JOURNAL OF MATERIALS SCIENCE 25 (1990) 4614–4621

Preparation of silicon carbide powders by chemical vapour deposition of the $(CH_3)_2SiCl_2$–H_2 system

LIDONG CHEN, TAKASHI GOTO, TOSHIO HIRAI
Institute for Materials Research, Tohoku University, Sendai 980, Japan

Silicon carbide (SiC) powders were prepared by chemical vapour deposition (CVD) using $(CH_3)_2SiCl_2$ and H_2 as source gases at temperatures of 1273 to 1673 K. Various kinds of SiC powders such as amorphous powder, β-type single-phase powder and composite powder were obtained. The composite powders contained free silicon and/or free carbon phases of about a few nanometres in diameter. All the particles observed were spherical in shape and uniform in size. The particle size increased from 45 to 130 nm with decreasing reaction temperature and gas flow rate, as well as with increasing reactant concentration. The lattice parameter of the β-SiC particles decreased with increasing reaction temperature. All the lattice parameters were larger than those of bulk β-SiC.

1. Introduction

Silicon carbide (SiC) is a promising material for engineering applications due to its mechanical strength and thermal shock resistance at high temperatures. In electrical applications it is useful due to its superior electrical resistance and thermal conductivity [1]. In order to obtain a high-density SiC body by a sintering process, the starting powders must have high purity, non-agglomeration, fine particle size with narrow size distribution and equiaxed morphologies [2]. Chemical vapour deposition (CVD) technique is the most suitable method for preparing such powders [3].

In the preparation of SiC powders by CVD, the general approach is to use chemical reactions between the silicon source gas ($SiCl_4$, SiH_4, etc.) and the carbon source gas (CH_4, C_2H_4, etc.) [4, 5]. We have reported the preparation of hollow β-SiC particles using SiH_4 and CH_4 as source gases and investigated their properties and structures [6]. A simpler process to synthesize SiC powders involves the pyrolysis reactions of organo-silicon compounds containing both elements of silicon and carbon. Until now, $(CH_3)_4Si$ [7], CH_3SiCl_3 [7], CH_3SiH_3 [8] and $[(CH_3)_2Si]_2H_2$ [9] have been used as source materials. However, the powder yield is too small when CH_3SiCl_3 vapour is used, and $(CH_3)_4Si$ is easily decomposed but forms a large amount of free carbon. CH_3SiH_3 generally produces a large amount of free silicon. In order to obtain β-SiC not containing free silicon, a high temperature is required above 1873 K. $(CH_3)_2SiCl_2$ is known to have a sufficiently large negative Gibb's free energy and is easy to handle. However, no reports on the preparation of SiC powders using $(CH_3)_2SiCl_2$ are available. In the present work, $(CH_3)_2SiCl_2$ was used to prepare SiC powders by CVD at temperatures between 1273 and 1673 K. The effects of deposition conditions on the structure and properties of the product powder were investigated.

2. Experimental procedure

The CVD reaction was carried out in a flow-type reactor at a total gas pressure (P_{tot}) of 0.1 MPa. The schematic diagram of the CVD apparatus is shown in Fig. 1. The reaction chamber consisted of an outer mullite tube which encased an inner reaction-sintered (RS) SiC tube. Liquid $(CH_3)_2SiCl_2$ (99.9%) was used as the source material and was bubbled with H_2 gas (99.999%). The source gases were introduced into the reaction chamber through stainless steel nozzles. Powder was collected in a flask having a 65 mesh brass filter. Reaction temperature (T_{rea}) ranged from 1273 to 1673 K. The total gas flow rates (FR) were 6.3×10^{-6} and $2.0 \times 10^{-5}\,m^3\,sec^{-1}$. $(CH_3)_2SiCl_2$ concentrations were 7.0 and 14.5 mol %.

The shape and structure of the particles were observed by transmission electron microscopy (TEM) (Jeol: JEM-2000EX). The specific surface area was determined by three-point BET method using a sorptograph (Shimadzu: ADS-1B). The infrared absorption spectra (IR) were obtained by the KBr pellet method using a spectrometer (Japan Spectroscopic: IR-G) in a wave number range from 400 to 4000 cm^{-1}. The crystal phases were identified and the lattice parameters were determined using X-ray diffractometry (Rigaku: RAD-IIB, nickel filtered, Cu$K\alpha$). The powder density was measured by pycnometry using toluene. The amounts of silicon, carbon, hydrogen and oxygen in the powders were measured by chemical analyses. The chlorine content was analysed by energy dispersive X-ray spectrometry (EDX) (Tracor Northan: TN5500-UTW).

0022-2461/90 $03.00 + .12

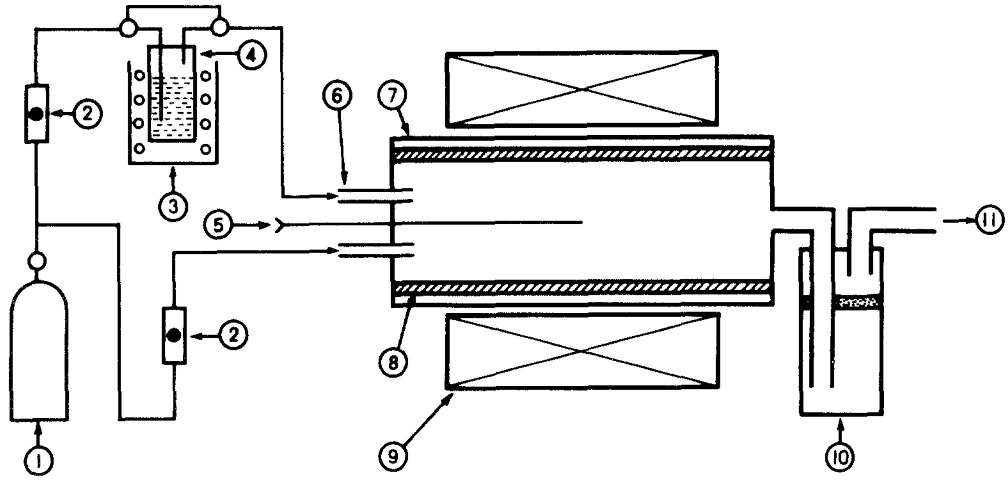

Figure 1 Schematic diagram of the apparatus for synthesizing β-SiC powder. (1) H_2 gas, (2) flow meter, (3) constant temperature bath, (4) $(CH_3)_2SiCl_2$ reservoir, (5) thermocouple, (6) stainless steel nozzle, (7) mullite tube (internal diameter 35 mm), (8) RS-SiC tube (internal diameter 20 mm), (9) SiC resistance furnace, (10) collecting flask and filter, (11) gas outlet.

3. Results and discussions

3.1. Formation and composition of SiC particles

Figs 2a and b, respectively, show the X-ray diffraction patterns of the powders prepared at $[(CH_3)_2SiCl_2] = 7.0$ mol %, FR $= 2.0 \times 10^{-5}$ m^3 sec^{-1} and those prepared at $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR $= 6.3 \times 10^{-6}$ m^3 sec^{-1}. It is clear from Fig. 2a that the powder prepared at 1673 K is single-phase β-SiC and those prepared below 1573 K contain some free silicon. The diffraction peaks become broader as the reaction temperature decreases. In Fig. 2b, the presence of some free carbon in the β-SiC powder is identified at 1673 K. The broad diffraction peak shows that the free carbon is in an amorphous state at this temperature. The β-SiC powders obtained at 1473 to 1573 K contain both free silicon and free carbon. Below 1373 K, much broader diffraction peaks from free silicon and SiC are observed, and both SiC and silicon phases are amorphous-like.

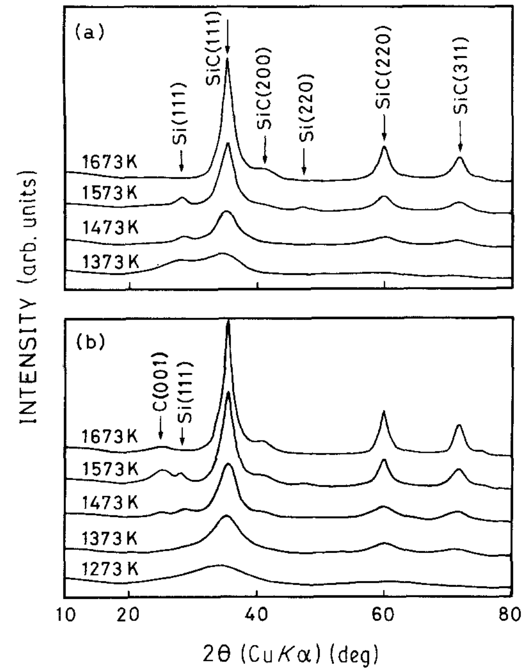

Figure 2 X-ray diffraction patterns of powders. (a) $[(CH_3)_2SiCl_2] = 7.0$ mol%, FR $= 2.0 \times 10^{-5}$ m^3 sec^{-1}, (b) $[(CH_3)_2SiCl_2] = 14.5$ mol%, FR $= 6.3 \times 10^{-6}$ m^3 sec^{-1}.

Fig. 3 shows the effect of the reaction temperature on the chemical composition (C/Si molar ratio). The C/Si molar ratio increases with increasing reaction temperature and $(CH_3)_2SiCl_2$ concentration and with decreasing total gas flow rate. The powder obtained at $[(CH_3)_2SiCl_2] = 7.0$ mol %, FR $= 2.0 \times 10^{-5}$ m^3 sec^{-1} and $T_{rea} = 1673$ K was found to be single-phase β-SiC through chemical and X-ray analyses. The powder obtained at $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR $= 6.3 \times 10^{-6}$ m^3 sec^{-1} and $T_{rea} = 1473$ K seems nearly stoichiometric (C/Si $\simeq$ 1) as shown in Fig. 3. However, the powder prepared under these conditions contained both free carbon and free silicon in β-SiC powder as shown in Fig. 2. The C/Si molar ratio for this case is almost one, because the amount of free silicon is nearly equal to that of free carbon. The chemical analysis showed that the powders contain about 1 wt % O and 0.1 wt % H at all preparation conditions. The EDX analyses indicated the presence of chlorine in the powders prepared at $[(CH_3)_2SiCl_2] = 14.5$ mol %. The amount of chlorine decreased with increasing reaction temperature. The presence of chlorine was not detected for the powders prepared at $[(CH_3)_2SiCl_2] = 7.0$ mol %.

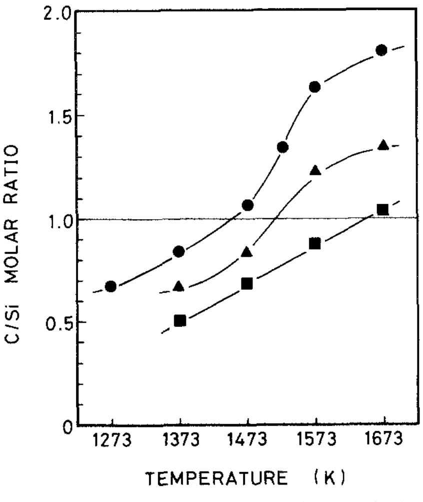

Figure 3 Effect of reaction temperature on the chemical composition of powders. (●) $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR $= 6.3 \times 10^{-6}$ m^3 sec^{-1}; (▲) $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR $= 2.0 \times 10^{-5}$ m^3 sec^{-1}; (■) $[(CH_3)_2SiCl_2] = 7.0$ mol %, FR $= 2.0 \times 10^{-5}$ m^3 sec^{-1}.

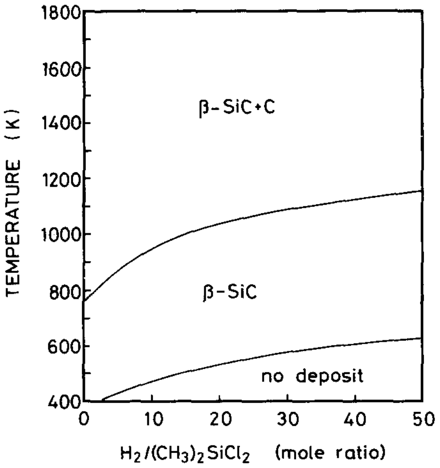

Figure 4 Calculated CVD phase diagram of the $(CH_3)_2SiCl_2$–H_2 system.

To date, there has been no report of the use of $(CH_3)_2SiCl_2$ as a source material for the preparation of SiC powder by CVD, except as used in CVD-SiC films [10–15]. Verspui [11] prepared β-SiC films containing a small amount of free silicon in the temperature range 1473 to 1673 K using $(CH_3)_2SiCl_2$. Muench and Pettenpaul [12] also prepared β-SiC films and reported that free silicon was co-deposited below 1673 K and free carbon was co-deposited above 1873 K. Thus, in the temperature range 1673 to 1873 K their deposits contained neither free silicon nor free carbon. Both earlier and present results indicate a common tendency that free silicon is co-deposited with β-SiC at lower temperatures and free carbon is co-deposited at higher temperatures.

Fig. 4 shows an equilibrium CVD phase diagram for the $(CH_3)_2SiCl_2$–H_2 system calculated using an optimization method [16]. The deposition region of single-phase β-SiC is present in the temperature range ~ 500 to 1000 K. A no-deposit region is indicated below 500 K. Free carbon will be co-deposited with β-SiC above 1000 K, and the deposition of free carbon becomes easier at higher $(CH_3)_2SiCl_2$ concentrations (i.e. lower $H_2/(CH_3)_2SiCl_2$ ratio). In the present experiment, the amount of free carbon increased with the $(CH_3)_2SiCl_2$ concentration as shown in Fig. 3. This tendency is in agreement with the predictions of thermodynamic calculations. However, the experimental temperature where free carbon is co-deposited with β-SiC was 300 to 400 K higher than the calculation, and the co-deposition of free silicon at lower temperatures was not predicted by the calculation. These differences may have been due to a kinetic restriction in the decomposition process of $(CH_3)_2SiCl_2$.

Rai-Choudhury and Formigoni [10] have studied the growth process of β-SiC films from $(CH_3)_2SiCl_2$ by CVD using a pyrolysis mechanism. They proposed that $(CH_3)_2SiCl_2$ decomposes to elemental silicon and CH_4 gas in a hydrogen atmosphere, and then this CH_4 gas decomposes to elemental carbon and hydrogen gas. The reaction of elemental silicon with carbon produces a β-SiC film on the substrate surface

$$(CH_3)_2SiCl_2(g) + 2H_2(g) \rightarrow Si(s) + 2CH_4(g) + 2HCl(g) \quad (1)$$

$$CH_4(g) \rightarrow C(s) + 2H_2(g) \quad (2)$$

$$Si(s) + C(s) \rightarrow SiC(s) \quad (3)$$

If the reaction rate of Equation 1 is faster than those of Equations 2 and 3, free silicon would remain in β-SiC. Many reports, including the present work, indicated that free silicon is frequently contained in deposited β-SiC films [11, 12] or powders. Therefore, the reaction rate of Equation 1 must be faster than that of Equation 2. According to Le-Chaterier's law, the presence of excess hydrogen gas will accelerate the reaction of Equation 1, but will retard that of Equation 2. This prediction agrees well with the experimental results that show the amount of free

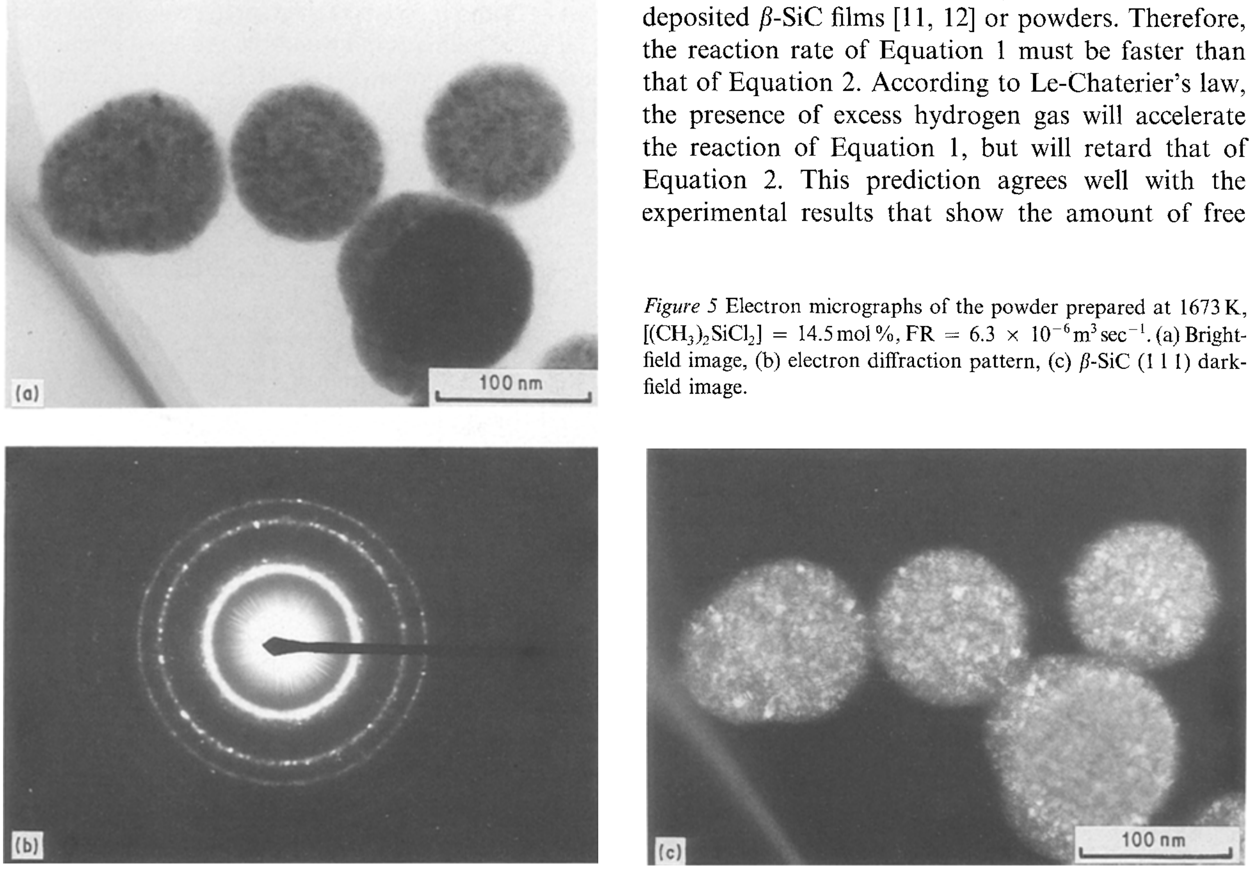

Figure 5 Electron micrographs of the powder prepared at 1673 K, $[(CH_3)_2SiCl_2]$ = 14.5 mol %, FR = $6.3 \times 10^{-6} m^3 sec^{-1}$. (a) Bright-field image, (b) electron diffraction pattern, (c) β-SiC (1 1 1) dark-field image.

silicon increases with increasing hydrogen partial pressure. On the other hand, both free silicon and free carbon are co-deposited with β-SiC powder under the conditions $[(CH_3)_2SiCl_2] = 14.5\,mol\,\%$, FR $= 6.3 \times 10^{-6}\,m^3\,sec^{-1}$ and $T_{rea} = 1473$ to $1573\,K$, as shown in Fig. 2. However, according to Gibbs' phase rule, three phases cannot coexist in the Si–C system at an equilibrium state. The coexistence of three phases in the present work must have been due to the existence of unreacted silicon and carbon in the SiC powders. This result suggests that the reaction rate of Equation 3 may be slower than those of Equations 1 and 2.

Okabe *et al.* [7] and Endo *et al.* [9] prepared β-SiC powders by CVD using the $(CH_3)_4Si$–H_2 and $[(CH_3)_2Si]_2H_2$–H_2 systems, respectively. They proposed a polymerization mechanism in which the source gases polymerize to high-molecular polycarbosilanes and these polycarbosilanes decompose to β-SiC particles. However, as shown earlier, the present experimental results can be better explained by the pyrolysis mechanism. It is necessary to conduct an *in situ* analysis of gas species in order to explain better whether the pyrolysis or polymerization mechanism is suitable for the formation of SiC particles from the $(CH_3)_2SiCl_2$–H_2 system.

3.2. Shape and structure of particles

Fig. 5 shows the electron micrographs of the particles prepared at $[(CH_3)_2SiCl_2] = 14.5\,mol\,\%$, FR $= 6.3 \times 10^{-6}\,m^3\,sec^{-1}$ and $T_{rea} = 1673\,K$. Figs 5a, b and c represent a bright-field image, an electron diffraction pattern of a selected area, and a β-SiC (1 1 1) dark-field image, respectively. The β-SiC particles were solid (not hollow) and spherical as shown in Fig. 5a. The diffraction pattern (Fig. 5b) and the β-SiC (1 1 1) dark-field image (Fig. 5c) indicate that the β-SiC particles are polycrystalline, and the crystallite sizes are several nanometres in diameter. The β-SiC crystallite sizes measured by TEM observation were in good agreement with those calculated from the broadening of the X-ray diffraction peaks. The chemical analysis revealed that the powder shown in Fig. 5 contained about 20 wt % free carbon. X-ray and electron diffraction analyses indicated that the free carbon was amorphous. However, TEM observation showed that there is no particle that consists of just free carbon, thus the free carbon exists within the SiC particles. Endo *et al.* [9] prepared β-SiC particles containing free carbon by CVD using $[(CH_3)_2Si]_2H_2$. They suggested that the free carbon exists in an amorphous state in the intergranular region (grain boundary) of the β-SiC crystallite.

Fig. 6 shows the electron micrographs of the particles prepared at $[(CH_3)_2SiCl_2] = 7.0\,mol\,\%$, FR $= 2.0 \times 10^{-5}\,m^3\,sec^{-1}$ and $T_{rea} = 1373\,K$. The particles were spherical and uniform in size. The electron diffraction pattern indicates that the particles are amorphous. Earlier, in Figs 2 and 3, it was shown that the powder consisted of amorphous silicon (39 wt %) and amorphous SiC. In order to study further the dispersing state of free silicon in the particles, the amorphous powder was heat treated at 1423 K in argon for 2 h. Even after heat treatment, neither the particle size nor its composition changed.

Fig. 7 shows electron micrographs of the heat-treated particles. Figs 7a to d represent a bright-field image, a selected-area electron diffraction pattern, a β-SiC (1 1 1) dark-field image and a silicon (1 1 1) dark-field image, respectively. The electron diffraction showed the presence of crystalline silicon and β-SiC phases. Figs 7c and d show that the silicon crystallites of several nanometres in diameter are dispersed within the β-SiC crystallites to form β-SiC/Si composite particles.

Fig. 8 shows the effect of reaction temperature on the particle size measured by TEM. The (TEM) particle sizes closely match the values calculated from the BET specific surface area. The particle size decreased with increasing reaction temperature and gas flow rate and with decreasing $(CH_3)_2SiCl_2$ concentration.

For particles formed by CVD, the particle size can be calculated using Equation 4 based on the fusion–coalescence mechanism [17, 18]. In Equation 4, it was assumed that the nuclei of particles collide with each other by Brownian motion and particles are formed by coalescence soon after the nuclei collide

$$d = 1.88(6kT/\rho)^{1/5}\psi^{2/5}t^{2/5}(T/T_0)^{-4/5} \quad (4)$$

where k is the Boltzmann's constant, T is the temperature in the furnace, ρ is the particle density, ψ is

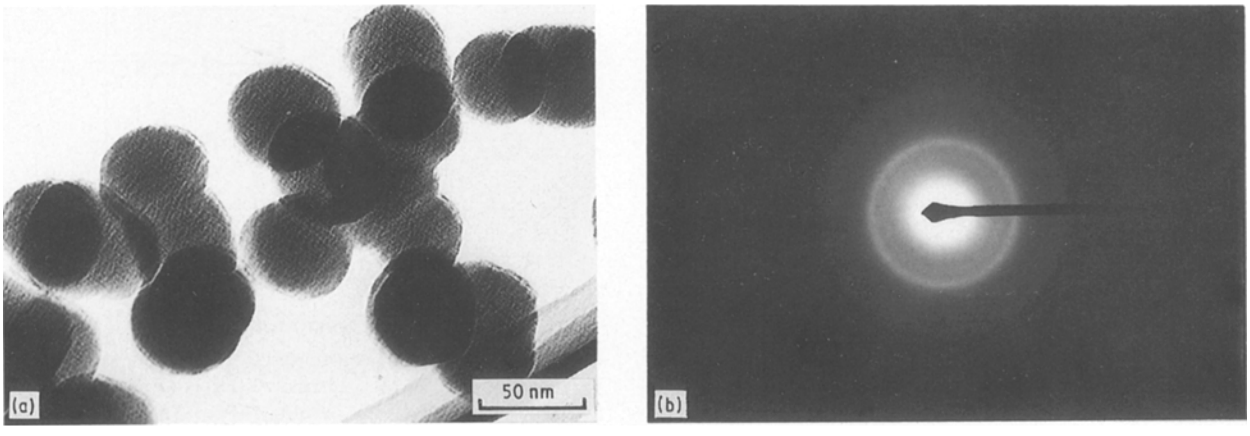

Figure 6 Electron micrographs of the powder prepared at 1373 K, $[(CH_3)_2SiCl_2] = 7.0\,mol\,\%$, FR $= 2.0 \times 10^{-5}\,m^3\,sec^{-1}$. (a) Bright-field image, (b) electron diffraction pattern.

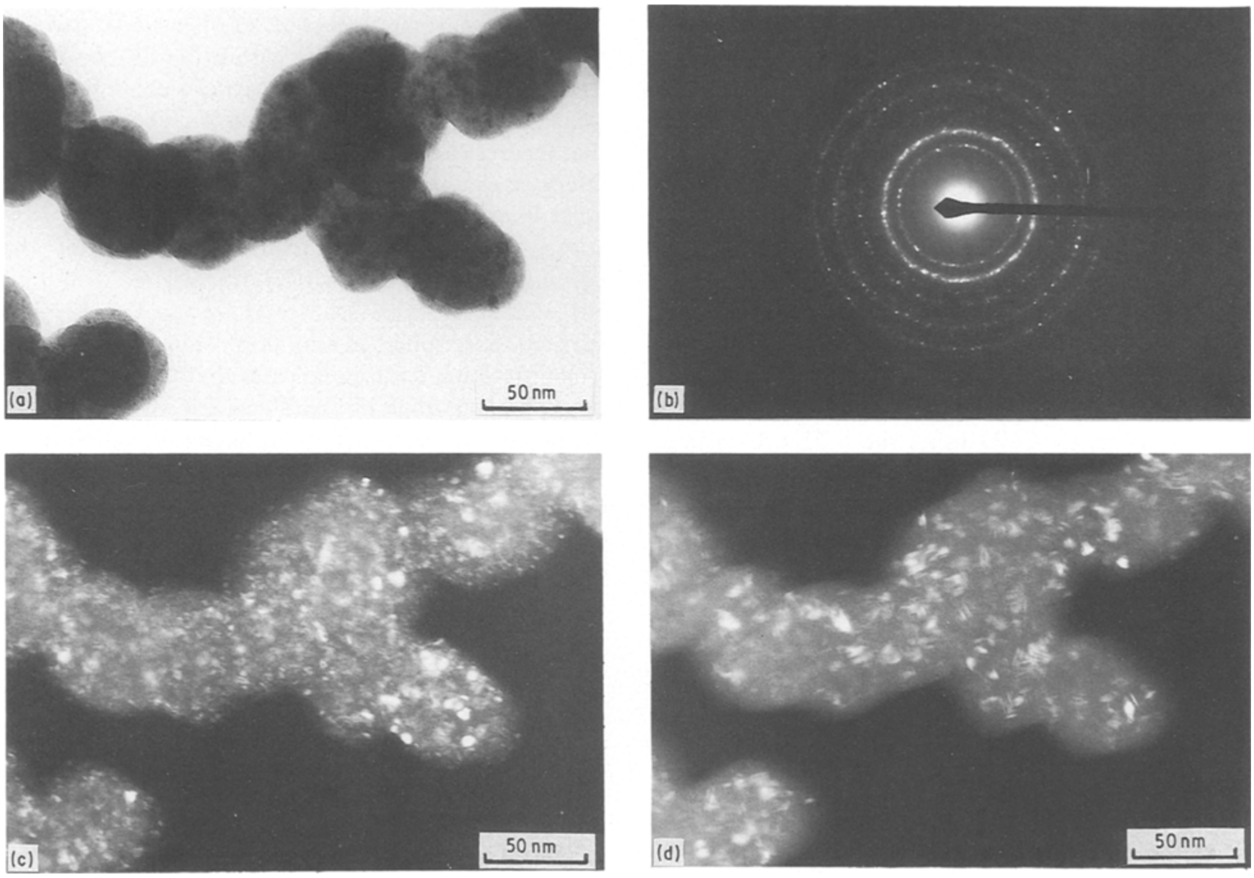

Figure 7 Electron micrographs of the powder shown in Fig. 6 after heat-treatment at 1423 K in an argon atmosphere for 2 h. (a) Bright-field image, (b) electron diffraction pattern, (c) β-SiC (1 1 1) dark-field image, (d) Si (1 1 1) dark-field image.

the volume fraction of particles, T_0 is the standard temperature (298 K), and t is the effective exposure time in the furnace under a standard temperature. Equation 4 predicts a decrease in particle size with increasing reaction temperature and gas flow rate, and with decreasing reactant gas concentration. This prediction agrees well with the present results as shown in Fig. 8.

Fig. 9 shows a comparison between the experimental and calculated results. The experimental values were about 1/5 to 1/6 of the calculated values. Suyama and Kato [19] and Morooka *et al.* [18] reported that the particle size of TiO_2 prepared by CVD was also 1/5 to 1/6 of the calculated values. The reason for the lower experimental values is explained by the fact that some nuclei do not coalesce to form new particles even if they collide [20].

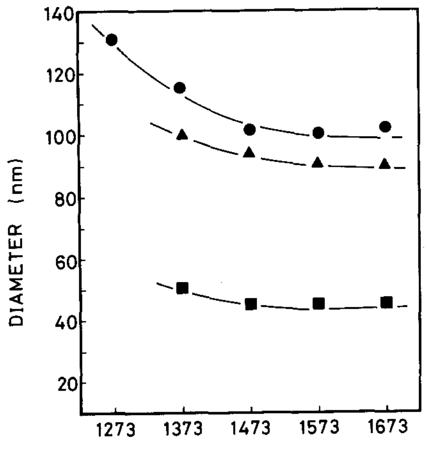

Figure 8 Effect of reaction temperature on particle size. (●) $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR = $6.3 \times 10^{-6}\,m^3\,sec^{-1}$; (▲) $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR = $2.0 \times 10^{-5}\,m^3\,sec^{-1}$; (■) $[(CH_3)_2SiCl_2] = 7.0$ mol %, FR = $2.0 \times 10^{-5}\,m^3\,sec^{-1}$.

Fig. 10 shows the effect of reaction temperature on powder density. The values calculated from the composition and theoretical densities of SiC, silicon and carbon ($\rho_{SiC} = 3.21 \times 10^3\,kg\,m^{-3}$, $\rho_{Si} = 2.33 \times 10^3\,kg\,m^{-3}$, $\rho_C = 1.85 \times 10^3\,kg\,m^{-3}$) are also shown in Fig. 10. The densities of powders prepared at

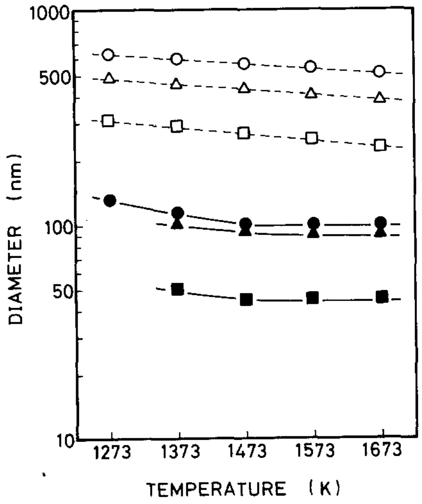

Figure 9 Comparison between experimental and calculated particle size. (○, ●) $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR = $6.3 \times 10^{-6}\,m^3\,sec^{-1}$; (△, ▲) $[(CH_3)_2SiCl_2] = 14.5$ mol %, FR = $2.0 \times 10^{-5}\,m^3\,sec^{-1}$; (□, ■) $[(CH_3)_2SiCl_2] = 7.0$ mol %, FR = $2.0 \times 10^{-5}\,m^3\,sec^{-1}$. (○, △, □) Equation 4; (●, ▲, ■) experimental.

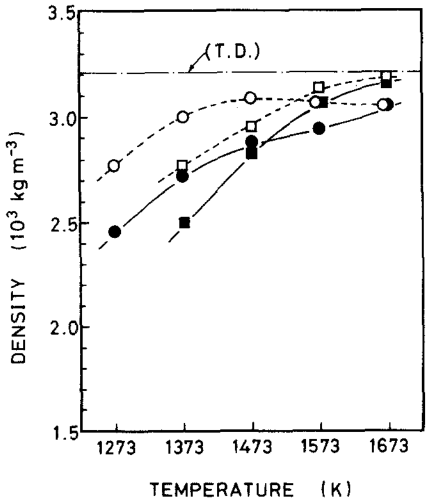

Figure 10 Effect of reaction temperature on powder density. (○, ●) $[(CH_3)_2SiCl_2]$ = 14.5 mol %, FR = 6.3×10^{-6} $m^3 sec^{-1}$; (□, ■) $[(CH_3)_2SiCl_2]$ = 7.0 mol %, FR = 2.0×10^{-5} $m^3 sec^{-1}$. (○, □) Calculated from powder composition; (●, ■) experimental. T.D. theoretical density of β-SiC (3.21×10^3 kg m^{-3}).

T_{rea} = 1673 K are in good agreement with the calculated values. This result indicates that dense particles are formed at T_{rea} = 1673 K. The densities of the powders prepared below 1573 K were lower than the calculated values. This difference between the measured and the calculated values increased with decreasing reaction temperature. This result indicates that lower reaction temperatures give a larger number of pores in the particles. The BET specific surface area, particle sizes and crystallite sizes of the powders prepared in the present work are summarized in Table I.

3.3. Infrared absorption and lattice parameter of β-SiC

Fig. 11 shows the effect of reaction temperature on the lattice parameter of β-SiC contained in powders. The lattice parameters decreased with increasing reaction temperature; however, all the values obtained in the present work were larger than that of bulk β-SiC crystal (0.435 89 nm) [21]. It was found that the higher the $(CH_3)_2SiCl_2$ concentration, the larger the lattice parameters became.

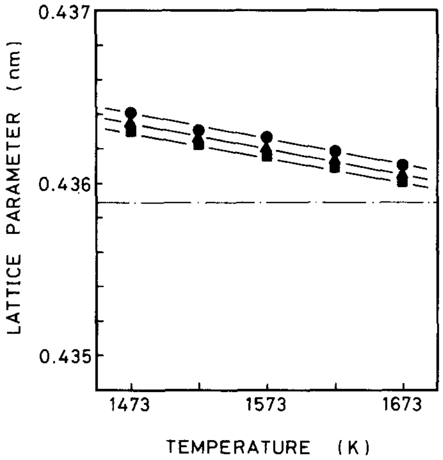

Figure 11 Effect of reaction temperature on the lattice parameter of β-SiC. (●) $[(CH_3)_2SiCl_2]$ = 14.5 mol %, FR = 6.3×10^{-6} $m^3 sec^{-1}$; (▲) $[(CH_3)_2SiCl_2]$ = 14.5 mol %, FR = 2.0×10^{-5} $m^3 sec^{-1}$; (■) $[(CH_3)_2SiCl_2]$ = 7.0 mol %, FR = 2.0×10^{-5} $m^3 sec^{-1}$. (—·—) JCPDS [21].

There is no known report published on the lattice parameters of β-SiC particles prepared by CVD using organo-silicon compounds. Hasegawa and Okamura [22] synthesized β-SiC fibre (containing SiO_2 and free carbon) by a polymerization and pyrolysis process using $(CH_3)_2SiCl_2$ as a starting material. They reported that the *d* value of β-SiC for the fibre decreased with increasing pyrolysis temperature [23]. This tendency agrees with the present results. Pai *et al.* [24] and the present authors [6] reported that the lattice parameters of β-SiC powders prepared by CVD using the CH_4–SiH_4–H_2 system were larger than that of bulk β-SiC when free silicon was co-deposited with β-SiC. Pai *et al.* [24] conjectured that a solid solution of silicon in the β-SiC lattice could be formed, thus increasing the value of lattice parameter. However, no other previous work has confirmed the evidence of a solid solution of silicon in β-SiC and it is generally considered that β-SiC is governed by strict stoichiometry [25].

Our earlier report suggested that the lattice mismatch between silicon and β-SiC (a_{Si} is about 20% larger than $a_{\beta\text{-SiC}}$) may have given larger lattice parameters of β-SiC powders [6]. Many researchers [26, 27] observed β-SiC film deposited on a silicon substrate by TEM and revealed that the lattice of β-SiC was significantly distorted at the β-SiC/Si interface. Many dangling bonds are formed due to the existence of nanometre-sized pores and the large surface area of the structure. These conditions may also have contributed to the increase of the lattice parameter.

Fig. 12 shows typical infrared absorption spectra. For all the powders, an absorption peak due to an Si–C bond is observed between 800 and 900 cm^{-1}.

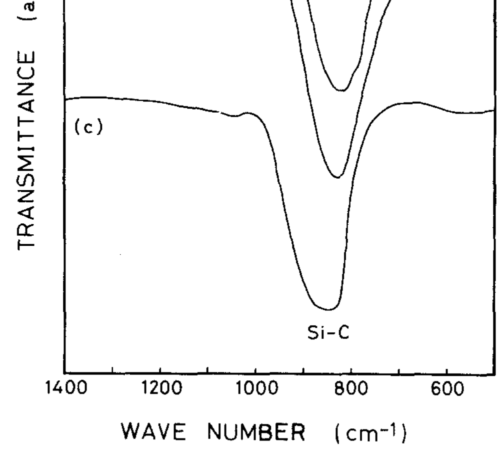

Figure 12 Infrared absorption spectra of the powders. (a) $[(CH_3)_2SiCl_2]$ = 14.5 mol %, FR = 6.3×10^{-6} $m^3 sec^{-1}$, T_{dep} = 1273 K; (b) $[(CH_3)_2SiCl_2]$ = 7.0 mol %, FR = 2.0×10^{-5} $m^3 sec^{-1}$, T_{dep} = 1373 K; (c) $[(CH_3)_2SiCl_2]$ = 7.0 mol %, FR = 2.0×10^{-5} $m^3 sec^{-1}$, T_{dep} = 1673 K.

TABLE I Deposition conditions and some properties of powders

Reaction temperature (K)	Total gas flow rate ($m^3 sec^{-1}$)	$(CH_3)_2SiCl_2$ concentration (mol %)	S_A ($m^2 g^{-1}$)	d_{BET} (nm)	d_{TEM} (nm)	$d_{X\text{-}ray}$ (nm)
1273	6.3×10^{-6}	14.5	19	128	130 ± 40	0.9
1373			18	123	115 ± 20	1.8
1473			19	111	101 ± 17	2.5
1573			25	82	99 ± 17	3.6
1673			26	76	102 ± 20	4.8
1373	2.0×10^{-5}	14.5	21	105	100 ± 20	1.8
1473			23	93	95 ± 10	2.7
1573			20	101	90 ± 15	4.0
1673			32	63	90 ± 10	4.7
1373	2.0×10^{-5}	7.0	53	45	50 ± 10	1.2
1473			28	76	45 ± 20	1.8
1573			40	49	45 ± 20	2.8
1673			52	37	45 ± 10	4.0

Small peaks are observed at 1273, 1010 and 600 cm^{-1} for the powders prepared at $[(CH_3)_2SiCl_2] = 14.5$ mol % and $T_{rea} = 1273$ to 1473 K. These peaks correspond to the Si–CH_3, C–H [28] and Si–Cl [29] bonds, respectively. However, no peaks except for the Si–C bond are observed for the particles prepared at $[(CH_3)_2SiCl_2] = 14.5$ mol %, $T_{rea} = 1573$ to 1673 K, and for those prepared at $[(CH_3)_2SiCl_2] = 7.0$ mol %, $T_{rea} = 1273$ to 1673 K. The absorption peak between 800 and 900 cm^{-1} due to the Si–C bond shifts to a higher frequency as the reaction temperature is increased. This behaviour can be predicted by a model of surface phonon mode for infrared spectra. The calculation gives an absorption peak at about 870 cm^{-1} [30]. The position of the absorption peak depends mainly on the lattice parameter and amount of free silicon contained in the powder. The absorption peak at about 870 cm^{-1} arising due to the surface phonon mode will shift to a lower frequency with increasing lattice parameter and free silicon content. This tendency is in agreement with the present results as shown in Figs 3 and 11.

4. Conclusions

Silicon carbide powders (β form) were prepared by CVD using the $(CH_3)_2SiCl_2$–H_2 system at reaction temperatures of 1273 to 1673 K. The structures and properties of the powders were investigated. The following results were obtained.

1. Single-phase β-SiC powder was obtained at $[(CH_3)_2SiCl_2] = 7.0$ mol %, FR $= 2.0 \times 10^{-5} m^3 sec^{-1}$ and $T_{rea} = 1673$ K.

2. The C/Si molar ratio in the powders increased with increasing reaction temperature and $(CH_3)_2SiCl_2$ concentration, and with decreasing gas flow rate. Free silicon and/or free carbon of nanometre size are dispersed within β-SiC polycrystalline particles to form composite particles.

3. The particles were spherical in shape and uniform in size. The particle size increased from 45 to 130 nm with decreasing reaction temperature and gas flow rate, and with increasing reactant concentration. The particle size dependence on the deposition conditions was explained by the fusion–coalescence model.

4. The lattice parameter for β-SiC decreased with increasing reaction temperature. All of the values found in the present study were larger than that of bulk β-SiC crystal. It is speculated that the strain and dangling bonds in the β-SiC particles may affect the lattice parameter.

5. The infrared absorption peaks of β-SiC particles due to the surface phonon mode were observed between 800 and 900 cm^{-1}, and they shifted to a higher frequency with increasing reaction temperature. This tendency was explained as an effect of decreasing β-SiC lattice parameter and free silicon content.

Acknowledgements

The authors thank Mr F. Chida for measurements of infrared absorption spectra, Messrs H. Ohta, T. Sekiguchi and M. Kikuchi for TEM observations and EDX analysis and Professor R. Watanabe for helpful discussions. This research was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Scientific and Culture, under contract nos. 60 430 019 and 60 850 130.

References

1. Y. TAKEDA *et al.*, in "Advances in Ceramics, Vol. 7", edited by M. F. Yan and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1983) p. 253.
2. H. K. BOWEN, *Mater. Sci. Engng* **44** (1980) 1.
3. A. KATO, J. HOJO and Y. OKABE, *Mem. Fac. Engng Kyushu Univ.* **41** (1981) 319.
4. W. R. CANNON *et al.*, *J. Amer. Ceram. Soc.* **65** (1982) 330.
5. Y. OKABE, J. HOJO and A. KATO, *J. Chem. Soc. Jpn* **2** (1980) 188.
6. L. D. CHEN, T. GOTO and T. HIRAI, *J. Mater. Sci.* **24** (1989) 3824.
7. Y. OKABE, J. HOJO and A. KATO, *J. Less-Common Metals* **68** (1979) 29.
8. W. BÖCKER and H. HAUSNER, *Ber. Dt. Keram. Ges.* **55** (1978) 233.
9. M. ENDO *et al.*, *Yogyo-Kyokai-Shi* **95** (1987) 114.
10. P. RAI-CHOUDHURY and N. P. FORMIGONI, *J. Electrochem. Soc.* **116** (1969) 1440.
11. G. VERSPUI, in "Proceedings of the 6th International Conference on CVD", Atlanta, October 1977, edited by L. F. Donaghey, P. Rai-Choudhury and R. N. Tauber (Electrochemical Society, Princeton, New Jersey, 1977) p. 366.
12. W. V. MUENCH and E. PETTENPAUL, *J. Electrochem. Soc.* **125** (1978) 294.

13. L. AGGOR and W. FRITZ, *Chemie Ing. Technol.* **43** (1971) 472.
14. L. M. IVANOVA, G. A. KAZARYAN and A. A. PLETYUSHKIN, *Izvest. Akad. Nauk SSSR, Neorg. Mater.* **2** (1966) 223.
15. E. FITZER, in "Proceedings of the International Symposium of Factors in Densification and Sintering of Oxide and Non-oxide Ceramics", Hakone, Japan, October 1978, edited by S. Somiya and S. Saito (Gakujutsu Bunken Fukyu-Kai, Tokyo, Japan, 1979) p. 40.
16. T. GOTO and T. HIRAI, *J. Chem. Soc. Jpn* **11** (1987) 1939.
17. F. S. LAI *et al.*, *J. Colloid Interface Sci.* **39** (1972) 395.
18. S. MOROOKA *et al.*, *Kagaku Kogaku Ronbunshu* **13** (1987) 159.
19. Y. SUYAMA and A. KATO, *J. Amer. Ceram. Soc.* **59** (1976) 146.
20. S. MOROOKA, Y. KATO and A. YOSHIZAWA, *Kemikaru Enjiniyaringu* **2** (1986) 29.
21. "Powder Diffraction File", JCPDS International Centre for Diffraction Data, File No. 29-1129.
22. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **18** (1983) 3633.
23. S. YAJIMA *et al.*, *J. Amer. Ceram. Soc.* **59** (1976) 324.
24. C. H. PAI *et al.*, *J. Mater. Sci.* **24** (1989) 3679.
25. D. P. BIRNIE, W. C. MACKRODT and W. D. KINGERY, in "Advances in Ceramics, Vol. 23", edited by C. R. A. Catlow and W. C. Mackrodt (American Ceramic Society, Westerville, Ohio, 1987) p. 571.
26. K. KUROIWA and T. SUGANO, *J. Electrochem. Soc.* **120** (1973) 138.
27. Y. NAKAJIMA, in "Tankakeiso Seramikkusu (SiC ceramics)", edited by S. Somiya and Y. Inomata (Uchida Rokakuho, Japan, 1988) p. 44.
28. H. WIEDER, M. CARDONA and C. R. GUARNIERI, *Phys. Status Solidi (b)* **92** (1979) 99.
29. H. A. SZYMANSKI and R. E. ERICKSON, "Infrared Band Handbook" (IFI/Plenum, New York, Washington, London, 1970) p. 1034.
30. L. D. CHEN, T. GOTO and T. HIRAI, in Abstracts of the 26th Symposium on Basic Science of Ceramics, Nagoya, Japan, 20–22 January (1988) p. 114.

Received 8 May
and accepted 29 September 1989