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Low-temperature synthesis of sinterable SiC powders by carbothermic reduction of colloidal SiO_2

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β-SiC powders were synthesised by carbothermic reduction of carbon-black doped silica gel. The morphological characteristics of the resulting powders depend on the morphology of precursor carbon black as well as the reaction conditions. A model for particle coarsening during carbothermic reduction is presented, suggesting that surface diffusion may be responsible for the formation of polycrystalline aggregates, while at higher reaction temperatures volume diffusion is operative. Processing consisting of decarburization, HF treatment and sedimentation but no milling is required to convert crude reaction products into sinterable powders. After doping with boron and carbon they can be sintered to 98–99% of theoretical density which, in general, is better than or comparable to results obtained with commercial β-SiC powders which were also included in the present study.

1. Introduction

Advanced ceramic materials based on silicon carbide require extremely fine and chemically pure starting powders. In general, the average particle size should be about 0.5 μm, while particles coarser than 3–5 μm are harmful. An oxygen content up to 1 wt % and 0.5 wt % nitrogen and metallic impurities can be tolerated.

Various methods have been used to produce submicrometre SiC powders, and can be roughly classified into two categories: (a) carbothermal reduction of silica (including the classical Acheson process) and (b) pyrolysis of silane compounds. Extensive milling and purification procedures are necessary in order to convert Acheson α-SiC into sinterable powder. Laser- or plasma-driven chemical vapour deposition (CVD) methods were shown to produce very fine and pure SiC powders [1, 2]; however, it is difficult to envisage the industrial application of these methods in the near future. In contrast, the synthesis of β-SiC by carbothermal reduction of SiO_2 can be easily scaled up, and the process designed for continuous rather than batch production [3, 4]. Fine particles can be obtained, in principle, directly since the particle size of the resultant SiC can be controlled by the size of the carbon and silica particles in the reaction mixture [5].

Accordingly, in order to optimize the appearance of submicrometre SiC particles and improve the kinetics of carbothermal reduction, several authors have used fine starting reactants (colloidal silica and carbon black) and a reaction mixture prepared by the sol–gel technique, or by pyrolysis of silicon- and carbon-containing compounds [6–8]. Most reported data indicate, however, that in spite of finely dispersed and well-homogenized reaction mixtures, milling of the resulting β-SiC powders was necessary prior to sintering or hot-pressing in order to obtain high final densities [5, 9]. This implies that SiC particles grow extensively during carbothermic reduction, which in turn is reflected in the reduced sinterability of the powder.

In the present study an attempt was made to synthesize sinterable β-SiC powders by carbothermic reduction in high yield, without the need of a milling step. It is demonstrated that particle size and reaction yield can be controlled efficiently, provided the reaction mechanisms, the thermodynamic background as well as the kinetic parameters are adequately understood.

2. Experimental procedure

The procedure involves (i) powder preparation, (ii) processing and (iii) sintering. Colloidal silica (Cab-O-Sil, Cabot, $S = 200\ m^2\ g^{-1}$) and two grades of carbon black: (a) Hoechst, $S = 70\ m^2\ g^{-1}$ and (b) Cabot, $S = 560\ m^2\ g^{-1}$ were used as starting materials for carbothermic reduction. In some experiments, 0.6 wt % of amorphous boron was also added to the reaction mixture. The mixtures were homogenized in acetone, which was subsequently removed by evaporation with constant stirring in order to maintain a uniform distribution of the reaction components. Carbothermic reduction was performed in a graphite crucible *in vacuo* (≈ 1 Pa), at temperatures between 1150 and 1500 °C for 0.5 to 2 h.

The chemical purification of the synthesized powders involved the removal of excess carbon by heating the powders in air at 750 °C for 24 h, while two procedures were used in order to remove SiO_2: washing of powders with hydrofluoric acid at 60–90 °C or exposing them to a flow of dry gaseous HF at 600 °C.

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Further processing of the synthesized powders involved gravitational sedimentation and vacuum filtration. Slurries for sedimentation studies, as well as for the measurement of particle size distribution, were prepared by dispersing β-SiC powders in water at pH = 11, adding Lomar-D (Diamond Shamrock, Chemical Product AG) as a wetting agent.

Vacuum filtration was performed using a 0.8 μm membrane filter (Sartorius, SM 11404). After filtration, in order to achieve the flocculation of β-SiC particles, the pH of the slurry obtained was adjusted to be neutral. The flocculated β-SiC particles were then collected by centrifugal sedimentation (0.5 h, 5000 min^{-1}, 10 °C).

The examination of the resulting powders involved chemical analysis of free carbon and oxygen [10, 11], X-ray diffraction to identify the crystalline phases in the powders, determination of BET surface area and the analysis of particle size distribution. TEM was used to reveal the morphology of ultrasonically dispersed powders and, especially, the mechanism of coarsening.

In order to study the efficiency of the processing procedures, as well as the importance of different powder characteristics, sintering experiments were also performed using several commercial materials (HCS B-10; Superior Graphite HSC-100 GL; Mitsui Toatsu MSC-20; Ibiden UF 0090) and β-SiC powders prepared in the laboratory. Special emphasis was placed on the effects of particle size distribution and oxygen pick-up during storage on their sinterability.

Powders for sintering studies were doped with constant additions of 0.6 wt % B and 4 wt % C. Boron was added in the elemental form while phenolformaldehyde resin was used as a carbon precursor. Samples were mixed in a planetary ball-mill using a polyethylene jar and balls, isostatically pressed and heated in flowing argon for 4 h at 450 °C to permit carbonization and vaporization of organics. Sintering was performed at 2000–2200 °C for 5 to 60 min in a static argon atmosphere.

Densities of sintered specimens were measured by liquid displacement. The microstructures of samples were examined by reflected-light microscopy after polishing. An etchant consisting of a mixture of equal volumes of 50% KOH (aqueous solution) and a saturated aqueous solution of $K_3Fe(CN)_6$ held at its boiling point was used.

3. Results and discussion

3.1. Low-temperature carbothermal reduction

It has been suggested that the real mechanism of carbothermal reduction is rather complex, but the following reactions seem to be the most important [5]:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \qquad (1)$$

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \qquad (2)$$

The change of free energy ΔG for the above reactions as a function of temperature and pressure is shown in Fig. 1.

Obviously, the temperature where Reactions 1 and 2 become thermodynamically feasible depends strongly on the pressure in the reactor. The reaction temperature (and hence the driving force for particle coarsening) can be strongly reduced by decreasing the pressure from normal to 1–2 Pa. The drop of reaction rate at a lower temperature can be minimized by using finer starting reactants. In this way, at 1300 °C approximately 50% conversion into SiC can be achieved in less than 1 h [12]. However, the loss of SiO(g), caused by pumping off the gaseous products of carbothermic reduction in order to keep the vacuum constant, results in a low reaction yield.

The conversion of $SiO_2(s)$ into SiO(g) (x) and the loss of SiO(g) component (y) during carbothermic reduction can be calculated on the basis of Reactions 1′ and 2′:

$$SiO_2(s) + C(s) \rightarrow x(1-y)SiO(g) + xySiO(g) + (1-x)SiO_2(s) + (1-x)C(s) \qquad (1')$$

$$x(1-y)SiO(g) + 2.3^*C(s) \rightarrow x(1-y)SiC(s) + x(1-y)CO(g) + (2.3-2x+2xy)C(s) \qquad (2')$$

which give for the summary or overall reaction

$$SiO_2(s) + 3.3^*C(s) \rightarrow \overbrace{\underbrace{x(1-y)SiC(s) + (1-x)SiO_2(s)}_{\text{weight of specimen after removal of free carbon}} + (3.3-3x+2xy)C(s)}^{\text{weight of specimen after carbothermic reduction}} + xySiO(g) + (2x-xy)CO(g) \qquad (3)$$

Using the stoichiometry of Reaction 3, x and y can be calculated on the basis of the weight of the specimen after carbothermic reduction and after removal of free carbon. Note that two important assumptions are made in this calculation: (a) the rate-limiting step of carbothermic reduction is the formation of SiO(g) [12]; and (b), conversion of SiO(g) into SiC by Reaction 2 is complete. Values calculated for the weight loss data are presented in Fig. 2. Above 1275 °C both parameters show a tendency to level off. At lower temperatures a significant loss of SiO(g) component with simultaneous decrease of conversion were observed, which resulted in a low yield of β-SiC.

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* 10 wt % of excess of carbon is assumed.

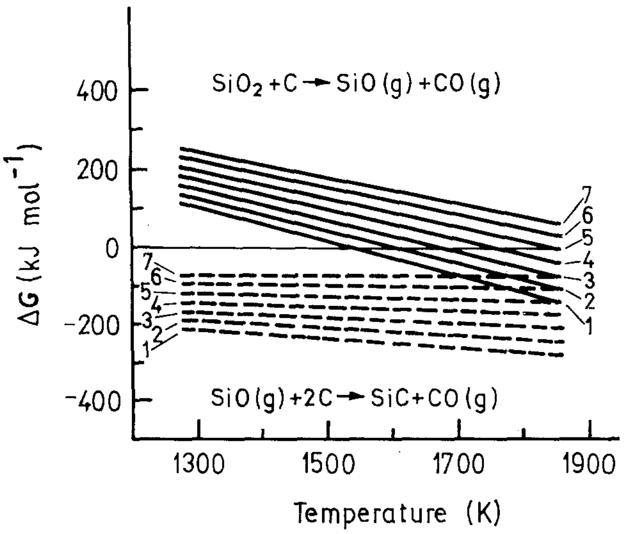

Figure 1 Change of free energy ΔG for Reactions 1 and 2 as a function of temperature and pressure. Pressure: (1) 0.133 Pa, (2) 1.33 Pa, (3) 13.3 Pa, (4) 133 Pa, (5) 1.3 kPa, (6) 13.3 kPa, (7) 133 kPa.

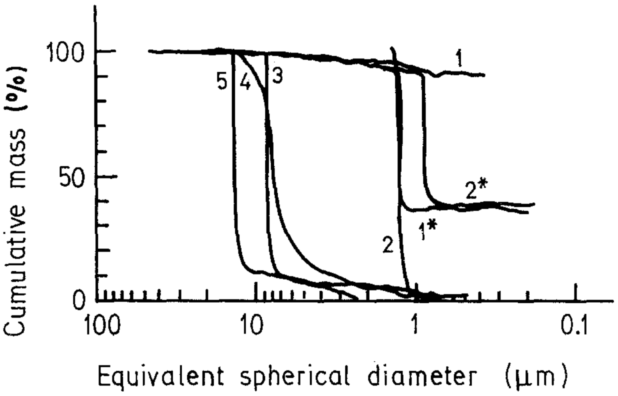

Figure 3 Influence of temperature of carbothermic reduction on the particle size distribution of β-SiC powders. Reaction time 30 min. Carbon black A: (1) 1170 °C (yield 12%), (2) 1220 °C, (3) 1270 °C (yield 82%), (4) 1310 °C, (5) 1350 °C (yield 95%). Carbon black B: (1*) 1170 °C (yield 55%), (2*) 1220 °C.

The influence of the temperature on the particle size, and the size distributions of the β-SiC powders prepared from both carbon grades, are presented in Fig. 3. Note that the increase of average particle size is especially pronounced in the range 1200–1300 °C. Below 1200 °C powders consisting mostly of submicrometre particles were obtained; however, the reaction yield was rather low. A rather uniform particle size distribution is characteristic for most of the powders. The analysed size of the particle corresponds to the size of agglomerates, which will be more thoroughly discussed in the next section. As illustrated in Fig. 4, the specific surface area of β-SiC powder decreases with the reaction temperature, the decrease being especially pronounced in the range between 1200 and 1300 °C, in accordance with Fig. 3. Similar results, obtained on pressed discs of β-SiC, were reported by Greskovich and Rosolowski [13] and, recently, by Elder and Krstić [14]. It is worth noting that the temperatures of carbothermic synthesis of SiC which are reported in the literature are almost exclusively above 1450 °C.

If the particle size of SiC is determined by the particle size of the carbon species, in accordance with the suggested reaction mechanism, finer carbon black should result in finer SiC powder. As shown in Fig. 3 (curves 1* and 2*), by employing grade B carbon black, the fraction of submicrometre β-SiC particles was increased after reaction at 1220 °C. However, at low temperatures (e.g. 1170 °C) finer SiC powders can be prepared using reaction mixtures containing the coarser grade A carbon black. Evidently, beyond some critical SiC primary particle size, extensive formation of aggregates and stronger agglomerates must occur, in spite of the relatively low reaction temperature. One can conclude that the application of an extremely fine carbon source is not necessarily an effective way of improving the morphology of the resultant SiC powder. However, the reaction yield can be substantially

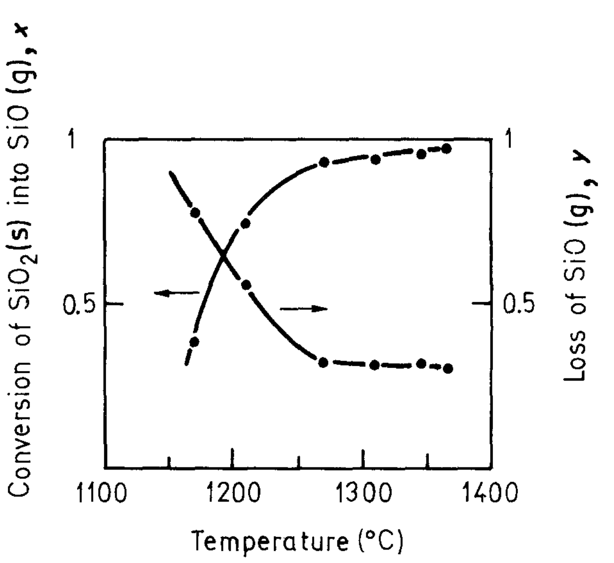

Figure 2 Conversion of SiO_2(s) into SiO(g) and loss of SiO(g) component versus temperature of carbothermic reduction (time of synthesis 30 min, pressure 1 Pa, carbon source: carbon black A).

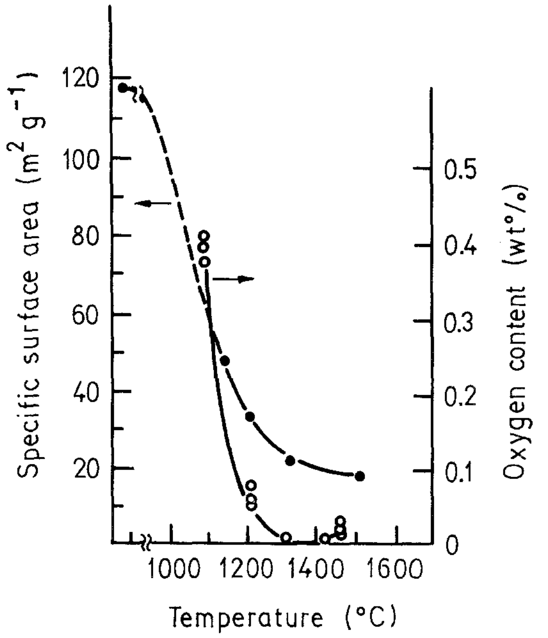

Figure 4 Specific surface area and oxygen content of β-SiC powders versus temperature of carbothermic reduction.

increased, especially when the temperature of the carbothermic reduction is rather low.

3.2. Particle coarsening during carbothermic reduction

The morphology of the SiC powders which were synthesized at different temperatures using both grades of carbon black, as well as from the reaction mixture with added amorphous boron, was examined by TEM. In order to investigate the influence of the morphology of carbon black on the morphology of resultant β-SiC particles, both grades of carbon black were also characterized by TEM. For grade A the average size of agglomerates and primary particles was estimated to be approximately 1000 nm and 50–100 nm, respectively. In the case of grade B an estimate of 10–20 nm for the size of primary particles and 400–500 nm for the agglomerates could be made. It should be noted that the size of primary particles is rather uniform in both grades of carbon black.

The morphology of β-SiC powders synthesized at 1220 °C using both grades of carbon black is shown in Fig. 5. In both β-SiC powders primary β-SiC crystallites[†], polycrystalline aggregates and agglomerates could be discerned. However, the usage of different carbon black results in significant differences in the size of these constituents. In addition, a small portion of SiC whiskers (mostly longer than 1 μm) and larger monocrystalline particles (≈ 200 nm) was formed by some of the mechanisms which are operative in whisker growth [16].

β-SiC powder synthesized using carbon black A has crystallites approximately 50 nm in size and agglomerates approximately 1000 nm in size (Fig. 5a). The use of finer carbon black (grade B) results in much finer β-SiC crystallites, whereas the size of agglomerates does not differ significantly (Fig. 5b). It is important to note that in both cases the size of the crystallites corresponds to the size of the parent carbon black particles. Note that sedimentation analysis of the same powders (Fig. 3, curves 2 and 2*) revealed the presence of a large proportion of monodisperse particles with a size approximating to the size of agglomerates as determined by TEM. This indicates that the intra-agglomerate bonds were rather strong and could not be disrupted by the adjustment of the zeta-potential in order to obtain maximum deflocculation. By heating β-SiC powders synthesized at low temperatures, i.e. 1170–1220 °C, at 1500 °C, large (up to 1 μm) monocrystalline particles of β-SiC were formed. As will be discussed more thoroughly below, surface diffusion may be responsible for the formation of polycrystalline aggregates, as well as for the strong intra-agglomerate bonds. At higher reaction temperatures volume diffusion must be operative, as shown by the presence of large monocrystalline particles.

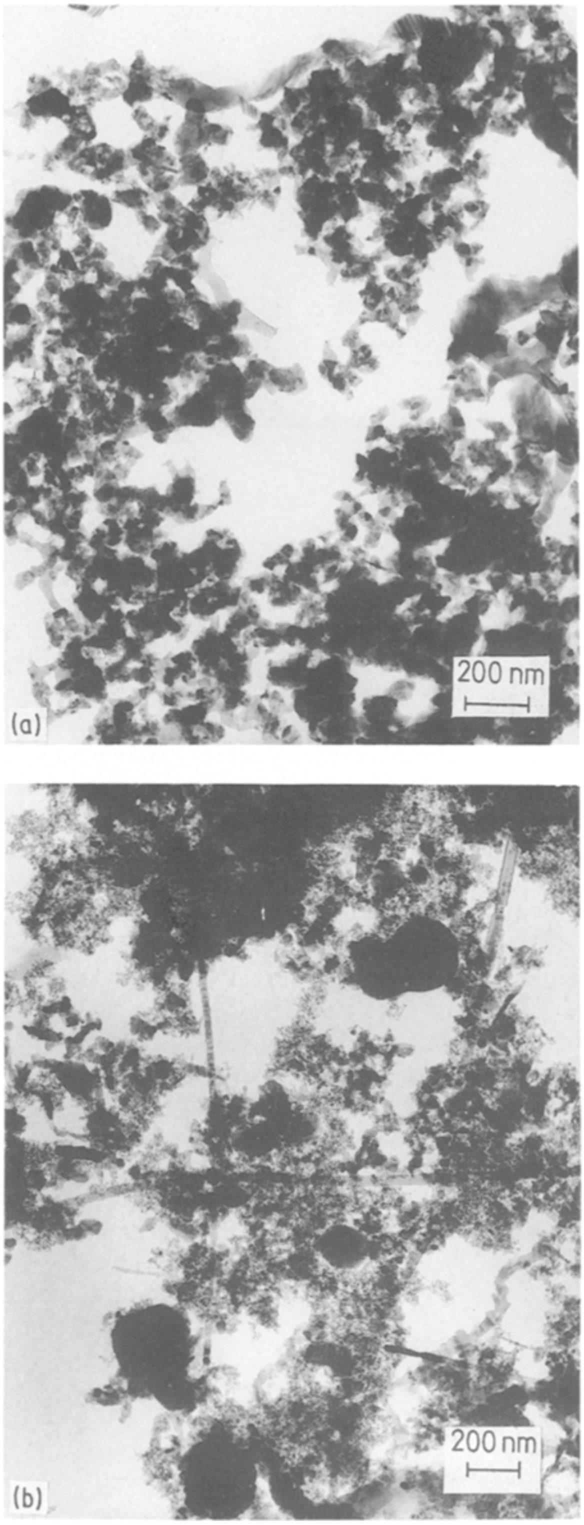

Figure 5 TEM micrographs of β-SiC powders synthesized at 1220 °C for 0.5 h *in vacuo* (1 Pa) using carbon black: (a) grade A, (b) grade B.

According to Greskovich and Rosolowski [13], strong evidence exists that during sintering of SiC surface diffusion may be responsible for observed surface area reduction, i.e. coarsening at temperatures ⩽ 1500 °C, but can be suppressed by the addition of boron. Hence, boron was added to $SiO_2 + C$ reaction mixture and the particle size distribution of resultant

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[†] According to Pampuch and Haberko [15] a crystallite is a coherently diffracting region of a lattice, an aggregate is a non-porous particle composed of crystallites, and an agglomerate is a more or less porous cluster of crystallites or aggregates.

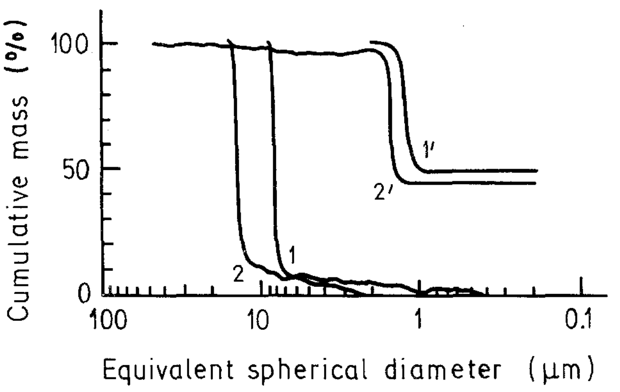

Figure 6 Influence of boron addition on the particle size distribution of β-SiC powders. Reaction time: 30 min. Undoped samples: (1) 1270 °C, (2) 1350 °C. Doped samples: (1′) 1270 °C, (2′) 1350 °C.

SiC powders compared with the particle size distribution of undoped samples (Fig. 6). Obviously, much finer particles were obtained when boron was present, suggesting that surface diffusion is the main mechanism of particle coalescence and growth during carbothermic synthesis of SiC at low reaction temperatures, i.e. 1200–1400 °C. Accordingly, by adding boron to the silica and carbon black mixture, the reaction temperature can be kept sufficiently high to increase the yield, while simultaneously the fraction of submicrometre particles increases because boron will reduce the effectiveness of the particle surface as a diffusion path.

From Fig. 6 it is also evident that, in spite of boron addition, the coarsening of β-SiC particles during carbothermal reduction is not completely eliminated. For example, in β-SiC powder synthesized at 1350 °C for 0.5 h using a reaction mixture with 0.6 wt % B, more than 50% of particles grew to 1 µm.

A possible explanation for this non-uniform particle growth could be (i) inhomogeneous boron distribution in the starting reaction mixture or (ii) different boron vapour removal ratios in the upper in lower part of the graphite crucible, as a consequence of continuously pumping off gaseous products during carbothermal reduction.

The following mechanism of growth and agglomeration of β-SiC particles during carbothermic reduction could thus be proposed (Fig. 7).

1. Direct chemical transformation of non-agglomerated and agglomerated particles of carbon black into β-SiC crystallites without significant change of size.
2. The coalescence of individual β-SiC crystallites into polycrystalline aggregates and agglomerates by surface diffusion which results in changes of particle size and morphology.
3. The formation of large monocrystalline β-SiC particles (> 1 µm) by bulk diffusion which is especially pronounced at temperatures higher than 1500 °C.

As is evident from Fig. 7, several routes of coalescence and growth are possible, according to features observed by TEM: (i) direct formation of SiC agglomerates from agglomerated particles of carbon black, (ii) formation of polycrystalline aggregates of SiC which bond subsequently into strong agglomerates, (iii) formation of individual SiC crystallites which coalesce into aggregates and agglomerates, and (iv) at higher temperature aggregates and agglomerates transform into monocrystalline particles by bulk diffusion. Due to the correspondence in the size of agglomerates in starting carbon black and the resultant SiC as established in the case of powders synthesized around 1200 °C, it seems that reaction route (i) is dominant, at least in the range of low reaction temperatures.

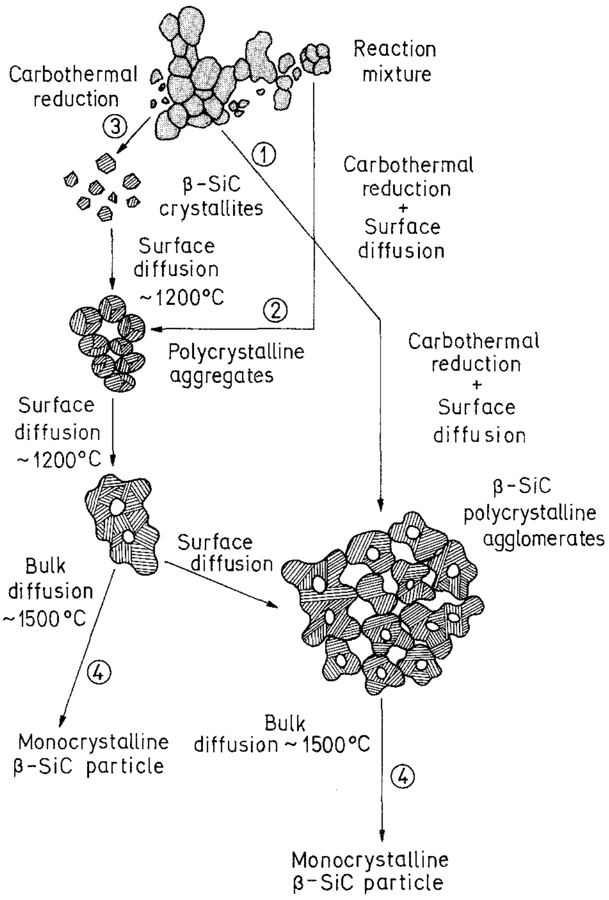

Figure 7 Schematic representation of growth and agglomeration of β-SiC particles during carbothermal reduction.

3.3. Processing of β-SiC powders

An appreciable amount of unreacted carbon and silica (up to 35% C and 30% equivalent oxygen) was present in the reaction product after carbothermic reduction, especially if the synthesis was performed at low temperatures, e.g. 1150–1200 °C. After heating in air for 24 h at 750 °C, the residual free carbon content was 0.08 ± 0.01 wt %, irrespective of the starting free carbon concentration.

The oxygen concentration and specific surface area of the SiC powders after treatment with gaseous HF as a function of the temperature of carbothermic reduction are shown in Fig. 4. Obviously, a correlation exists between the oxygen content and the specific surface area of the β-SiC powder. The purification method turned out to be very efficient, especially in comparison with other methods [6, 17]. This is demonstrated by the low oxygen content ($\ll 0.1$ wt %) of the coarser SiC powders synthesized at temperatures above 1250 °C. The higher oxygen content of the finer powders prepared at lower reaction temperatures is explained by reoxidation of these powders, which could take place rather easily due to their fineness. In order to determine oxygen pick-up during storage in air, one of the commercial β-SiC powders (HSC-100 GL) was exposed to an air atmosphere after HF treatment for 100 h. As the result of this exposure, a significant increase of oxygen content from 0.1 to 0.5 wt % was found. Recently, Matje and Schwetz [18] reported that physisorption of water, followed by chemisorption and formally by the formation of SiO_2, was observed on the surface of submicrometre SiC powders during storage at room temperature. The repeated HF treatment of SiC powders just prior to sintering could thus enhance densification (see section 3.4 below).

Sedimentation in a liquid medium represents a generally recognized method of classification of solid particles. In our studies, a 10% water slurry of β-SiC was used. As is evident from Fig. 8, the effect of sedimentation can be increased by adjusting the pH of the slurry to 11 where the maximum in zeta-potential was reported [19]. Further enhancement of sedimentation can be obtained by improving the wettability of hydrophobic SiC particles by the addition of surfactant [20]. Lomar-D (naphthalene sulphonic acid condensate) was used in the present investigation.

An attempt was made to evaluate quantitatively the sedimentation process for the case of a cut-off size of 1 µm, the time of sedimentation being 120 h. It was calculated that the efficiency of separation of particles with $d < 1$ µm was about 60%. This figure confirms that classification by sedimentation in liquid media is not very effective in the submicrometre range. Coarse particles with $d > 1$ µm were also present in the classified powder fraction. Complete removal of the fraction of coarse particles ($d > 1$ µm) could be accomplished only by filtration.

The influence on the sinterability of residual Lomar-D which remains occluded on the surface of the particles was also examined. A significant drop in the final density, of about 5–7%, was noted if the washing of sedimented powders was insufficient. Thus the washing of powders by a flocculation–ultracentrifugation–redispersion sequence was necessary in order to obtain an adequate purity of the powder.

3.4. Sintering studies

Sintering experiments were performed in order to assess the relative importance of particle size and size distribution, as well as chemical purity, particularly oxygen concentration, on the densification of β-SiC. Four different commercial β-SiC powders and our own β-SiC powder prepared by carbothermic reduction were used.

The particle size distributions of the respective powders are shown in Fig. 9. A broad distribution with approximately 40% of particles having diameters in the range 1–10 µm is characteristic of B-10 and HSC-100 GL powders. In contrast, MSC-20 and UF 0090 powders exhibit a rather narrow size distribution, predominantly in the sub-micrometre range. The particle size distribution of our own β-SiC IJS powder differs significantly, the main characteristics being comparable proportions of ultrafine particles (< 0.2 µm) and uniformly sized agglomerates (≈ 1.5 µm).

Due to the differences in oxygen and free carbon contents of the powders in the as-received condition, they were chemically treated immediately before sintering. Thus it is believed that the differences in the sinterability will result predominantly from the different particle size distributions of the respective powders. Since it was shown that during storage of powders in humid air oxygen pick-up is possible [18], powders were exposed to an air atmosphere after HF treatment for different periods of time and then sintered. Results are presented in Fig. 10 showing the relative sintered density as a function of sintering temperature and time of storage. As expected, higher densities were obtained in the case of finer powders with a narrower particle size distribution. Under the same conditions β-SiC IJS powder sintered only to 80% T.D. in spite of the relatively high fraction of very fine particles. Consequently, in the case of β-SiC powders, particles with diameters above approximately 1 µm are detrimental to densification.

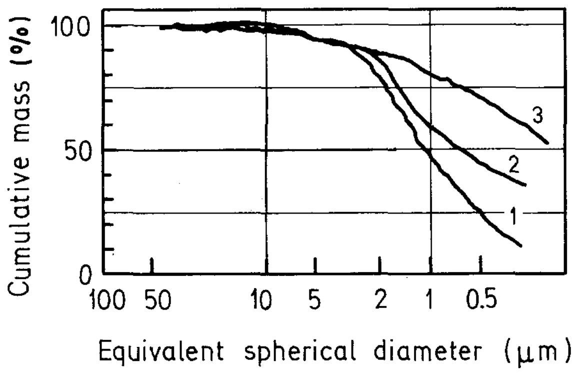

Figure 8 The influence of sedimentation conditions on the particle size distribution of B-10 SiC powder; fraction taken from the upper part of the column. (1) As-received B-10 powder, (2) after 120 h sedimentation at pH 11, (3) same as (2) + 3 wt % Loman-D.

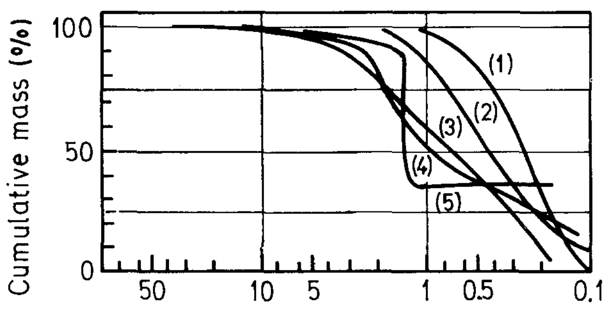

Figure 9 Particle size distribution of investigated β-SiC powders. (1) Ibiden UF 0090, (2) Mitsui Toatsu MSC-20, (3) Superior Graphite HSC-100 GL, (4) H. C. Starck B-10, (5) β-SiC IJS.

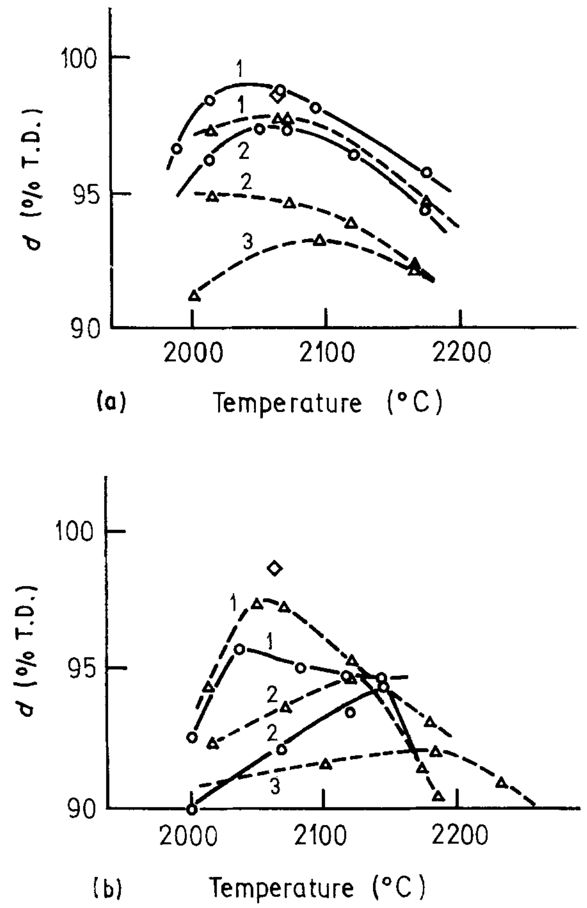

Figure 10 Effect of temperature and time of storage after HF treatment on the sintered density of powders: (a) (○) MSC-20, (△) UF-0090, (◇) β-SiC IJS; (b) (○) B-10, (△) HSC-100 GL, (◇) β-SiC IJS. (1) Immediately after treatment, (2) after 100 h, (3) after 2 months.

The influence of storage time is also evident. The highest densities were obtained if sintering was performed immediately after purification with HF. Samples which were stored before sintering for 100 h or more sinter to lower densities, and the density maximum moves towards a higher temperature in the case of the coarser B-10 and HSC 100 GL powders. These rather pronounced effects are somewhat surprising, especially with regard to the role which free carbon plays in the sintering of SiC. It seems that at a very low oxygen concentration, which was achieved with repeated HF treatment, other factors that are also known to control the densification of β-SiC become less critical, resulting in improved sinterability, provided of course that the general requirements for sinterable SiC powders are fulfilled. In contrast to expectations, UF-0090 powder does not exhibit the best densification behaviour. It is hypothesized that rapid oxygen pick-up occurs after cleaning with HF due to the great fineness of that powder, which in turn is reflected in its reduced sinterability.

Obviously, β-SiC powders can be sintered to high final densities, provided that very strict requirements regarding powder morphology and chemistry are fulfilled. Tedious processing of powders prior to sintering is thus unavioidable. If low reaction temperatures can be used for the preparation of β-SiC, as exemplified by carbothermic synthesis, powders which contain a high fraction of submicrometre particles can be obtained. Processing consisting only of classification and removal of excess carbon and oxygen may be sufficient for producing powders with high sinterability. To test this, β-SiC IJS powders were processed by sedimentation, filtration, and chemical purification. Upon sintering at 2060 °C in argon, densities > 98.5% TD were obtained, in contrast to unprocessed powders, which sintered only to 80% TD, as mentioned earlier.

4. Conclusions and summary

Carbothermic reduction of SiO_2 by carbon black can be successfully employed in order to synthesize fine β-SiC powders with a high yield of submicrometre particles. As established by TEM, the size of β-SiC primary crystallites corresponds to the size of carbon black particles. However, it was observed that the use of finer carbon black results in rapid growth of polycrystalline aggregates. Surface diffusion may be responsible for the formation of polycrystalline aggregates, as well as strong intra-agglomerate bonds. At higher reaction temperature, e.g. 1500 °C, volume diffusion is likely to be operative. By adding boron to the reaction mixture particle coarsening is inhibited, suggesting that boron impedes material transport in SiC by surface diffusion.

In order to obtain powders with good sinterability further processing is unavoidable, consisting in the removal of excess carbon by oxidation and excess silica by subsequent HF treatment, as well as the elimination of particles larger than 1 μm by sedimentation and/or filtration. After doping with carbon and boron, densities exceeding 98% of theoretical density can be obtained by pressureless sintering.

Sintering studies on several commercial β-SiC powders demonstrate that once the powders are adequately chemically processed, the main differences in the sinterability arise from differences in particle size and size distribution. Also noticeable is the effect of storage time after HF treatment on densification. Oxygen pick-up is likely to occur during prolonged exposure to an air atmosphere, resulting in reduced sinterability of SiC powders.

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