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Preparation of nanocrystal SiC powder by chemical vapour deposition

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Nanosized silicon carbide powders of high purity and low oxygen content have been prepared by thermal chemical vapour deposition (CVD) of dimethyldichlorosilane at pyrolytic temperatures, 1100–1400 °C. The nanosized silicon carbide particles prepared at 1400 °C consist of small crystallites of β-SiC arranged randomly in the particles. At pyrolytic temperature below 1300 °C, the particles consist of amorphous phase and β-type SiC crystallites. The average particle size changed from 70 nm to 40 nm and the average size of the β-SiC crystallite changed from 7.3 nm to 1.8 nm depending on the pyrolysis conditions. The C/Si molar ratios of the product powders changed from 0.5 to 1.07 with the CVD conditions. The near theoretical values of C/Si molar ratio of the product powders within 0.95–1.05 can be controlled by CVD conditions such as pyrolytic temperature and reactant concentration. Finally, the product powders were characterized by chemical analysis, X-ray diffraction, electron microscopy, and infrared spectroscopy.

1. Introduction

Nanocrystalline materials are single- or multi-phase polycrystals, the crystal size of which is of the order of a few nanometres, so that about 50 vol % of the material consists of grain or interphase boundaries which will have some important effects on the intrinsic properties of the materials, including physical, electrical and mechanical properties [1]. In the early 1980s, Gleiter [2] paid attention to the fact that these materials are morphologically quite different from their large-grained counterparts and may, therefore, possess quite different performances due to the high volume per cent of atomics at the interfaces in nanocrystalline materials. So far, much interest has been directed towards nanocrystalline materials with a novel atomic arrangement and boundary structure, which has generated significantly increased research activity and resulted in improvement of nanosized ceramic powder synthesis processing. Thermal chemical vapour deposition (CVD) [3–5], laser-induced chemical vapour deposition (LICVD) [6–9] and plasma chemical vapour deposition (PCVD) [10–14] have been used as the main processing routes for the preparation of various nanosized ceramic powders, especially SiC and Si_3N_4 powders.

As is known, silicon carbide has excellent mechanical properties and chemical stability at high temperature and superior electrical resistance and thermal conductivity, which has resulted in the wide application of SiC as engineering and electrical materials. On the other hand, SiC nanosized powder is the main reinforcement of nanocomposites materials. In view of this, a synthesis technique of nanocrystal SiC powder by a thermal chemical vapour deposition system is reported here and a series of highly pure SiC nanocrystal powders was obtained. The product powders were characterized by chemical analysis, X-ray diffraction (XRD), electron microscopy (TEM and HREM) and infrared spectroscopy. The particle size and shape, the microstructure of particles, the oxygen content and the C/Si molar ratio of the product powders were determined.

2. Experimental procedure

The experimental apparatus consists of a source gas supply and a control system, a thermal-wall reactor chamber and a product powder collector, as shown schematically in Fig. 1. In the present work, dimethyldichlorosilane ($(CH_3)_2SiCl_2$, DMS) was used as the source of both silicon and carbon elements, and hydrogen gas was used as source gas and carrier gas. The flow rate of DMS was controlled by the hydrogen flow rate under a stable temperature water bath. The mixed DMS and hydrogen gases were injected into the reactor chamber through a quartz nozzle. The pyrolytic

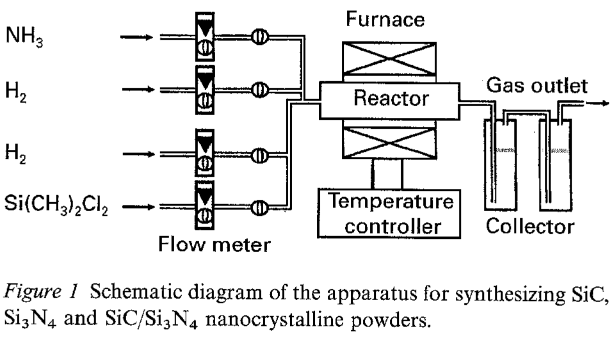

Figure 1 Schematic diagram of the apparatus for synthesizing SiC, Si_3N_4 and SiC/Si_3N_4 nanocrystalline powders.

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temperatures were in the range 1100–1400 °C; the product powders were collected by the collector system.

Many experimental results [15, 16] have indicated that when preparing SiC from DMS using a pyrolysis mechanism, the $(CH_3)_2SiCl_2$ molecule was pyrolyzed first and then transformed into Si(s) and CH_4(g) which was decomposed into C(s) and hydrogen with time. Then the Si(s) and C(s) combined to yield SiC(s). The reactions from $(CH_3)_2SiCl_2$(g) to SiC(s) are given below

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

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

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

The present work confirms than, because the reaction rate of Equation 1 was faster than Equation 2 at a pyrolytic temperature below 1300 °C, excessive Si(s) remained in the product powder.

The prepared SiC powders were characterized by chemical analysis, infrared (IR) spectroscopy, and electron microscopy (for example, TEM and HREM). The amount of crystalline SiC was determined by X-ray diffraction (XRD). The average particle size and crystallite size of β-SiC were examined by TEM and XRD, respectively.

3. Results and discussion

3.1 Particle size and microstructure

The effects of pyrolytic temperatures, DMS concentrations, flow rates of the source gas and the total gas pressure in the reactor chamber on the crystal phase, microstructure of particles, particle size, C/Si molar ratio and oxygen content of the product powders, were studied. The concentration of DMS was adjusted from 3.5–10.5 mol %, and the flow rate of the source gas, DMS, ranged from 1.0–2.5 l min^{-1}. The TEM and HREM observations indicated that all the product powders prepared under different pyrolysis conditions were of spherical shape and uniform particle-size distribution. Fig. 2 shows a transmission electron micrograph and diffraction pattern of SiC powder prepared at 1400 °C, 3.5 mol % DMS concentration and 1.5 l min^{-1} flow rate, which indicated that the SiC powder was of an average particle size about 45 nm and consisted of SiC polycrystals. The polycrystalline structure of the product powder were determined further by high-resolution electron microscopy (HREM) as shown in Fig. 3. Fig. 3a–d show the HREM microstructure of the product powders prepared under a DMS concentration of 3.5 mol % and the source gas flow rate of 1.5 l min^{-1} at the pyrolytic temperatures of 1100 °C, 1200 °C, 1300 °C and 1400 °C, respectively. Fig. 3d indicates that the SiC particles consist of β-SiC crystallites arranged randomly in the particles and the average size of β-SiC crystallite making up the powder was about 6–8 nm. At the lower pyrolytic temperature, the product powder consisted of a morphous phase and crystallites. At the pyrolytic temperature of 1100 °C, the particles consisted mainly of amorphous phase in which a few SiC crystallites were distributed, which was confirmed by HREM (Fig. 3a) and XRD, as discussed in Section 3.3. With decrease of the pyrolytic temperatures, the average particle size and the average crystallite size of β-SiC making up the particles was reduced from 60 nm to 47 nm and from 7.3 nm to 1.8 nm, respectively; the number of SiC crystallites decreased and the fraction of amorphous phase increased. The average diameter of the particles and the average β-SiC crystallite size of the product powders prepared under different pyrolytic conditions are listed in Table I. The particle size changed from 70 nm to 40 nm and the crystallite size from 7.3 nm to 1.8 nm.

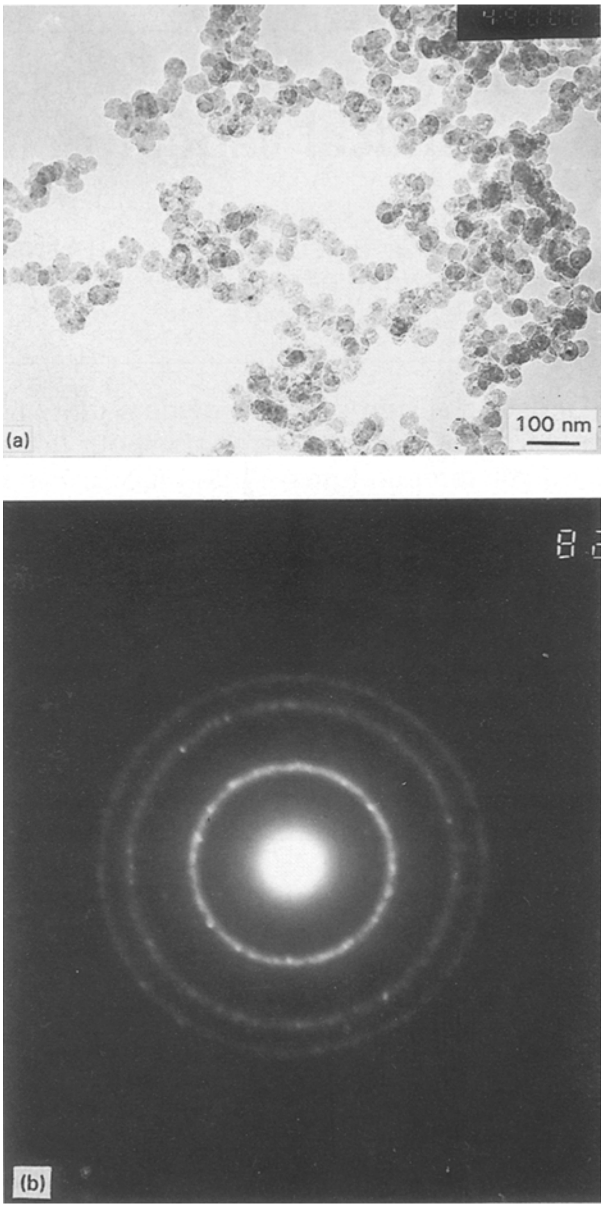

Figure 2 (a) Transmission electron micrograph and (b) diffraction pattern of SiC powder prepared at 1400 °C under a DMS concentration of 3.5 mol % and a flow rate of 1.5 l min^{-1}.

3.2. Chemical composition and crystal phase

Table II shows the C/Si molar ratio, crystal phase and oxygen content of the product powders under various

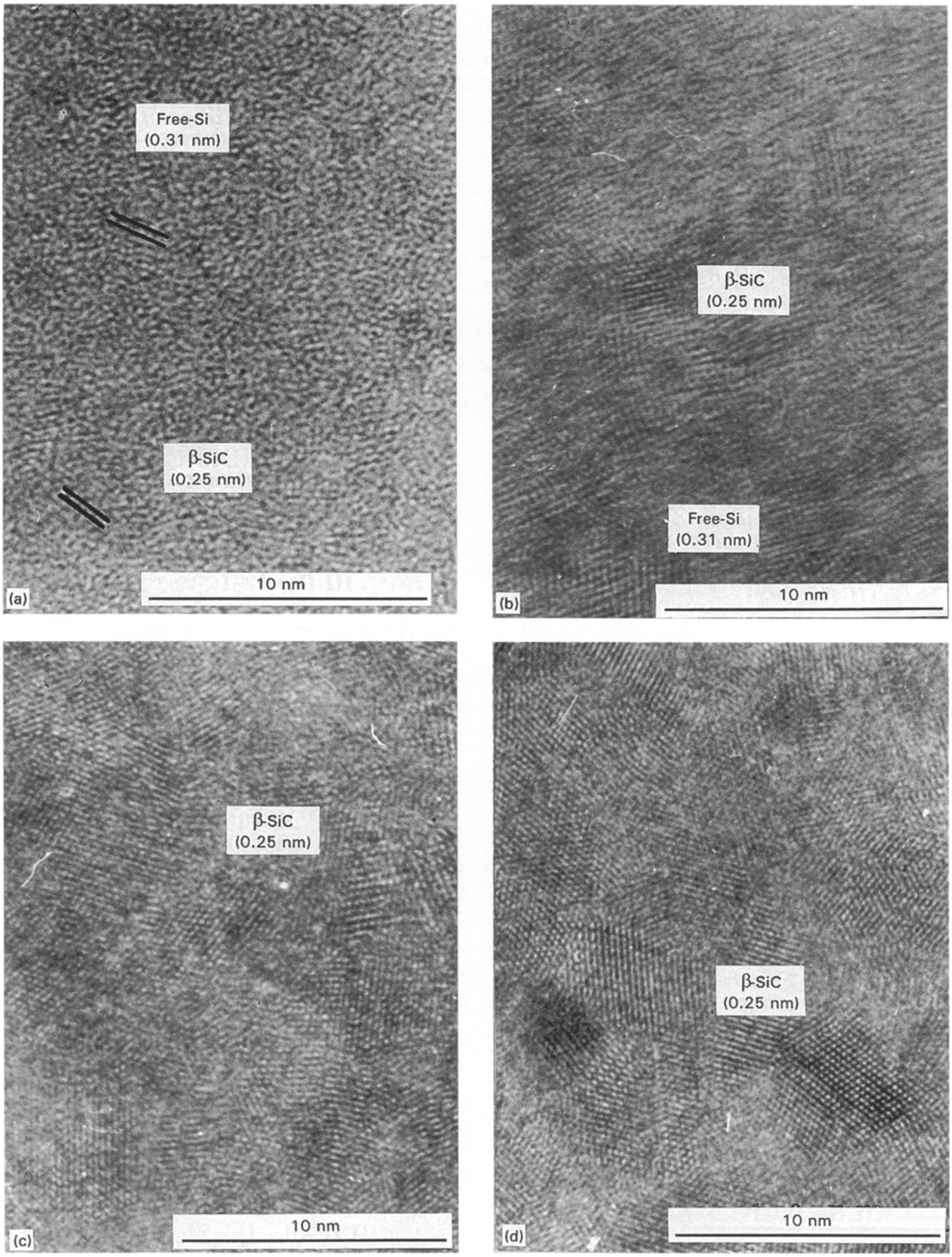

Figure 3 High-resolution electron micrographs of product powders prepared under a DMS concentration of 3.5 mol % and a source gas flow rate of 1.5 l min^{-1} at (a) 1100 °C, (b) 1200 °C, (c) 1300 °C and (d) 1400 °C.

pyrolysis conditions. With the DMS purified by distillation, the oxygen content of the product powder are less than 0.90 wt % which is of benefit to sintering and mechanical properties. The C/Si molar ratios of the product powders were plotted as linear functions of the source gas concentration and the pyrolytic temperature in Fig. 4. These results show that the C/Si molar ratios were near the theoretical values of SiC at the pyrolytic temperature of 1400 °C with the $(CH_3)_2SiCl_2$ concentration from 7.0–10.5 mol % and

TABLE I Particle size and crystallite size of product vs pyrolysis conditions

Temperature (°C)	Concentration of DMS (mol %)	F.R. of DMS (L/min)	Pressure (atm)	Particle size (nm)	Crystallite size (nm)
1400	3.5	1.5	1.0	45	6.1
1400	7.0	1.5	1.0	60	6.7
1400	10.5	1.5	1.0	70	7.3
1400	3.5	1.0	1.0	45	5.9
1400	3.5	2.0	1.0	45	6.1
1400	7.0	1.5	0.5	40	—
1300	7.0	1.5	1.0	55	4.6
1200	7.0	1.5	1.0	50	3.4
1100	7.0	1.5	1.0	47	1.8

TABLE II C/Si molar ratio and oxygen content of the product powder versus pyrolysis conditions

No.	Temperature (°C)	Concentration DMS (mol %)	DMS flow rate (L/min)	Pressure (atm)	CSi (mol mol^{-1})	Total O content (wt %)	Crystal phase
1[a]	1400	3.5	1.5	1.0	0.968	0.86	β
2[a]	1400	7.0	1.5	1.0	0.994	0.88	β
3[a]	1400	10.5	1.5	1.0	1.065	0.84	β
4	1400	3.5	1.0	1.0	0.961	1.24	β
5	1400	3.5	2.0	1.0	0.978	1.18	β
6[a]	1400	7.0	1.5	0.5	1.009	0.73	β
7[a]	1400	7.0	1.0	0.5	1.037	0.86	β
8	1300	7.0	1.5	1.0	0.848	1.15	A[b] + β
9	1200	7.0	1.5	1.0	0.665	1.73	A[b] + β
10	1100	7.0	1.5	1.0	0.503	1.68	A[b] + β

[a] Souce DMS was purified by distillation.

[b] A = amorphous.

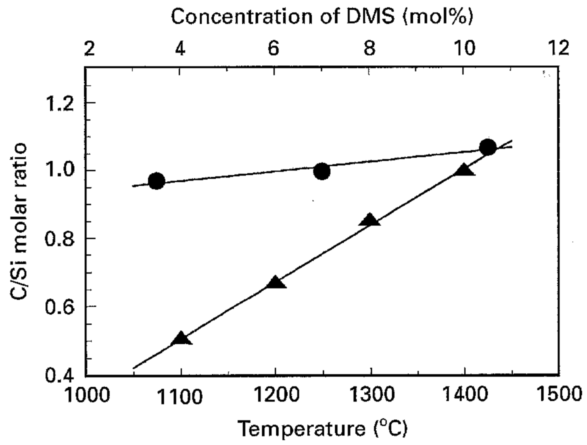

Figure 4 C/Si molar ratios of the product powders as a function of the (●) source gas concentration and (▲) the pyrolytic temperature.

increased slightly with increasing $(CH_3)_2SiCl_2$ concentration. This agrees well with the pyrolysis mechanism. According to the transformation reactions of dimethyldichlorosilane into silicon carbide, the increase in concentration of $(CH_3)_2SiCl_2$ will accelerate the reaction rate of Equations 1, 2 and 3, simultaneously. But excess hydrogen will accelerate the reaction rate of Equation 1 and retard that of Equation 2. At a stable pressure of the total source gas, with decreasing concentration of DMS, the partial pressure of hydrogen increased and Reaction 1 was accelerated and Reaction 2 was retarded, which resulted in the increase of free-silicon in particles and a decrease of the C/Si molar ratio of the product powders. On the other hand, the C/Si molar ratio decreased significantly when the product powders were prepared at a lower pyrolytic temperature than 1300 °C, and the powders consisted of SiC and free silicon. It was thought that at a temperature lower than 1300 °C, the reaction rate of Equation 1 was much faster than that of Equation 2 and so excessive Si(s) were deposited in the product powders. The diffraction patterns of the free Si(1 1 1) crystal surface with a lattice constant of 0.314 nm were identified in Fig. 3a and b.

3.3. X-ray diffraction (XRD) and infrared spectra

Fig. 5 shows the X-ray diffraction patterns of the powders prepared at pyrolytic temperatures of 1100, 1200, 1300 and 1400 °C. With increasing pyrolytic temperature, the intensities of the β-SiC peaks increased and the peaks narrowed gradually. At 1100, 1200 and 1300 °C, two small peaks of Si(2 2 0) and Si(1 1 1) were observed, but no peaks of Si(2 2 0) and Si(1 1 1) were found at 1400 °C. The X-ray diffraction results showed that the crystallite size of β-SiC and the crystallization from amorphous SiC to β-SiC increased and the amount of free silicon remaining in the particles was reduced with increasing pyrolytic temperature. This XRD result coincided with the chemical analysis and electron microscopy observations mentioned in Sections 3.1 and 3.2. In the XRD pattern at 1400 °C, two

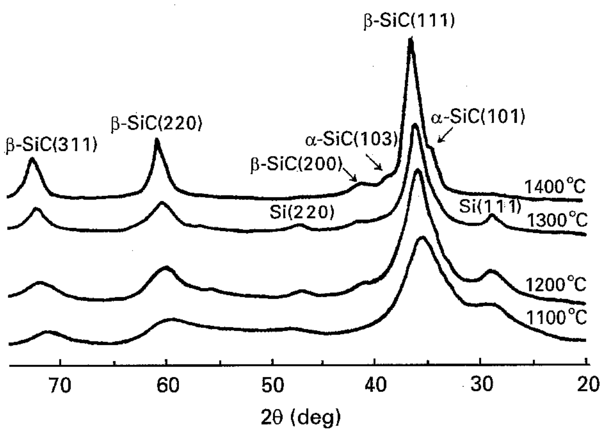

Figure 5 X-ray diffraction pattern of product powders prepared under a DMS concentration of 3.5 mol % and a source gas flow rate of 1.5 l min^{-1} at 1100 °C, 1200 °C, 1300 °C and 1400 °C.

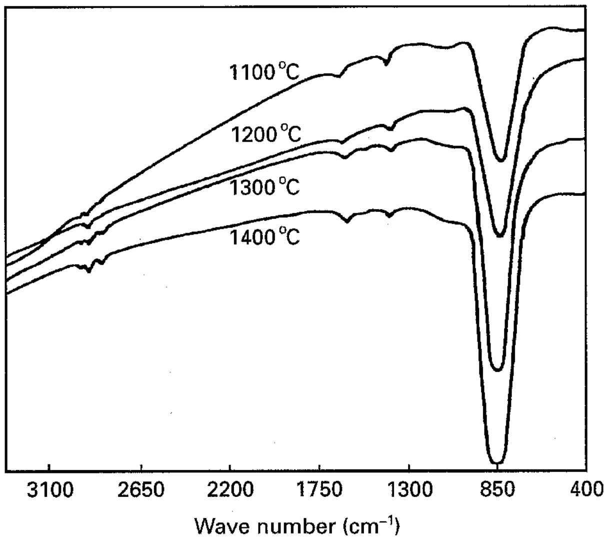

Figure 6 Infrared spectra from product powders at different pyrolytic temperatures.

weak peaks of α-SiC(1 0 3) and α-SiC(1 0 1) were observed, which demonstrated the onset of the transformation from β-SiC to α-SiC during the nucleation and growth of SiC powder at 1400 °C.

Fig. 6 shows the infrared absorption spectra (KBr pellet) of nanosized product powders prepared at different temperatures. A very strong absorption peak from 700–970 cm^{-1} corresponding to Si–C bond vibration can be observed. The width of this peak varies little with the pyrolytic temperature, but the intensities (transmittance) were increased significantly with increasing pyrolytic temperature. This is thought to be due to the variable C/Si (SiC/(SiC + Si)) molar ratio and the crystallized amount of amorphous SiC to β-SiC. The crystallized SiC resulted in a stronger vibration absorption than amorphous SiC and the higher the fraction of SiC in the particles, the more intense is the peak corresponding to the Si–C bond vibration. The band from 1050–1100 cm^{-1} corresponded to the Si–O bond vibration mode. It can be found that the Si–O vibration absorption peaks were weak and wide which coincide with the very low oxygen content in the product powder listed in Table II. The weak and sharp peaks responded to 1395, 1548 and 1630 cm^{-1} which arose from the vibration absorption of $-CH_x$ groups, indicating that a small amount of the remaining $-CH_x$ group was absorbed on the surface of the product powder.

4. Conclusion

Nanocrystalline silicon carbide powders were prepared by thermal chemical vapour deposition using $(CH_3)_2SiCl_2$ and hydrogen as source gases at pyrolytic temperatures from 1100–1400 °C. The microstructure of the particles and the properties of the powders were characterized by TEM and HREM observation, infrared spectroscopy and X-ray diffraction. The nanosized silicon carbide particles prepared at 1400 °C consist of small crystallites of β-SiC arranged randomly in the particles. At a pyrolytic temperature below 1300 °C, the particles consist of amorphous phase and β-type SiC crystallite. The average particle size of the product powders changed from 40 nm to 70 nm and the average size of β-SiC crystallite in the particles changed from 7.3 nm to 1.8 nm depending on the pyrolytic temperatures. The C/Si molar ratios of the product powders were determined by chemical analysis. The results indicated that the C/Si molar ratios changed from 0.5 to 1.07 on increasing the pyrolytic temperature from 1100 to 1400 °C. This variation of C/Si molar ratio with the pyrolytic temperature was proved by infrared absorption spectra. The effect of DMS concentration on the particle size and C/Si molar ratio was investigated. The particle size increased from 45 nm to 75 nm but only a slight variation of C/Si molar ratio was generated with change of the DMS concentration from 3.5 mol % to 10.5 mol %. The near theoretical values of C/Si molar ratio of the product powders within 0.95–1.05, can be controlled by CVD conditions such as pyrolytic temperature and reactant concentration.

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