Journal of the European Ceramic Society 20 (2000) 1939–1946

Silicon carbide powder synthesis by chemical vapour deposition from silane/acetylene reaction system

Štefan Kavecký [a,*], Beata Janeková, Jana Madejová, Pavol Šajgalík [b]

[a]Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Račianska 75, SK-838 12 Bratislava, Slovakia
[b]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-842 36 Bratislava, Slovakia

Received 28 June 1999; received in revised form 4 February 2000; accepted 12 February 2000

Abstract

Amorphous fine silicon carbide powders have been prepared via the chemical vapour deposition from reaction mixture SiH_4–C_2H_2 in a vertical tubular flow reactor in the temperature range 900–1250°C. Powder particles prepared at temperature 1100°C and C_2H_2/SiH_4 mol ratio 1.2 are equiaxial, quasispherical and agglomerated. The mean particle size of the powder is approx. 0.1–0.2 μm. The maximum agglomerate size is about 0.3 μm. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical properties; CVD; Grain size; Powders; SiC

1. Introduction

In the past few years, a great deal of interest has been focused on non-oxide ceramics, mainly on silicon carbide and nitride. Silicon carbide belongs to this category of materials due to its excellent chemical and thermal shock resistance, superior electrical properties, mechanical strength, chemical stability, and high thermal conductivity. Silicon carbide retains a large fraction of room temperature strength up to relatively high temperatures without a significant deterioration in its structural integrity. Strong covalent bonding between the constituent elements in this material gives rise to a combination of properties, such as low thermal expansion coefficient, high Young's modulus and hardness that are important for designing high-performance materials. Consequently the materials made from SiC have opened new areas in the field of materials designed such as those seen in metal- and ceramic-matrix composites.[1] Silicon carbide powder is also one of the most important catalyst supports recently used to replace the alumina support in heterogeneous catalysis.[2] SiC nanosized powder is frequently used as a main constituent of ceramic nanocomposite materials. Significant improvements in strength and toughness have been reported for Al_2O_3 containing fine SiC particles.[3] The dispersion of nanosized SiC particles into Si_3N_4 matrix can lead to considerable improvement in composite strength.[4,5]

In recent years, starting powders for the ceramic materials have at least one component of particles in the nanometer range (<100 nm). Such a way prepared ceramic materials attract attention mainly due to their enhanced low-temperature densification, excellent mechanical properties, and/or appearance of superplasticity.[6] Physical and chemical properties of starting powders are depending on the particle size, mainly in cases when the ratio of powder free surface to the powder bulk is extremely high. Ultrafine ceramic powders are usually used for design of materials for new applications, as materials with extreme high temperature applications, multifunctional materials, materials with superplastic behaviour, etc.

The usual synthesis techniques for producing SiC nanoparticles include mechanical milling of solid phases, solution chemistry and vapour-phase synthesis. The methods which are frequently used for SiC synthesis are as follows: carbothermal reduction of silica,[7] chemical vapour deposition (CVD), laser-induced chemical vapour deposition (LICVD),[8] plasma chemical vapour deposition (PCVD) and polymer pyrolysis.[9] A number of studies have been reported on the PCVD synthesis of

---

* Corresponding author. Tel.: +42-17-49268281; fax: +42-17-44253301.
E-mail address: ummskave@savba.sk (Š. Kavecký).

0955-2219/00/$ - see front matter
PII: S0955-2219(00)00071-6

ultrafine SiC powder. These used a wide range of reaction routs, for example $Si+CH_4$, and SiH_4+CH_4.[10] In another study, nanosized SiC powders of high purity and low oxygen content have been prepared by thermal CVD of dimethyldichlorosilane,[11] methyltrichlorosilane and or tetrachlorosilane.[12]

Generally, the vapour-phase reaction method as powder preparation technique is characterised by: (1) high purity of powder products due to the use of gaseous reactants which are purified easily by distillation; (2) highly discrete particles or unaggregated powders; (3) ease of preparation of ultrafine powders with narrow particle-size distribution by manipulating reaction conditions; and (4) versatility for the direct preparation of powders of metals and nonoxide in addition to oxides by control of the reacting atmosphere.[13]

In view of the above mentioned characteristics, a vapour-phase reaction (CVD process) was chosen for a synthesis of fine amorphous SiC powder in present paper. Influence of reaction temperature and molar ratio of C_2H_2 to SiH_4 on the particle size, morphology and the quality of the product in the system SiH_4–C_2H_2–N_2 is studied and discussed.

2. Experimental

Fig. 1 illustrates the experimental set up of the CVD apparatus which was used in the present study. Reactor consisted of an alumina ceramic tube with inner diameter of 46 mm and length of 500 mm (Alsint 99.7 wt% Al_2O_3) placed vertically in a molybdenum wound resistance furnace. The vertical temperature distribution of the reaction zone is uniform on the distance ±5 cm from the middle of the furnace at 1000°C.[14] These data together with the total gas flow through the reactor, which was varied between 130 and 178 $cm^3\ min^{-1}$ (all volumes are given at 22°C), could be used for estimation of the residence time of the reactants at various temperatures possible if a piston flow is assumed. That means the time available for the reaction in the isothermal reaction zone ranges from 54 to 78 s.

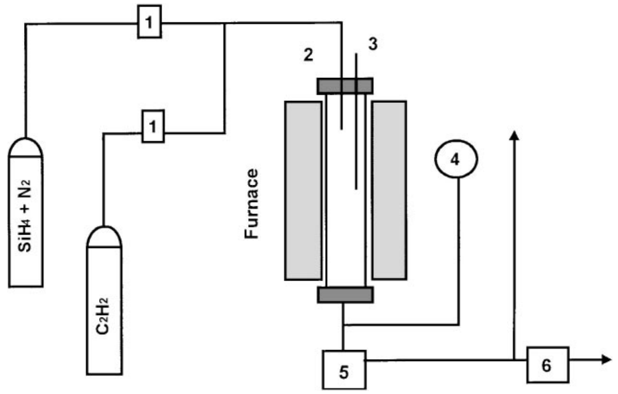

Fig. 1. Schematic diagram of CVD apparatus for synthesis of silicon carbide from a silane–nitrogen–acetylene gas mixture: 1. mass flow meter; 2. reactor; 3. thermocouple; 4. manometer; 5. sample collecting chamber; 6. rotary pump.

Input of acetylene (C_2H_2, purity 99.5 wt%) and electronic grade silane (15 wt% of SiH_4 in nitrogen, purity 99.99 wt%) through alumina tubes was localised in the upper (colder) part of the furnace. Gases were spontaneously premixed at this part, then they flowed through a tubular hot-wall reactor in which the reaction took place. The reaction temperatures used in the present study were 900, 1100, 1200 and 1250°C. The precipitate of reaction was filtered from the mist with help of a glass grit in the multiple sample collector in the bottom part of the apparatus. The details of the experimental set up of the hot wall reactor are described in an earlier work.[15] Various reaction conditions were selected in present study. The first set of experiments were carried out by varying the molar ratio of C_2H_2 to SiH_4 (r) in the range 0.9–2.1, while the reaction temperature (1100°C) was kept constant. The second set of experiments was carried out in the temperature range between 900 and 1250°C at fixed mol ratio (r) of C_2H_2 to SiH_4 at 1.2 and flow rate 130 $cm^3\ min^{-1}$. Reaction conditions are listed in Table 1. The gas pressure within the reactor was kept at 110 kPa during all experiments.

SiC powder product of reactions was collected and investigated by scanning electron microscopy (SEM), infrared (IR) spectroscopy, differential thermal analysis (DTA), chemical analysis and X-ray diffraction (XRD) analysis. The morphology, shape and size distribution of the powders were studied by SEM C Jeol JSM-35.

FTIR spectroscopy (Nicolet Magna 750) was used for characterisation of the composition of the amorphous powder product. TG in air/nitrogen atmosphere was used for setting the presence of free carbon and estimation of its content. Nitrogen content in the reaction powder product was determined by the chemical analytical method described in Ref. 16. XRD was used for qualitative analysis of main phases, the powder product after crystallisation consists of.

Table 1
Reaction condition

Sample no.	Temperature (°C)	Ratio C_2H_2:SiH_4	Ratio C:Si	Flow rate ($cm^3\ min^{-1}$)	Colour
1	900	1.2:1	2.4:1	130	Brown
2	1100	1.2:1	2.4:1	130	Black
3	1200	1.2:1	2.4:1	130	Black
4	1250	1.2:1	2.4:1	130	Black
5	1100	1.6:1	3.1:1	178	Black
6	1100	0.9:1	1.8:1	163	Brown–black
7	1100	2.1:1	4.2:1	143	Brown–black

3. Results and discussion

3.1. Characterisation of SiC powder — powder morphology

The reactor shown in Fig. 1 was used in present study for production of SiC amorphous fine powder. The following reaction is expected to take place in the reaction zone:

$$2SiH_4(g) + C_2H_2(g) \rightarrow 2SiC(s) + 5H_2(g) \qquad (1)$$

The powder formation process changes with reaction conditions, mainly with reaction temperature, even in the same system. Chemical analysis exclude the presence of nitrogen in the reaction product, even the nitrogen was the carrying gas of SiH_4 in the present case. This result means that no formation of Si_3N_4 is supposed at the reaction conditions.

IR analysis of the reaction products 1, 2 and 4 (Table 1) show that the major peak at 827 cm^{-1} corresponds to the Si–C vibrations (Fig. 2). This fact allows us to suppose that the reaction product is SiC amorphous powder. The other proof of production of SiC powder is the XRD pattern. Fig. 3 shows crystallised powder 4 (crystallised at 1580°C in Ar), the peaks corresponding to the β-SiC are visible, some minor amount of SiO_2 are also documented. The other minor species in the final product are discussed in the next paragraphs.

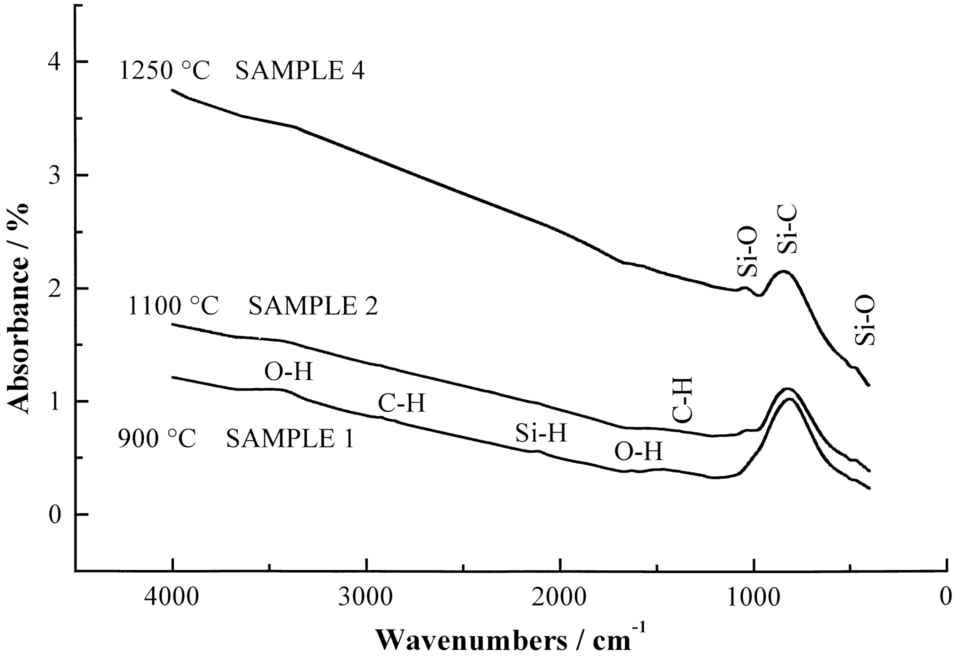

Fig. 2. Infrared spectra of SiC powder samples 1, 2 and 4 (Table 1) (temperatures 900, 1100 and 1250°C, ratio C_2H_2/SiH_4 1.2:1, flow rate 130 cm^3 min^{-1}).

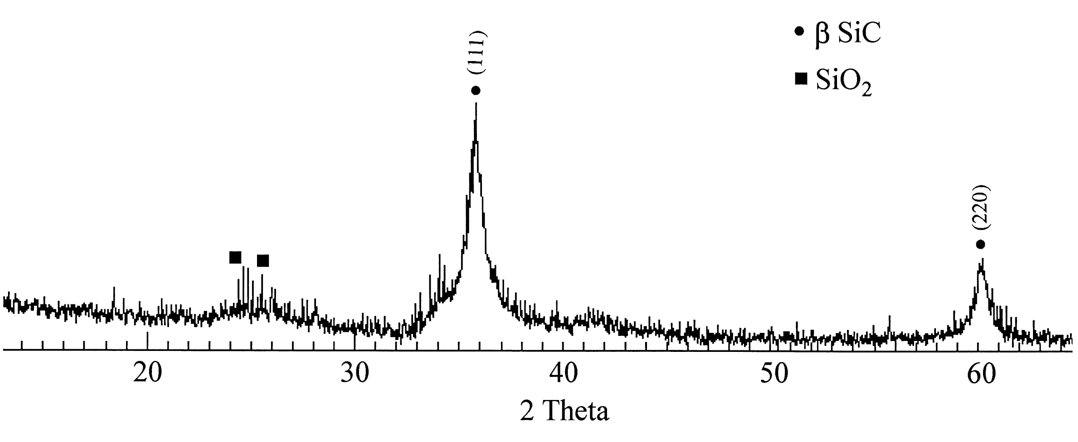

Fig. 3. XRD pattern of SiC powder sample 4 (Table 1) (temperature 1250°C, ratio C_2H_2/SiH_4 1.2:1, flow rate 130 cm^3 min^{-1}), crystallised at 1580°C for 2 h in argon.

The control of particle size is of prime importance in the production of powders. The prepared SiC powders generally consist of spherical, solid loosely agglomerated particles.

Fig. 4a and b shows the micrographs of powder products as a result of reaction conditions 1 and 2 (Table 1), respectively. The product of reaction performed at the condition 1 (Table 1) was not completely powdered. This product was brown. As can be seen from Fig. 4a, a large number of agglomerates are present. The particle size distribution is quite wide: the maximum size of particle is about 0.5 μm, the minimum is about 0.1 μm. Size of observed agglomerates is up to 1 μm. The large liquid wetted areas of particles is rarely observed (Fig. 4c). This indicates the presence of undecomposed and unreacted organic intermediate products pyrolysis of acetylene and silane. This statement is confirmed by IR spectrum, where the bands assigned to vibrations of the C–H and Si–H bonds are documented (Fig. 2).[17]

As can be seen from Fig. 4b (powder product of conditions 2, Table 1) grains of powder 2 are equiaxial and quasispherical. The mean particle size of this powder is approx. 0.1–0.2 μm. The narrow particle size distribution of powder 2 is also visible. Agglomeration of particles is substantially lower than in the above mentioned case. The maximum agglomerate size is about 0.3 μm.

3.2. The effects of pyrolytic temperatures

The formation of SiC powder grains/particles from reactant gases is a rather complicated atom transport process involving nucleation and growth. Both the nucleation and growth rates are considered to be function of the reaction temperature. As was mentioned above, from the morphological point of view, the temperature 1100°C is an optimum. The particle size distribution is narrow and particles are quasi-spherical. Slight increase of grain size and broadening of the particle size distribution of sample 4 (Table 2) with increasing temperature suggests that the growth increased faster than the nucleation rate with temperature (Fig. 5). The growth of particles which are in intimate contact makes the distribution broader at higher temperature (Fig. 4, indicated by arrow). This effect is more pronounced in Fig. 6, which shows the morphology of powder 2 after crystallisation at 1580°C in argon for 2 h. The powder was pressed into a pellet before crystallisation, i.e. more particles were in contact. Abnormal grain growth and sintering of two SiC spheres is clearly visible.

3.3. Powder formation — effect of C_2H_2/SiH_4 mol ratio on the composition of SiC powders

As the system, which produces powders by CVD has a large equilibrium constant, the metal-carrying reactant

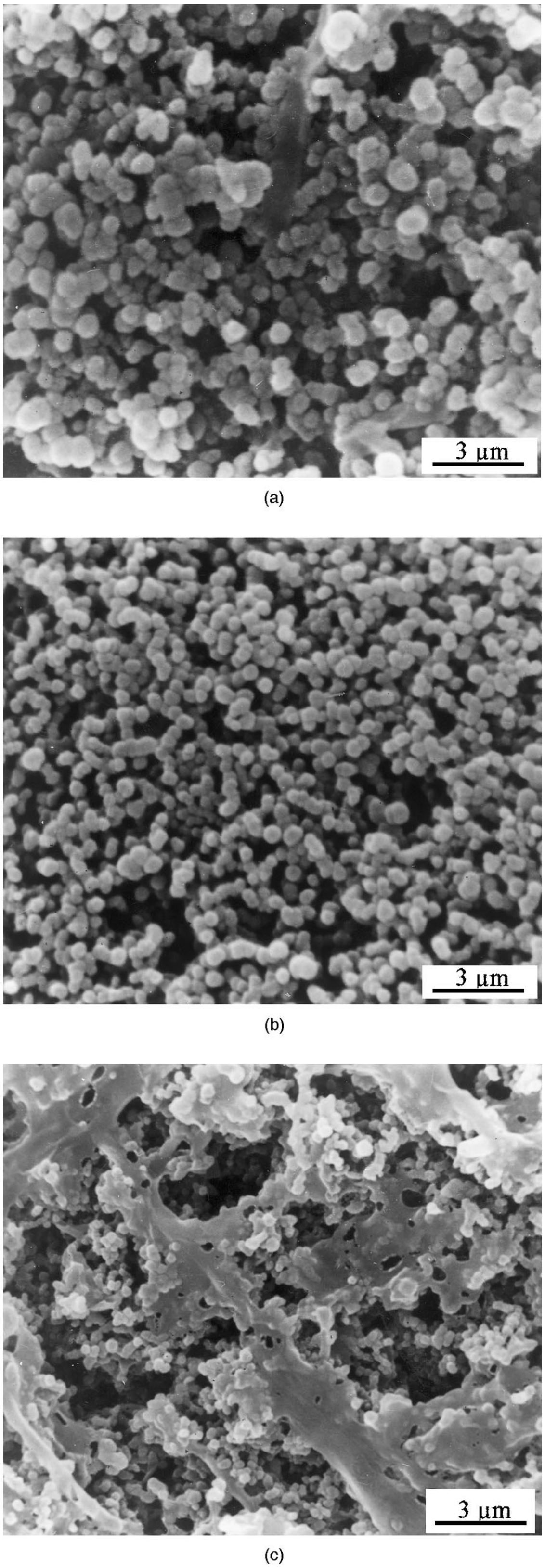

Fig. 4. Micrographs of powder products prepared: (a) sample 1 (Table 1) (temperature 900°C, ratio C_2H_2/SiH_4 1.2:1, flow rate 130 cm^3 min^{-1}); (b) sample 2 (Table 1) (temperature 1100°C, ratio C_2H_2/SiH_4 1.2: 1, flow rate 130 cm^3 min^{-1}); (c) another view of the same sample as in (a).

Table 2
Thermodynamic data of some reactions at preparation of SiC powder

	ΔG^o (kJ mol^{-1})			K_T		
Reactions	1100°C	1200°C	1300°C	1100°C	1200°C	1300°C
1. $2SiH_4$ (g) + C_2H_2 (g) = 2SiC (s) + $5H_2$ (g)	−587.1	−600.2	−613.4	2.1×10^{22}	1.9×10^{21}	2.3×10^{20}
2. SiH_4 (g) = Si (s) + $2H_2$ (g)	−156.1	−166.0	−175.9	8.6×10^{5}	7.7×10^{5}	6.9×10^{5}
3. C_2H_2 (g) = 2C (s) + H_2 (g)	−149.9	−144.7	−139.5	5.1×10^{5}	1.4×10^{5}	4.3×10^{4}

can, in practice, be completely converted into the products by adjusting the other reactant until in excess. Complete conversion of the metal source is also important to obtain a pure carbide powder, because the unreacted metal-carrying compound is often hydrolysed to contaminate the powder.

The chemical process for the formation of SiC powders in the SiH_4–C_2H_2–N_2 system is rather complicated. The following reaction mechanism, similar to that in Ref. 18, is proposed. At elevated temperatures, SiH_4 and C_2H_2 are decomposed to produce Si and C, respectively. Free Si react with free C to form gaseous SiC which nuclei instantly and grows to stabile over-critical size, but due to the narrow homogeneity range of SiC, SiC–C and SiC–Si system may also be formed. The following chemical equations can be written in sequence to describe the steps leading to SiC powder production:

$$SiH_4(g) \rightarrow Si(g) + 2H_2(g) \tag{2}$$

$$C_2H_2(g) \rightarrow 2C(g) + H_2(g) \tag{3}$$

$$Si(g) + C(g) \rightarrow SiC(g) \tag{4}$$

$$SiC(g) \rightarrow SiC\ (nucleus) \tag{5}$$

$$SiC\ (nucleus) \rightarrow SiC(s) \tag{6}$$

$$Si(g) \rightarrow Si(s) \tag{7}$$

$$C(g) \rightarrow C(s) \tag{8}$$

The reactions (2)–(8) should be considered as an ideal case, the kinetics of these reactions is not known. On the other hand, the simple thermodynamic calculation[19] shows that formation of SiC according to Eq. (1) is advantageous (see Table 2).

The IR spectrum, in addition to Si–C band, shows the bands at 1050 and 476 cm^{-1} due to Si–O stretching and bending vibrations. Moreover, a small peak at 1385 cm^{-1} is attributed to C-H deformation vibration, which indicates that these bonds survive the reaction conditions, i.e. reaction (3) was in this case not completed. This indicates higher flow rate as optimum. Some residual, not reacted carbon was also observed. TG curve of sample 2 is shown in Fig. 7. The weight loss at about 600°C in air is attributed to the oxidation of free carbon. As it is documented at this figure, about 7 wt% of free carbon was in the reaction product. This carbon excess is as a result of the reaction conditions (Table 1) the set ratio C:Si was 2.4:1. In order to be sure that

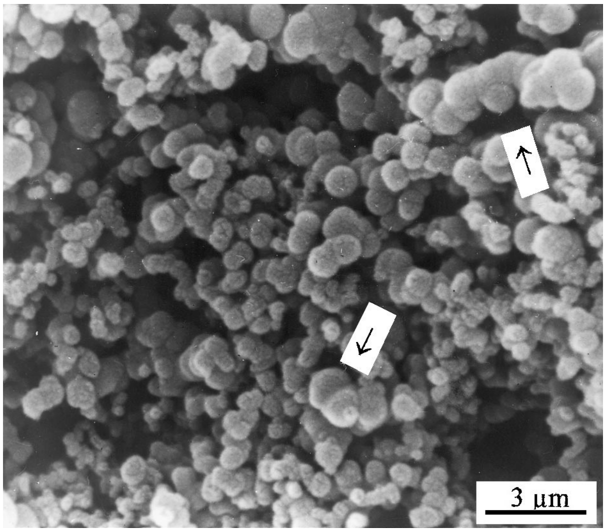

Fig. 5. Morphology of SiC powder, sample 4 (Table 1) (temperature 1250°C, ratio C_2H_2/SiH_2 1.2:1, flow rate 130 cm^3 min^{-1}).

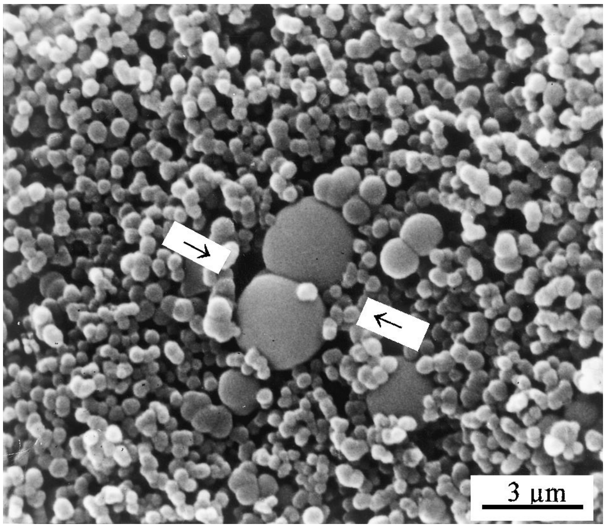

Fig. 6. Morphology of powder sample 2 (Table 1) (temperature 1100°C, ratio C_2H_2/SiH_4 1.2:1, flow rate 130 cm^3 min^{-1}) after crystallisation at 1580°C in argon for 2 h.

other compounds which can be dissipated at this temperature and thus accompany the oxidation of carbon, the same DTA measurement was performed in nitrogen. No weight loss at temperatures between 400 and 800°C was observed, only decrease was observed up to 400°C, which is connected with evaporation of adsorbed water and other hydroxyl groups. This effect is observed also at DTA measured in air (Fig. 8).

The equilibrium constant for the formation of Si(s) from SiH_4 at temperatures higher than 1100°C is some times larger than that of C(s) from C_2H_2 (Table 2) This fact influences the reaction kinetics and the chemical composition of the product. As can be seen from the IR spectra of products 1, 2 and 4 (Fig. 2), Si–H band is present only at the lowest temperature (900°C; Fig. 2), while the C–H band is present up to 1100°C. Only product prepared at 1250°C is free of these bands (Fig. 2).

This, in fact, indicates that either the temperature of complete decomposition of C_2H_2 is in the interval between 1100 and 1250°C or the flow rate is too high, and presence of C_2H_2 in hot zone of the furnace is too short. Si–O bands are present in all cases. These could

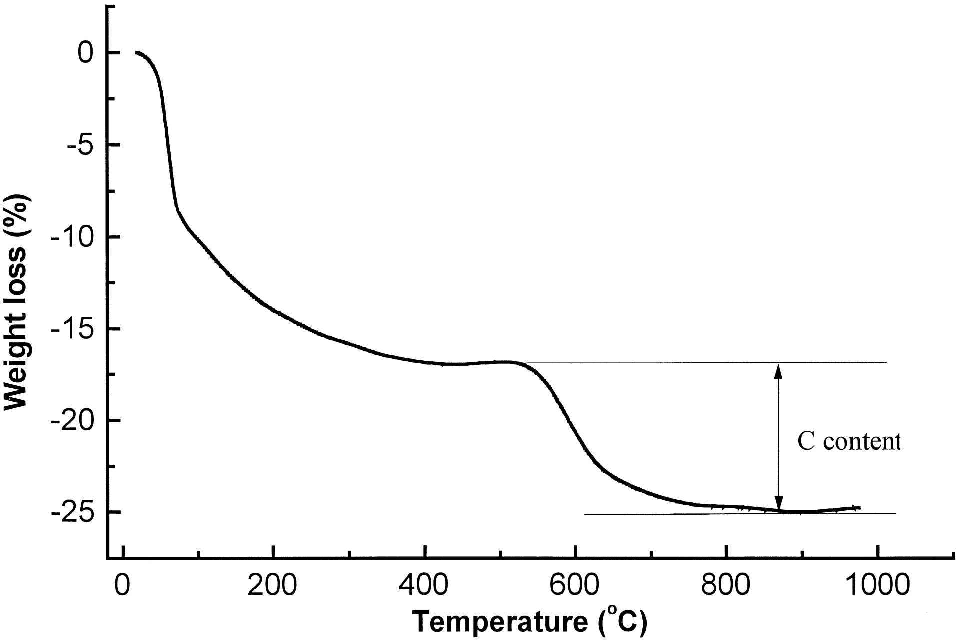

Fig. 7. TG curve of SiC powder sample 2 (Table 1) (temperature 1100°C, ratio C_2H_2/SiH_4 1.2:1, flow rate 130 cm^3 min^{-1}).

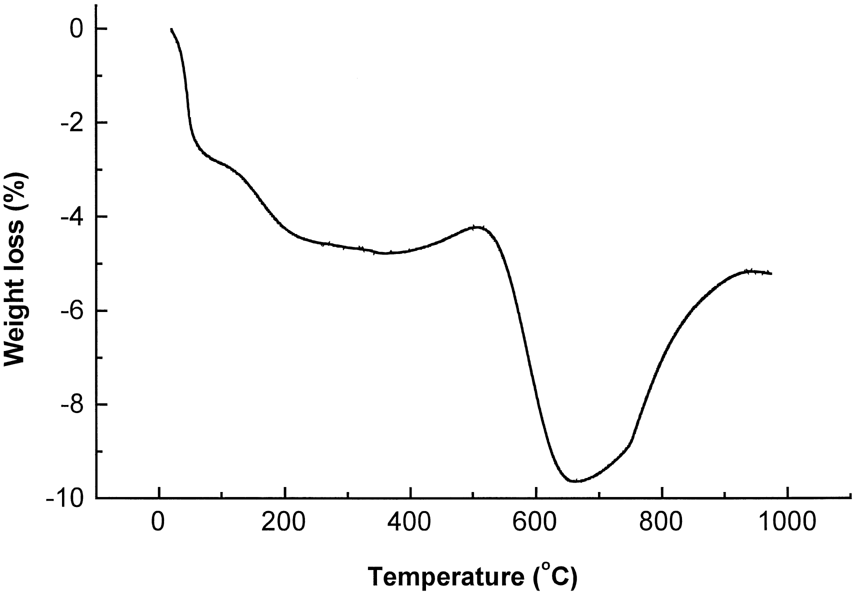

Fig. 8. TG curve of SiC powder sample 6 (Table 1) (temperature 1100°C, ratio C_2H_2/SiH_4 0.9:1, flow rate 163 cm^3 min^{-1}).

be attributed either to the surface oxidation of SiC or oxidation of the residual Si. From the thermodynamic point of view, the oxidation Si on the air:

$$Si(s) + O_2\ (g) \rightarrow SiO_2\ (s) \quad \left(\Delta G_{298\ K} = -856\ \text{kJ mol}^{-1}\right) \tag{9}$$

should be more advantageous as oxidation of SiC on the air (Eq. (10)):

$$SiC(s) + O_2\ (g) \rightarrow SiO_2\ (s) + C\ (s) \quad \left(\Delta G_{298\ K} = -786\ \text{kJ mol}^{-1}\right) \tag{10}$$

From this simple calculation can be concluded that some residual silicon is still present even at excess of carbon in the reactor. This also indicates that the flow rate of the gases through the hot zone of the reactor is too high and the reaction cannot be completed.

The C_2H_2/SiH_4 mol ratio partially affects powder colour which indicates a difference in phase composition of the powder product (as listed in Table 1) samples 2 and 5–7. In all these samples the temperature was kept constant at 1100°C, and the ratio C_2H_2:SiH_4 was changed from 0.9 to 2.1:1. Unfortunately, the gas flow rate in experiments producing the samples 5–7 was higher than in sample 2, which itself is too high, was mentioned before. That means the role of the ratio could be only estimated. IR spectra of samples 5–7 are similar with stretching and bending vibrations of Si–H and C–H. The intensity of these vibrations was smallest, almost negligible in case of powder 5 (Table 1). This spectrum is very similar to those for sample 2. The temperature and C_2H_2:SiH_4 ratio are similar but the flow rate is much higher in sample 5. The difference is in the TG curve of this sample, the residual free carbon is approx. 17 wt%. This amount is higher than in powder 2 (Table 1), which was only 7 wt%. That indicates that the optimum of C_2H_2:SiH_4 ratio is lower than in powder 2, i.e. lower than 1.2:1. The chemical composition of the final product is very sensitive to the C_2H_2:SiH_4 ratio. This must be optimised/set very precisely together with the total gas flow. As the TG curve of powder 6 (Table 1) in Fig. 8 indicates, low C_2H_2:SiH_4 ratio together with a high total gas flow (163 $cm^3\ min^{-1}$) caused that reaction (1) was not completed. The free carbon content in the powder 6 is about 5 wt% which is documented with the weight loss at 500°C, but the subsequent weight gain at 650°C indicates an enhanced oxidation of free silicon (Fig. 8).

4. Conclusions

Fine, submicrometer and quasispherical SiC powder was synthesised by CVD method in the SiH_4–C_2H_2 system even the nitrogen was used as a carrying gas. Presence of SiC was proved by IR and XRD analysis. Chemical analysis excluded formation of Si_3N_4 at the reaction conditions.

The morphology and chemical composition of the powder products is related to the C_2H_2:SiH_4 ratio in the initial gas mixture and temperature. From the morphological point of view the C_2H_2:SiH_4 ratio 1.2:1 and temperature 1100°C is an optimum.

Prepared SiC amorphous fine powder has a particle size in the range 0.1–0.5 μm and consists of spherical particles, partly agglomerated.

The IR spectrum of product reaction and the XRD pattern of its crystallised form are reliable evidence of SiC dominance in the reaction product.

The IR spectrum and DTA of products indicate that about 7 wt% of free carbon and also some residual silicon as in the reaction product, even at excess of carbon in the reactor consists of.

References

1. Changhong, D., Xianpeng, Z., Jinsong, Z., Yongjin, Y., Lihua, C. and Fei, X., The synthesis of ultrafine SiC powder by the microwave heating technique. *J. Mat. Sci.*, 1997, **32**, 2469–2472.
2. Benaissa, M., Werckmann, J., Ehret, G., Peschiera, E., Guille, J. and Ledoux, M. J., Structural studies of active carbon used in the growth of silicon carbide catalyst support. *J. Mat. Sci.*, 1994, **29**, 4700–4707.
3. Ohji, T., Hirano, T., Nakahira, A. and Niihara, K., Particle/matrix interface and its role in creep inhibition in alumina/silicon carbide nanocomposites. *J. Am. Ceram. Soc.*, 1996, **79**, 33–45.
4. Šajgalík, P., Rajan, K., Warbichler, P. Hofer, F. and Dusza, J., Silicon nitride based nano- and micro-composites with enhanced mechanical properties. *Key Engineering Materials*, 1999, **161–163**, 229–234.
5. Niihara, K., New design concept of structural ceramics–ceramic nanocomposite. *J. Ceram. Soc. Japan*, 1991, **99**, 974–982.
6. Sakka, T., Bidinger, D. D. and Aksay, I. A., Processing of silicon carbide–mullite–alumina nanocomposites. *J. Am. Ceram. Soc.*, 1995, **78**, 479–486.
7. Koc, R. and Cattamanchi, S., Synthesis of β-SiC powders using carbon coated fumed silica. *J. Mat. Sci.*, 1998, **33**, 2537–2549.
8. Suyama, Y., Marra, R. M., Haggerty, J. S. and Bowen, H. K., Synthesis of ultrafine SiC powders by laser-driven gas phase reactions. *Am. Ceram. Sci. Bull.*, 1985, **64**, 1356–1359.
9. Riedel, R. and Dressler, W., Chemical formation of ceramic. *Ceram. Int.*, 1996, **22**, 233–239.
10. Hollabaugh, C. M., Hull, D. E., Newkirk, L. R. and Petrovic, J. J., R.F.-plasma system for the production of ultrafine, ultrapure SiC powder. *J. Mat. Sci.*, 1983, **18**, 3190–3194.
11. Huang, Z. R., Liang, B., Jiang, D. L. and Tan, S. H., Preparation of nanocrystal SiC powder by chemical vapour deposition. *J. Mat. Sci.*, 1996, **31**, 4327–4332.
12. Zhu, C. W., Zhao, G. Y., Revankar, V. and Hlavacek, V., Synthesis of ultra-fine SiC powders in a d.c. plasma reactor. *J. Mat. Sci.*, 1993, **28**, 659–668.
13. Janiga, J., Pak, K. and Figusch, V., Synthesis of silicon nitride powder by gas-phase reaction. *J. Eur. Ceram. Sci.*, 1991, **8**, 153–160.
14. Kato, A., Vapor-phase synthesis of ceramics powders. In *Advances in Ceramics, Vol. 21, Ceramic Powder Science*. The American Ceramics Society, Inc., OH, 1987, pp. 181–192.

15. Sahu, S., Kavecký, Š. and Szépvolgyi, J., Preparation of fine amorphous Si_3N_4 powder in the system SiH_4–Ar–NH_3. *J. Eur. Ceram. Soc.*, 1995, **15**, 1071–1077.
16. Ličko, T. and Šajgalík, P., Preparation of α-Si_3N_4 powder and ceramics reinforced by β-Si_3N_4 whiskers. *Ceramics-Silikaty*, 1991, **35**, 127–145.
17. Baraton, M-I., Chang, W. and Kear, B. H., Surface chemical species investigation by FT-IR spectrometry and surface modification of nanosized SiCN powder synthesized via chemical vapour condensation. *J. Phys. Chem.*, 1996, **100**, 16647–16652.
18. Zhu, W. Z. and Yan, M., Synthesis of nanometer-sized SiC powders through chemical vapour deposition II. Effect of C_2H_4/SiH_4 mole ratio. *Mater. Chem. Phys.*, 1998, **55**, 68–73.
19. Pori, A., *HSC Chemistry, A Computer Program to Thermodynamic Equilibrium Calculations*. Pori, Finland, 1992.