The chemistry of the carbothermal synthesis of β-SiC : reaction mechanism, reaction rate and grain growth

The Chemistry of the Carbothermal Synthesis of β-SiC: Reaction Mechanism, Reaction Rate and Grain Growth

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Abstract

Evidence is given that in the present case the reaction mechanism of β-SiC formation from silica and carbon is a direct solid-state reaction in which silica migrates over the silicon carbide surface to the carbon. A high value (440 kJ/mol) of activation energy is obtained for this reaction. This high value indicates that the reaction rate is determined by the diffusion of C atoms in carbon. As soon as the silica layers surrounding the silicon carbide particles have disappeared grain growth of β-SiC occurs. The mechanism for grain growth of β-SiC seems to be surface diffusion of Si and C atoms in SiC. The measured value of the activation energy for grain growth of β-SiC is 450 kJ/mol. Grain growth of α-SiC results in platelets.

Der Reaktionsmechanismus der Bildung von β-SiC aus SiO₂ und Kohlenstoff konnte in diesem Fall auf eine reine Festkörperreaktion zurückgeführt werden bei der SiO₂ über die SiC Oberfläche zum Kohlenstoff wandert. Für diese Reaktion ergab sich eine hohe Aktivierungsenergie von 440 kJ/Mol. Dieser hohe Wert ist ein Indiz, daß die Reaktionsgeschwindigkeit durch die Diffusion der C-Atome im Kohlenstoff bestimmt ist. Sobald die SiO₂-Schicht, die die β-SiC Teilchen umgibt, verbraucht ist, findet im β-SiC Kornwachstum statt. Wahrscheinlich geschieht das Kornwachstum des β-SiC durch Oberflächendiffusion von Si- und C-Atomen im SiC. Die gemessene Aktivierungsenergie für Kornwachstum von β-SiC

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beträgt 450 kJ/Mol. Beim Kornwachstum von α-SiC entstehen Plättchen.

On met ici en évidence que le mécanisme réactif de la formation de β-SiC à partir de la silice et du carbone est une réaction directe à l'état solide au sein de laquelle la silice migre jusqu'au carbone à travers la surface du carbure de silicium. On obtient pour cette réaction une valeur élevée de l'énergie d'activation (440 kJ/mol). Cette valeur indique que la vitesse de la réaction est déterminée par la diffusion des atomes de C dans le carbone. Dès que les couches de silice qui entourent les particules de carbure de silicium disparaissent, le grossissement de grain du β-SiC commence. Le mécanisme mis en jeu dans la croissance de grain du β-SiC semble être la diffusion surfacique des atomes de Si et de C dans le SiC. La valeur mesurée de l'énergie d'activation de la croissance de grain du β-SiC est de 450 kJ/mol. La croissance granulaire du α-SiC conduit à la formation de plaquettes.

1 Introduction

Carbothermal synthesis of SiC is a relatively old process. It was developed at the end of the 19th century as the Acheson process. The overall reaction can be described as:

$$SiO_2 + 3C = SiC + 2CO$$
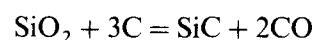
The raw materials for this process are quartz sand and petroleum cokes. The reaction is carried out by electrical resistance heating of the mixture of quartz

sand and petroleum cokes to temperatures up to 2300°C. The SiC produced in the Acheson process is obtained in the form of large chunks. The silicon carbide produced in this way has a hexagonal crystal structure: it is α-silicon carbide.[1]

In the 1970s it was discovered that submicron SiC powder can be (pressureless) sintered to densities higher than 95%.[1] A bright future was seen for products made from sintered silicon carbide. As the raw material for sintered silicon carbide is submicron silicon carbide powder, interest in the production of this powder was raised. The conventional way of producing submicron SiC powder is milling and leaching of Acheson-type SiC. As Acheson SiC is hard, strong and anything but fine, the milling of this material down to a submicron powder requires a great effort. Moreover, the purification of the powder by acid leaching is an unpleasant process. So, research was started into better and more economic processes for producing submicron SiC powder.

One out of many processes for making submicron SiC powder is a modified Acheson process. In this process the SiO_2 and C react at temperatures between 1200 and 1800°C instead of at temperatures between 2000 and 2300°C. Often submicron SiC powder is obtained without milling. Many articles have been written about this modified Acheson process in which different types of SiO_2 and C, different SiO_2: C ratios and different ways of mixing C and SiO_2 have been used.[2] Sometimes SiO_2–C mixtures are granulated prior to reaction. The reactions are carried out in different types of reactor. Often the conversion is not complete and free carbon and SiO_2 have to be removed during or after the reaction.[2,3] Sometimes the product is not a submicron powder.[4] Due to the low reaction temperature β-silicon carbide is obtained: a material with a cubic crystal structure. If impure raw materials are used it is necessary to remove the metallic impurities from the product. Due to all these differences in processing, raw materials and reaction conditions, many values for the activation energy, reaction mechanisms and hypotheses concerning the particle size of the powder are found in literature. Relations between kinetics, reaction mechanism and/or product size are rare. The most accepted reaction mechanism for the carbothermal synthesis of SiC at low temperatures is given in eqn (1):[2]

$$SiO_2 + C = SiO + CO$$

and   (1)

$$SiO + 2C = SiC + CO$$
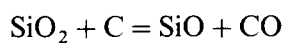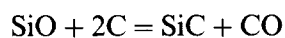
Reaction mechanisms including CO_2 or Si are also reported.[2] Solid-state diffusion as a reaction mechanism is usually rejected with the argument that the values of the coefficients of diffusion of Si and C atoms in silicon carbide or C atoms in carbon are too low.[2]

It is the aim of the authors to design a process for the carbothermal synthesis of β-SiC based on the following three characteristics:

—The use of pure raw materials in order to avoid purification of SiC afterwards;
—the production of submicron SiC powder without milling of SiC;
—the use of a small excess of carbon in order to obtain 100% conversion of SiO_2, removing the free carbon with a gasification reaction.

If this is achieved the process will be competitive with respect to other processes for the production of submicron SiC powder on a large scale, both in product quality and economic aspects. In this paper evidence is presented that, in the present case, the reaction mechanism is direct solid-state diffusion, that the activation energy of the synthesis is related to the diffusion of carbon and that after 99% conversion grain growth occurs (by surface diffusion) due to the absence of a silica layer around the SiC particles.

2 Pre-synthesis Processing

In the authors' view the most interesting SiO_2 raw materials are milled quartz sand and fumed silica. Milled quartz sand is cheap, pure (less than 500 ppm of metallic impurities) but not reactive. Fumed silica is pure (less than 300 ppm of metallic impurities), reactive but expensive. They also consider as the most interesting carbon raw material milled petroleum cokes and carbon black, especially gas black. Milled petroleum cokes are cheap but not reactive. They contain usually less than 5000 ppm of metallic impurities. Gas black is reactive, pure and some are moderately priced. It contains usually less than 300 ppm of metallic impurities. Experiments were carried out with gas black (Printex U) and an experimental type of precipitated silica. This experimental type of precipitated silica is similar in respect of purity and particle size to Aerosil Ox 50, a fumed silica. The gas black, silica and SiC powder were mixed in aqueous suspension. The scale of mixing was 3 microns. PVA (3 wt%) was added. The molar ratio of SiO_2:C was 1:3·2 β-SiC powder (5 wt% relative to the silica) was added to act as

nuclei (HSC-059 from Superior Graphite). After mixing, the slurry was filtered, the filtercake was dried and broken into particles with a diameter of less than 1 mm. Finally the powder was formed into tablets with a diameter and height of 5 mm and a bulk density of about $1 \cdot 0 \, g/cm^3$.

3 Experimental

The experiments to study the reaction mechanism were performed in an induction furnace, Linn HFG-12. The tablets were placed in a graphite crucible with a volume of $50 \, cm^3$. The crucible was covered with a porous graphite plate. The crucible was placed in the furnace, wrapped in the insulating alumina, and argon was purged around the insulation at a flow rate of $1 \, dm^3/min$. The tablets were heated for 15 min at 1000°C. In this way volatile matter, consisting mainly of CO, CO_2, H_2O and sulphur compounds, was removed. Next the temperature was raised to 1650°C and the sample was kept at this temperature for various periods. It took approximately 5 minutes to heat the crucible with the tablets from 1000 to 1650°C. After reaction and cooling the samples were studied with XRD, SEM and TEM. The material was mixed with a mixture of MMA and BMA, with 70 wt% MMA and 30 wt% BMA. After polymerisation the sample was prepared using an ultra-microtome and a diamond knife. The thickness of the sample was 70 nm. A Philips EM-420 of 120 kV with EDAX and STEM was used for TEM analysis. The oxygen content was measured with Strohlein equipment.

The kinetic experiments were performed in a Netzsch STA 429 thermobalance. The samples were placed on an alumina plate, covered with graphite foil. The heating rate was 40°C/min. The cooling rate was 20°C/min. A W versus W/Rh thermocouple was used in the thermobalance for temperature measurements. Helium was used as insert gas in the synthesis of SiC. As variables the gas flow rate, the number of

tablets, the temperature and the size of the tablets were studied.

The experiments to study grain growth were performed in the induction furnace mentioned previously using a $50 \, cm^3$ graphite crucible with a porous graphite cover. The crucible was placed in the furnace, wrapped in the insulating alumina. The furnace was either purged with Ar or operated in a vacuum of 5 mbar. Tablets of SiO_2-C-SiC mixtures were studied as well as tablets of HSC-SiC powder. The chemical composition of the HSC-SiC powder is given in Table 1. After the experiments the samples were studied with SEM and the O, N and C content were measured with Strohlein equipment.

4 Results

Table 2 gives the results of the experiments concerning the reaction mechanism: O content, conversion, SEM and XRD. The results from TEM were used to investigate the reaction mechanism. Figure 1 shows the composition of the starting mixture: spherical carbon black particles with a diameter of 35 nm and spherical amorphous silica particles with a diameter of 125 nm. Figure 2 shows

Table 1. The chemical composition of HSC-SiC powder

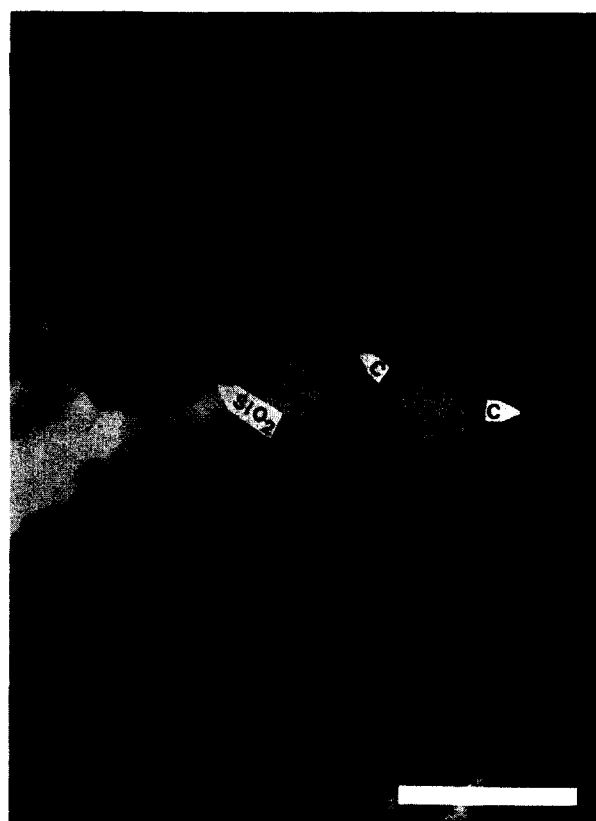| Contents	
C, wt%	30·7
O, wt%	0·8
N, wt%	0·2
F, ppm	500
Fe, ppm	160
Al, ppm	180
Ca, ppm	20

Fig. 1. Transmission electron micrograph of a mixture of gas black and silica. The length of the bar is 100 nm. The 35 nm spheres are gas black and the 125 nm spheres are silica.

Table 2. Results of experiments at 1650°C in Ar concerning the reaction mechanism

Number	Time (min)	O content (wt%)	Conversion (%)	Maximum particle size (micron)	Phases present
1	5	22	31	<0·3	β-SiC, amorphous C and SiO$_2$
2	10	3·3	90	<0·3	β-SiC, amorphous C
3	15	0·1	100	3	β-SiC, amorphous C
4	20	0·1	100	30	β-SiC, amorphous C

The conversion is calculated on the basis of the oxygen content.

the mixture at 30% conversion. It can be seen that the silica agglomerates are transformed into dense amorphous silica spheres with a diameter of 350 nm. The carbon black particles, however, have not changed in size: their diameter is still 35 nm. SiC particles can also be observed. Figure 3 shows the mixture at 90% conversion in which no more free silica particles are found. All silica is present as a layer surrounding the SiC particles. With EDAX it was shown that this amorphous layer contained Si and by reasoning where the oxygen might be, it became clear that the layer surrounding the SiC particles was silica. The carbon black particles which were not in contact with SiC particles have

not changed in size. Figure 4 shows a SiC particle in the mixture at 100% conversion. This figure shows that SiC particles are partially covered with layers of carbon. Also particles partially covered with a silica layer were observed.

The results concerning the kinetics as measured in the thermobalance are given in Figs 5 to 7. These figures are obtained by converting the weight loss, from 1200°C onwards, to the conversion, a. Figure 5 shows the influence of the gas flow rate on the reaction rate of the synthesis of SiC at 1510°C measured for one tablet. Figure 6 shows the influence of the number of tablets and the tablet size on the reaction rate of the synthesis of SiC at 1510°C
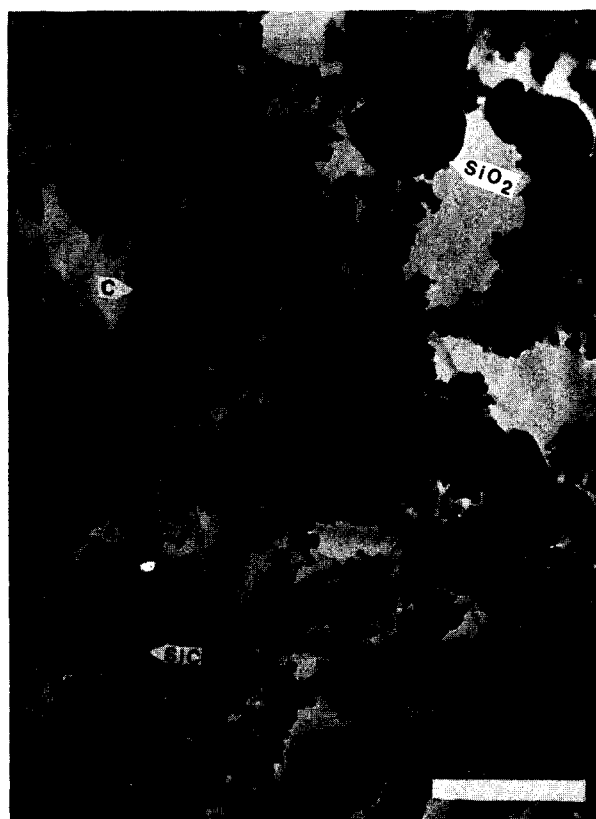
Fig. 2. TEM of a mixture of gas black, silica and SiC at 30% conversion. The length of the bar is 500 nm. The 35 nm spheres are gas black and the 350 nm spheres are silica. SiC particles can also be seen.

Fig. 3. TEM of a mixture of gas black, silica and SiC at 90% conversion. The length of the bar is 50 nm. The 35 nm spheres are gas black. The figure also shows submicron SiC particles which are covered with a layer of silica.
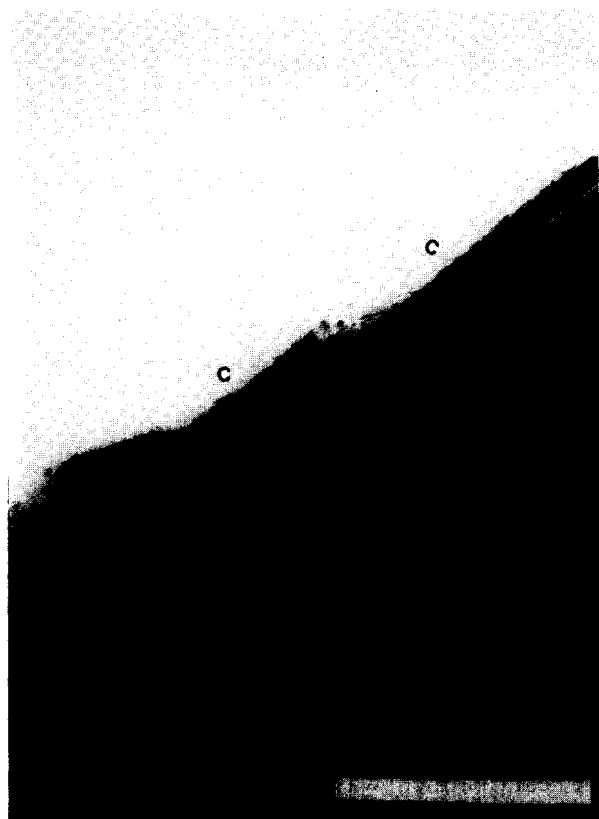
Fig. 4. TEM of a mixture of gas black and SiC at 100% conversion. The length of the bar is 50 nm. A layer of graphitized carbon on a SiC particle can be seen.

Fig. 6. The influence of the tablet size and the number of tablets on the reaction rate in the thermobalance at 1510°C. The reaction is the carbothermal synthesis of SiC in He at 1 atm. The gas flow rate is 100 cm³/min. Number of tablets: ●, 1 (broken); ○, 1; □, 3; △, 5.

and a flow rate of 100 cm³/min. From these two figures it was assumed that measurement of the chemical reaction rate was best approached by taking one broken tablet for the reaction and using a gas flow rate of at least 100 cm³/min. Under these conditions physical aspects do not influence the reaction rate. Figure 7 shows the influence of the temperature on the reaction rate of the synthesis of SiC of one broken tablet and a flow rate of He of
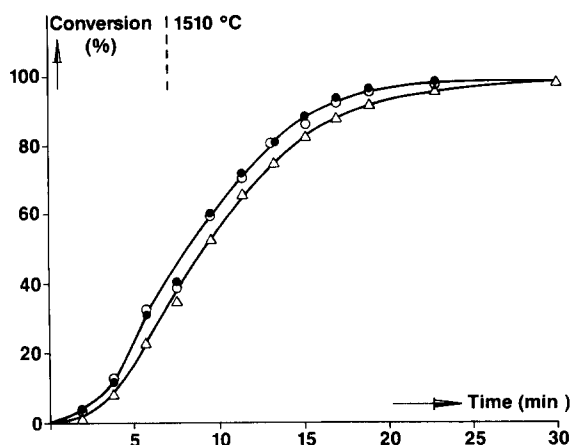

Fig. 7. The influence of the temperature on the reaction rate of one broken tablet in the thermobalance. The He flow is 100 cm³/min at 1 atm. The reaction is the carbothermal synthesis of SiC. Reaction temperature: ●, 1290°C; ○, 1340°C; △, 1410°C; □, 1460°C.

Fig. 5. The influence of the gas flow rate on the reaction rate of one tablet in the thermobalance at 1510°C. The reaction is the carbothermal synthesis of SiC in He at 1 atm. Gas flow rates: ●, 200 cm³/min; ○, 100 cm³/min; △, 50 cm³/min.

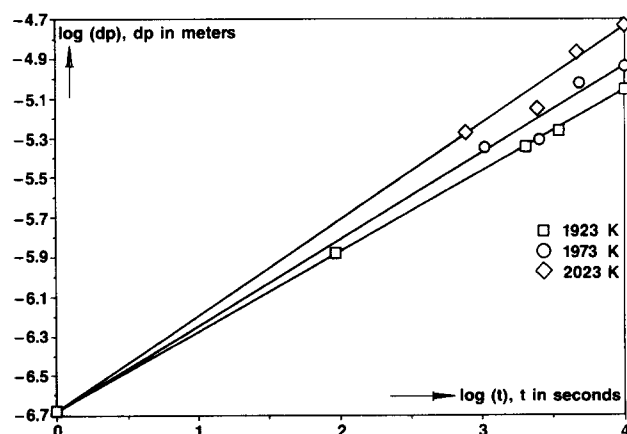**Fig. 8.** Normal grain growth of SiC with free carbon in Ar at 1 atm as log plot of maximum particle size versus time.

Table 3. Results of experiments concerning grain growth

Number	Time[a] (min)	Temperature (K)	Maximum particle size (micron)	O content (wt.%)	Remarks
0[b]	—	—	1·5	0·8	
1[b]	30	1 973	15	0·2	Argon
2[b]	30	2 073	60	0·1	Vacuum
3[b]	30	1 973	4	0·2	Vacuum
4[b]	60	1 873	2	0·1	Argon, 1 wt% B_4C
5[b]	60	1 973	2	0·1	Argon, 1 wt% B_4C
6[b]	60	2 073	100	0·1	Argon, 1 wt% B_4C
7[c]	10	2 073	<0·5	3·5	Vacuum
8[c]	60	2 073	8	0·1	Vacuum
9[c]	60	1 973	2	0·1	Vacuum
10[c]	15	1 973	<0·5	2	Argon
11[c]	60	1 973	5	0·1	Argon

[a] Including heating from 1000°C.
[b] Material: HSC–SiC.
[c] Material: SiC produced at DSM Research with 9 wt% free carbon.

100 cm³/min. The results as presented in Fig. 7 were used to calculate the activation energy of the carbothermal synthesis of SiC.

Figure 8 shows the grain growth of SiC with free carbon produced by a carbothermal reaction as a function of time in the induction furnace with a flow of argon around the crucible. The slope of the lines varies from 0·40 to 0·50. Figure 9 shows an electron micrograph of a powder after carbon burnout. From the results, as presented in Table 3, it can be seen that grain growth is less in vacuum and that the rate of grain growth is higher for HSC–SiC than for SiC powder (with free carbon) produced at DSM Research. HSC–SiC powder which was wet-mixed with B_4C powder shows hardly any grain growth at 1600 and 1700°C (see Table 3). However, at 1800°C grain growth occurred for this wet-mixed HSC–SiC powder. It was observed that grain growth of pure

SiC starts when the oxygen content of the powder becomes less than 1 wt%. Figure 10 shows grains of β-SiC doped with 0·3 wt% Al after grain growth. The heat treatment was 1800°C for 60 min in Ar. The figure shows a growth spiral on the surface of a SiC grain.

It was possible to produce a SiC powder with a specific surface area higher than 5 m²/g. The powder does not contain any α-SiC, less than 200 ppm metallic impurities, less than 0·1 wt% nitrogen and less than 0·5 wt% oxygen. This result is obtained by using pure, submicron raw materials, good mixing of the raw materials and direct cooling of the product when (almost) complete conversion is obtained. The HSC–SiC powder which was wet-mixed with boron carbide in a ball mill with α-SiC balls and heated at 1800°C for 1 h was converted to α-SiC. The shape of
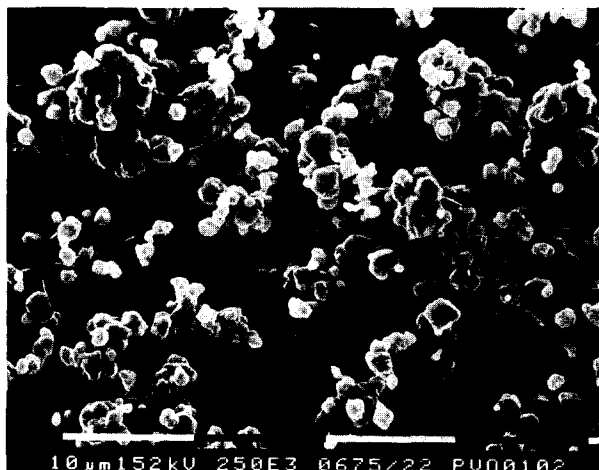
Fig. 9.   Scanning electron micrograph of a SiC powder after grain growth and removal of carbon.
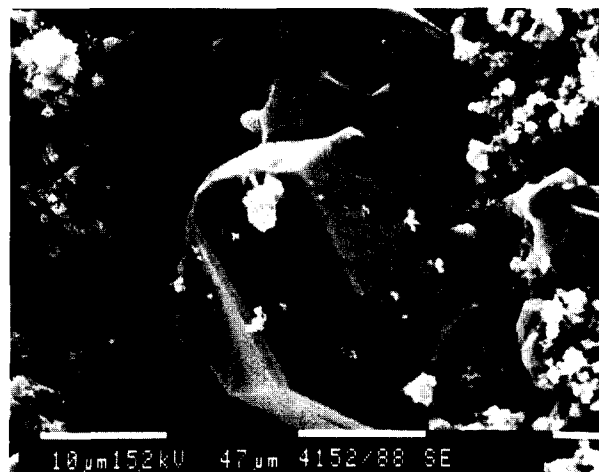
Fig. 10.   Scanning electron micrograph of DSM Research β-SiC powder with carbon after grain growth. The length of the bar is 10 microns.

Fig. 11. Scanning electron micrograph of HSC–SiC powder which was wet-mixed with 1 wt% B_4C after grain growth in Ar for 1 h at 1800°C. Platelets are formed.

the particles was plate-like; see the electron micrograph in Fig. 11.

5 Discussion

The results from TEM concerning the reaction mechanism seem to indicate that the silica migrates over the SiC particles towards the carbon. The carbothermal reaction takes place where the silica and the carbon meet. When SiO is first formed it is expected that all carbon black particles would take part in the reaction to give SiC:

$$SiO + 2C = SiC + CO$$
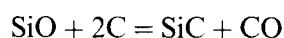
However, it is noted that only those carbon particles react which are in contact with SiO_2, which leads the authors to believe that the reaction mechanism is a direct solid-state reaction. When the activation energy is low, the rate-determining step is the diffusion of silica. When the activation energy is high, the rate-determining step is the diffusion of carbon. Typical diffusion distances for silica are 0·5 to 1 micron and for carbon the diffusion distances are 25 nm. At the end of the reaction (99% conversion) the SiC particles are not completely covered with silica and grain growth starts.

From Fig. 7 the activation energy of the carbothermal synthesis of SiC was calculated. Three calculation methods were used. The first method was based on slope of the curve at $t = 0$ s. The curves are fitted with the formula $da/dt = k$. From this fit a value for the activation energy for the synthesis of SiC of 310 kJ/mol is found. The second method is based on curve fitting with Jander's equation:

$$(1 - (1 - a)^{2/3})^2 = kt$$

This formula indicates that the reaction rate

decreases as the conversion increases and this is in agreement with the observations. From this fit a value for the activation energy for the synthesis of SiC of 440 kJ/mol is calculated. The third method is based on curve fitting with Carter's equation with $z = 2·1$. From this fit a value for the activation energy for the synthesis of SiC of 375 kJ/mol is obtained. The activation energy for the volume diffusion of oxygen in SiO_2 is 150 kJ/mol.[5] It is believed that the activation energy of 440 kJ/mol (or 310 kJ/mol) is related to the coefficient of surface or volume diffusion of carbon. The activation energy for volume diffusion of graphite is 680 kJ/mol.[5]

According to the literature the mechanism of grain growth of SiC is surface diffusion, as indicated by Greskovich & Rosolowski.[6] A silica layer around the SiC particles prevents surface diffusion. Free carbon, which forms graphite layers on the SiC surface, reduces grain growth. The fact that free carbon reduces grain growth of SiC is described in the literature.[7] This explains why grain growth of HSC–SiC is faster than grain of the SiC powder, with free carbon, produced at DSM Research. It is already known that B_4C reduces grain growth of SiC at relatively low temperatures.[6] The value for the activation energy of grain growth is calculated from Fig. 8. The curves were fitted with the formula:

$$d^2 - d_0^2 = kt$$

where d is the maximum grain diameter for a given time, d_0 the maximum grain diameter at $t = 0$, t the time and k the rate constant. This relation holds for normal grain growth.[5] For k as a function of the absolute temperature an Arrhenius relation is assumed. In this way a value of the activation energy for grain growth of 450 kJ/mol was calculated. This is in good agreement with Greskovich & Rosolowski.[6] The value of the activation energy for the coefficients of volume diffusion of Si and C atoms in β-SiC are both about 900 kJ/mol with Si atoms having the lowest coefficient of volume and surface diffusion. No liquid phase is present which can transport both Si and C. Thermodynamic calculations show that at 1 atm CO the reaction

$$SiC + CO_2 = SiO + CO$$
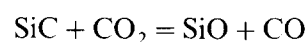
can result in gas transport and hence neck growth. In vacuum the partial pressure of CO_2 is too low to result in significant transport via the gas phase according to thermodynamic calculations. SiC platelets are obtained by grain growth of α-SiC. At 1800°C α-SiC is formed due to incorporation of B in the crystal structure and to the presence of α-SiC seeds due to ball wear.[8]

6 Conclusion

Evidence is given that in the present case the reaction mechanism of the carbothermal synthesis is direct solid-state diffusion. The silica migrates fast over the surface of the SiC particles to the carbon. The value for the activation energy of the synthesis of SiC is $440 \, kJ/mol$. This value is most likely related to the coefficient of diffusion of C atoms in carbon. When the conversion is almost complete (oxygen content lower than 1 wt%), grain growth of SiC occurs. The mechanism of grain growth is reaction of traces of silica plus surface diffusion of Si and C atoms in SiC. The rate of grain growth depends on the atmosphere, impurities, dopes and the temperature. Grain growth of SiC increases with increasing temperature. Free carbon and B_4C reduce grain growth at temperatures lower than $1700°C$. The rate of grain growth of SiC is less in vacuum compared to Ar. The grain growth is normal grain growth with a value for the activation energy of $450 \, kJ/mol$ at temperatures below about $1800°C$ in Ar. Platelets of SiC are formed by grain growth of α-SiC.

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