealing for 60 min at 2 150 °C

Treatment	*Polytype distribution*	$S/m^2\,g^{-1}$	$w/\mu m$	$h/\mu m$
—	100% 3C	18·7	0·05	0·05
60 min, 2 150 °C	90% 6H	0·05	75·0	15·0

S = specific surface area.
w = mean particle width (see Fig. 1).
h = mean particle height (see Fig. 1).

From the Arrhenius plot of the starting transition rates the activation energy of $590 \pm 125\,\mathrm{kJ\,mol^{-1}}$ was determined. This value is comparable with values found in the literature.[1] It is also similar to the value for the heat of sublimation of silicon carbide.[1]

The predominantly formed polytype was of the 6H type. The total amount of 4H and 15R was always below 10%.

The higher the temperature the better developed the particles, but the particle size seems to reach a maximum value. Above a certain temperature (>2100 °C) this maximum is independent of the annealing temperature. Below 2000 °C practically no grain growth was observed. Figure 3 shows the time dependence of the specific surface area of the powder for two different annealing temperatures.

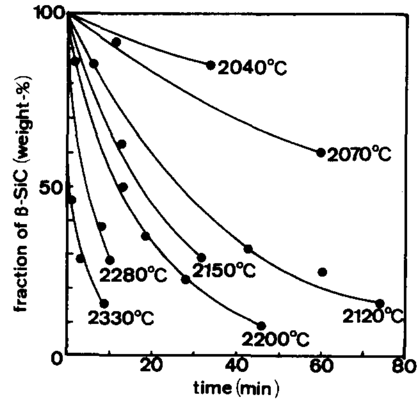


Fig. 2. Transformation of β-SiC at different annealing temperatures (powder BU, argon atmosphere).

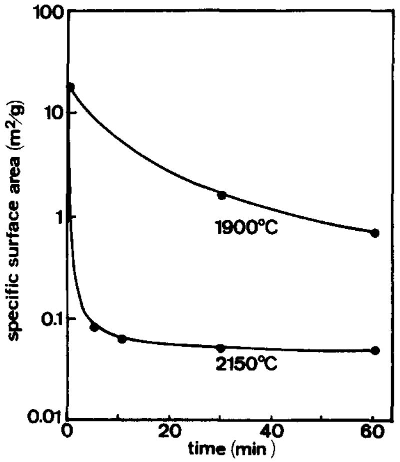


Fig. 3. Specific surface area of silicon carbide powder after annealing at different temperatures (powder BU, argon atmosphere).

These experiments illustrate very clearly that the time factor must be taken into consideration when comparing results which have not been obtained under the same conditions. Many existing contradictions in the literature can be traced to the neglect of the time factor (e.g. the time of annealing).

3.3. Influence of the specific surface area of the powder

The experiments were carried out with the very fine-grained powder BU, the very coarse-grained powder PB and with ground powder PB. The powders PB and BU have very similar specifications except that the particle size is totally different. It could be shown that the rate of transformation was proportional to the dimension of the specific surface area of the powder under otherwise similar conditions (Fig. 4).

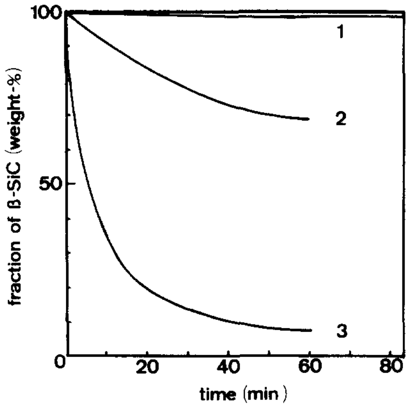


Fig. 4. Transformation of β-silicon carbide powders with different specific surface areas (argon atmosphere, 2200 °C). 1, powder PB, specific surface area = $0{\cdot}006\,m^2\,g^{-1}$; 2, powder PB (ground), specific surface area = $0{\cdot}8\,m^2\,g^{-1}$; 3, powder BU, specific surface area = $18{\cdot}7\,m^2\,g^{-1}$.

A graphical determination of the starting rate of transformation (slope of the transformation curve at the beginning) revealed that the rates are proportional to the starting specific surface areas of the employed powders. Due to the fact that in these experiments the specific surface areas are known exactly only at the start of the experiment, only the initial rates of transformation are compared. The specific surface areas at different stages of reaction could not be determined separately for the different polytypes. Only the overall values could be measured.

Powder annealed at a certain temperature where the transformation proceeded very slowly, due to the small specific surface area available, was ground and annealed again. The further transformation then occurred much faster than before. These results can be interpreted as showing that the transformation is controlled by surface mechanisms; it is certainly not only an *in situ* rearrangement of the crystal layers.

3.4. Influence of the impurity content of the powder

We next consider if the results found for the powder BU are also valid for the other starting materials consisting of β-silicon carbide. The experiments performed with the powder BU were repeated with the powder HB. Large differences in the resulting properties of the powders have been found (Table 4).

The question arose as to what causes these differences and would it be possible to obtain the same powder after annealing simply by changing the process conditions. The greatest difference between the two powders was in their aluminium content. Therefore, the next experiments were performed with powder BU doped with different amounts of aluminium. With a certain aluminium addition, powder BU could be induced to behave like powder HB with only minor remaining differences. These could be due to a different defect content of the two powders, which was not measured during this investigation.

Other impurity additions were also checked for their influence on the resulting powders. The influence of the following additions were studied: aluminium oxide, aluminium, boron, ferric oxide, silicon dioxide and carbon. Furthermore the transformation was carried out under a nitrogen or carbon monoxide atmosphere, both of which can also be regarded as impurities. Each addition was not restricted to one impurity at a time. The additions were varied between 0 and 2 wt %. It was found that not all of the impurities had the same effects on the behaviour of the powder. Some, such

TABLE 4
Comparison of the Behaviour of Powders BU and HB During Annealing

Powder code	*T/°C*	*Polytype distribution*	*w/μm*	*h/μm*	*S/m² g⁻¹*
BU	2 000	90 % 6H	75·0	15·0	0·05
HB	1 800	20 % 4H, 70 % 6H	40·0	10·0	0·1

T = starting temperature of transformation.
w = mean particle width (see Fig. 1).
h = mean particle height (see Fig. 1).
S = specific surface area after annealing at 2 200 °C.

as aluminium, aluminium oxide, boron and nitrogen, had a very strong influence, others had practically none at all. Oxygen, which is the major impurity in most starting powders, could not be investigated properly, due to the reducing power of the graphite in the annealing environment. No traces of oxygen in the powder could be detected, even after short annealing times.

The impurities which affected the resulting silicon carbide powder most strongly were those which form similar compounds and can presumably be incorporated more easily into the silicon carbide lattice. The effects of the impurities are described below in greater detail.

3.4.1. The rate of transformation

Figure 5 shows the transformation with and without addition of aluminium and aluminium oxide to the powders BU and HB, where the aluminium content of powder HB is higher due to the manufacturing process. It has been found that aluminium enhanced the rate of transformation independently of whether a powder had a relatively high aluminium content or a pure powder was doped with aluminium. Even very small amounts (0·05 wt %) had a significant influence. The rates of formation of both hexagonal polytypes, 4H and 6H, were promoted. No differences in the behaviour of powders doped with aluminium or aluminium oxide were found, only the total amount of aluminium was important.

The addition of boron also had a similar influence, but only the rate of formation of 6H was enhanced, although 4H was the more stable polytype.

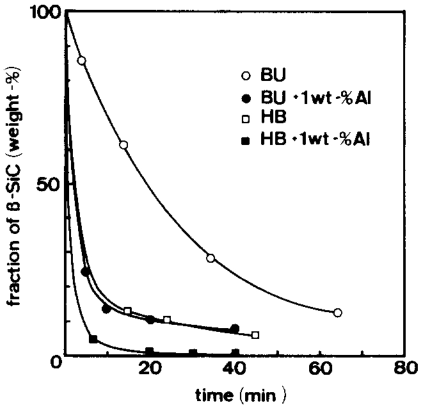


Fig. 5. Influence of the addition of aluminium (in the form of aluminium or aluminium oxide) on the transformation of powders BU and HB (argon atmosphere, 2150 °C).

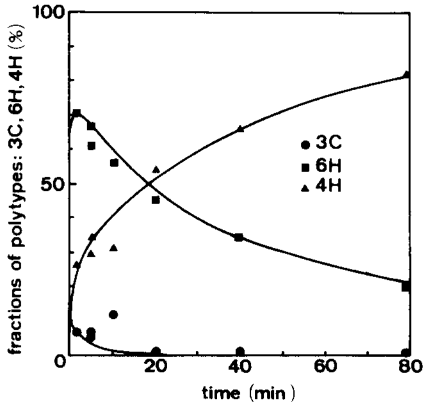


Fig. 6. Amount of different polytypes after annealing of powder BU doped with 2 wt % boron (argon atmosphere, 2150 °C).

Polytype 6H was formed only as an intermediate; after longer annealing times the predominant polytype was 4H. Fig. 6 shows the results.

Annealing the powder in a nitrogen atmosphere enabled comparison of the results with other investigations. It could be clearly demonstrated that nitrogen will retard the transition as shown by Kieffer *et al.*[4]

3.4.2. *The polytype distribution at 'equilibrium'*

Only the very fine-grained powders, which showed a large transformation rate, reached 'equilibrium states' (that is when no further changes occurred) in polytype distribution. Even if these powders were cooled, ground and annealed again, the polytype distribution did not change any more. Figure 7 shows the polytype distribution for different amounts of impurities of (a) aluminium and (b) boron.

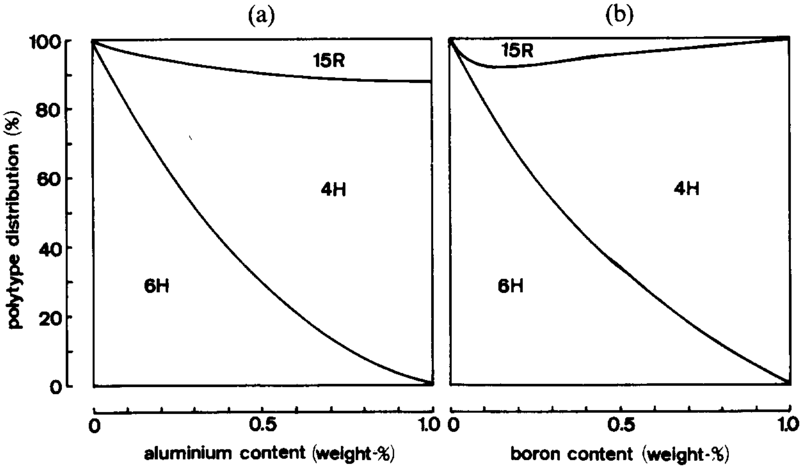


Fig. 7. Polytype distribution after annealing for typically 6 h (equilibrium state) for SiC powders BU, HB, PB, LB, BS and HA doped with different amounts of (a) aluminium and (b) boron.

Almost pure cubic silicon carbide powder (BU), which was transformed to practically pure 6H, can be ground and doped with aluminium and annealed again. The 6H powder is then transformed to 4H, the extent being dependent on the aluminium addition. This shows that some impurities stabilize certain modifications and that the effects of the impurities are not restricted to a kinetical influence only.

In order to distinguish between built-in and superficial impurities, the impurity content of the powder was measured twice after annealing. First without pretreatment and then again after washing the sample and removing superficial impurities (Tables 5 and 6). It was found that practically the

TABLE 5
Boron Content after Different Annealing Conditions of Powders BU and HB Doped with Boron

Boron addition/wt %	*T/°C*	*t/min*	*Boron content/wt %*	
			(1)	*(2)*
1·25	2 150	20	0·33	0·13
1·25	2 150	20	0·37	0·16
2·0	2 150	80	0·62	na
2·0	2 000	80	1·00	na

T = temperature of annealing.
t = time of annealing.
(1) = without pretreatment.
(2) = after pretreating with HF/H_2SO_4, $KHSO_4$-melt and HCl.
na = not analysed.

whole amount of aluminium was built into the powder (2 wt % maximum). Boron, on the other hand, could only be incorporated to a much smaller extent (0·5 wt %). The higher the annealing temperature the smaller the impurity content found after the treatment, with the same amount of impurities added before the annealing. A very long annealing time also causes a decrease in impurity content with the chosen experimental set-up.

3.4.3. The particle form

The impurity content was found to have a large influence on the grain

TABLE 6
Aluminium Content after Different Annealing Conditions of Powders BU and HB Doped with Aluminium

Aluminium addition/wt %	*T/°C*	*t/min*	*Aluminium content/wt %*	
			(1)	*(2)*
1·25	2 150	40	0·46	0·41
1·25	2 150	40	0·47	0·44
1·25	2 150	10	0·61	na
1·25	2 300	10	0·07	na

T = temperature of annealing.
t = time of annealing.
(1) = without pretreatment.
(2) = after pretreating with HF/H_2SO_4, $KHSO_4$-melt and HCl.
na = not analysed.

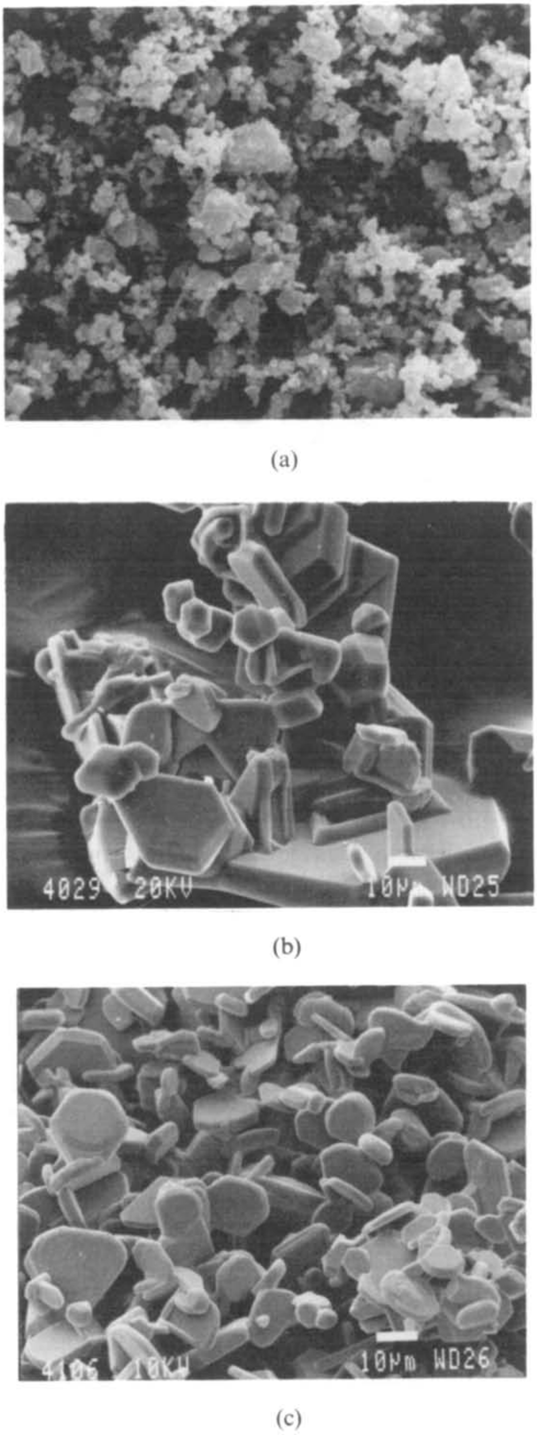
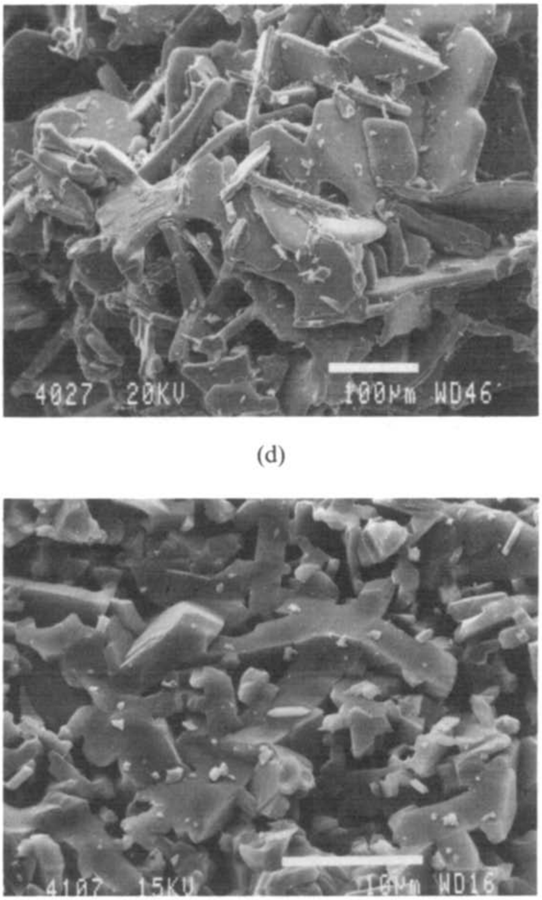


Fig. 8. (a) BU before annealing, 100% 3C (magnification ×3000); (b) BU after annealing (31 min, 2150°C, Ar), 52% 6H, 29% 3C (magnification ×530); (c) BU + 4 wt% Al after annealing (60 min, 2000°C, Ar), 77% 4H (magnification ×600).



(d)

(e)

Fig. 8—*contd.* (d) BU + 2 wt % B after annealing (40 min, 2150 °C, Ar), 34 % 6H, 44 % 4H (magnification × 125); (e) HB + 1 wt % Al + 1 wt % B after annealing (60 min, 2000 °C, Ar), 72 % 4H (magnification × 2000).

growth. SEM-pictures (Fig. 8) show the results. Figure 8(a) represents powder BU before annealing; powder HB has a similar appearance. Figure 8(b) shows the powder BU after annealing for 31 min at 2150 °C in an argon atmosphere. The hexagonal platelets can be seen, as shown diagrammatically in Fig. 1 for the standard experiment. No small particles as in the starting material can be recognized, although 30 % of the powder is still β-silicon carbide. This figure shows that β-silicon carbide particles also have grown under these process conditions.

In contrast to the behaviour of powder BU, there were particles in the powder HB which did not change their habit at all. The whole of powder HB showed a reduced grain growth. As already mentioned powder HB has a higher aluminium content than powder BU. Figure 8(c) shows powder BU doped with aluminium. Aluminium enhances the growth in the [0001] direction and slows down the growth perpendicular to the [0001] direction; very regular particles of smaller size are formed than in the standard experiment. However, it was not possible to simulate exactly the behaviour of powder HB; small differences remained. In the doped powder BU particles with the size of the starting material were not found; all the grains exhibited grain growth. It seems that only the aluminium incorporated in the grains influences the growth rates. At the beginning of the annealing of the doped powder the aluminium is only superficially distributed. Powder HB with an already higher aluminium content has the aluminium at least partially incorporated in the grains. However, at 'equilibrium' both powders looked the same.

Boron enhances the growth perpendicular to the [0001] direction. Large thin platelets are formed with fairly rounded edges (Fig. 8(d)). The edges appear to be molten. Both aluminium and boron enhance the sintering of the powder, but the strongest sintering was observed with the addition of aluminium and boron simultaneously, as can be seen in Fig. 8(e). In this case practically no single particles can be seen.

4. DISCUSSION

The described experiments show that the factors affecting grain growth, habit changes and transformation are manifold and strongly related to each other. The properties of the resulting powder are influenced by the time and temperature of annealing, and by the rate of heating and cooling, but the most important factor was found to be the impurity content of the powder.

The results obtained in this work confirm many of the conclusions drawn in the review of Jepps and Page.[1] In accordance with their assertions, it was also found that the content of special impurities in the powder is decisive for the formation of certain polytypes. It seems reasonable to assume that pure cubic silicon carbide transforms to the pure 6H polytype in the absence of impurities. All other polytypes are stabilized by different impurities. Furthermore, this work clearly demonstrates that the impurities also influence the rates of transformation and the grain growth. Also the particle form and size and the polytype are strongly influenced by the impurities. In addition the 'history' of the sample affects the behaviour of the resulting powder essentially through the impurity content.

Another important result was that the specific surface area was found to be one of the parameters which control the rates of transformation. The rate of transformation is proportional to the specific surface area of the powder, under otherwise identical conditions. This is further evidence that the transformation not only proceeds by an *in situ* rearrangement of the layers but also involves surface diffusion mechanisms.

The grain growth starts above 1900 °C; to a great extent, only nucleation is dominant below this temperature. Since for grain growth a certain vapour pressure is needed, this presumably indicates that the vapour phase is involved in the grain growth mechanisms. The starting temperature of grain growth can be shifted by impurities. In contrast to other studies a large grain growth of untransformed powder was also observed under conditions where, in spite of high annealing temperatures, no, or only slow, transformations of β-silicon carbide was observed (e.g. in a nitrogen atmosphere). No relationship between certain polytypes and particle forms was observed.

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