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Production of submicron SiC particles by d.c. thermal plasma: a systematic approach based on injection parameters

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Aiming at producing high temperature structural ceramics, ultra-fine SiC powders were synthesized by the gas phase reaction of silicon tetrachloride with methane in a d.c. thermal plasma. The influence of parameters as the $SiCl_4$ feeding rate, C/Si and H_2/C molar ratios and internal pressure on the powder properties were investigated. The SiC powders were characterized by chemical analysis, Fourier transform infrared spectroscopy, X-ray diffraction and scanning electronic microscopy. The experimental set-up allows the production of β-SiC powders at a rate of 200 g h^{-1} with particle size around 0.1 μm. The main impurities in the as-produced powder handled at ambient atmosphere are: oxygen (1.8–2.5%) and free carbon (3–4%). Interesting relationships were found between the $SiCl_4$ feeding rate and the H_2/C molar ratio and between the C/Si molar ratio and the internal pressure. The internal pressure plays a major role in controlling the particle size.

1. Introduction

Because of its hardness, high wear and corrosion resistance, thermal stability, and high thermal shock resistance, silicon carbide is a good candidate for high temperature structural ceramics. However to obtain dense parts with optimal mechanical properties, powders with specific characteristics like stoichiometry, purity, small particle size, narrow particle size distribution, equiaxed morphology and the absence of hard agglomerates [1] must be used as starting material. Dense materials with good reliability at a low sintering temperature and hopefully without sintering additive, should be produced with such powders controlled in morphology and chemistry.

Thermal plasma has been considered as a good means for producing ultra-fine powders because of its high temperature capability enabling fast reactions and cooling rates. Silicon carbide has been synthesized with d.c., RF and hybrid plasmas [2–11] using a variety of starting materials. Up to now, most of the work has been concerned with the plasma operating parameters and no special attention has been devoted to the other variables that could have a tremendous importance on the powder synthesis. This paper describes the synthesis of SiC ultra-fine powders in the $SiCl_4$–CH_4–Ar–H_2 system. It points out the influence of $SiCl_4$ feeding rate, Ar carrier gas flow rate, internal pressure and the reactant C/Si (CH_4/$SiCl_4$) and H_2/C (H_2/CH_4) molar ratios, on the synthesized SiC powder characteristics. The aim was to ascertain the importance of these parameters in order to develop a more systematic and reliable approach for the production of ultra-fine silicon carbide.

2. Experimental procedure

The test apparatus is schematically represented in Fig. 1. It consists basically in a commercial d.c. plasma torch slightly modified to be airtight. An injector allows reagents to be radially introduced in the tail flame of the plasma through four injection holes at 90° around the plasma tail flame. The Ar/$SiCl_4$ mixture is delivered near the exit of the plasma torch and the H_2/CH_4 mixture further downstream. A cooling chamber is located after the injector allowing cooling by gas expansion. All these components are water cooled.

The SiC powders are collected by solid-gas separation on a metallic filter of known porosity (10 μm). The filter is connected to a vacuum pump that serves to purge the system from oxygen and moisture before each test and to pump the collected powders to remove volatile impurities that could remain on the filter. The gases passing through the filter are neutralized in a caustic scrubber before being vented.

In a routine test about 60% of the powders are collected on the filter (only these powders are considered for the analysis) 20% pass through the filter and are trapped by the scrubber and finally 20% of the powders remain stuck on the walls of different components (especially near the end of the injector).

All experiments were carried out using an argon plasma (flow rate 20 SLPM) at a fixed current of 400 A giving a power comprised between 10 and 11.5 kW.

Gaseous silicon tetrachloride flow rate was controlled by a measuring pump. Liquid $SiCl_4$ was vaporized in a flash boiler at 150 °C and carried by argon gas.

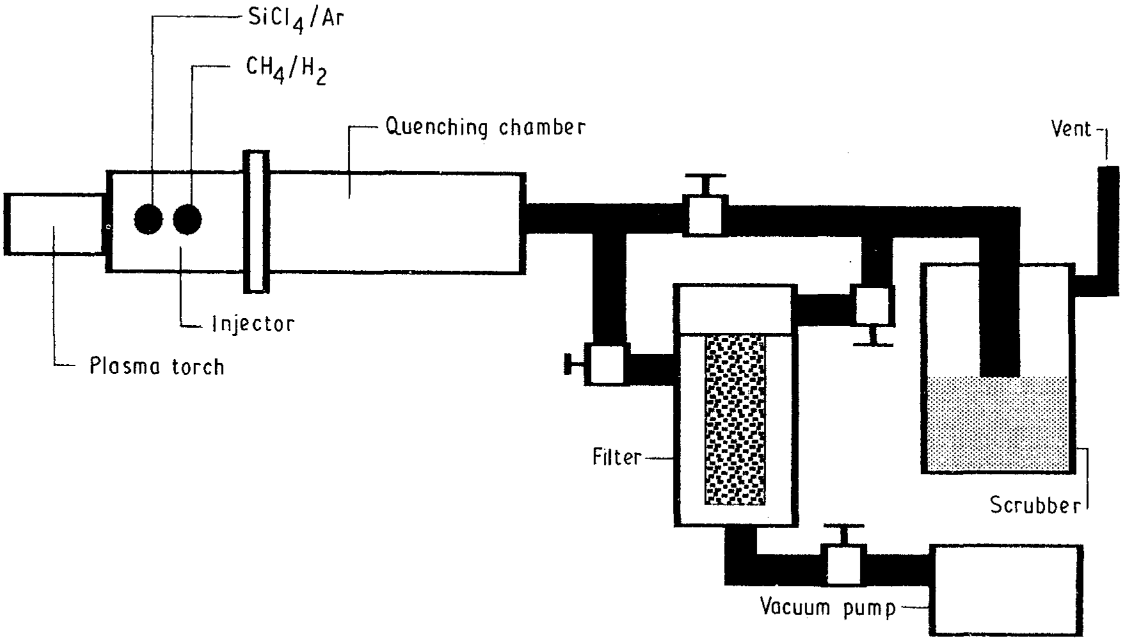

Figure 1 Schematic view of the experimental apparatus.

$SiCl_4$ (99% pure, Aldrich Chem. Co.), and all gases (Ar, CH_4 and H_2) were used without purification.

Infrared spectra were recorded on a Bomem Michelson 100 Fourier transform infrared spectrometer with samples prepared as KBr disc. X-ray diffraction patterns were recorded on a Philips PW 1840 diffractometer using the Cu radiation (wavelength: 15.425 nm). Total carbon and oxygen determination were performed on a LECO analyser. Free carbon analyses were run on a Coulometrics CO_2 coulometer burning the samples at 720 °C for 20 min. Scanning electron microscope (SEM) photographs were taken with a JEOL JSM 35CF.

3. Results and discussion

The production of silicon carbide powders by plasma gas phase reaction is not a simple process and many experimental parameters affect the properties of powders. All the parameters (plasma power and composition, different injection modes, etc.) that can have an influence were not studied in this paper. The attention was purposely limited to parameters that correspond to a reactor of determined geometry.

Previous workers [4–7] have reported that silicon carbide can be produced with a variety of reactant C/Si molar ratios generally in the range of 1 to 3. It was thought to determine the optimum experimental C/Si molar ratio by varying that ratio from test to test between 1 and 3 keeping constant the other parameters ($SiCl_4$ feeding rate, Ar carrier gas flow rate and the H_2/C molar ratio). The objective was first to obtain the lowest free carbon and oxygen content and the highest bonded carbon concentration.

3.1. Bonded and free carbon concentration in SiC powders

In Fig. 2 the variations of bonded carbon, free carbon and oxygen are reported as a function of the C/Si molar ratio in the as-produced SiC powder with different operating parameters. As shown, it is quite obvious that the oxygen and free carbon are low when the reactant C/Si molar ratio is around 1.3. A C/Si molar ratio exceeding 1.5 always increases free carbon and oxygen but mainly decreases the bonded carbon concentration.

3.2. Influence of carrier gas flow rate

The influence of the argon carrier gas flow rate was also examined. As shown in Fig. 3 optimum concentrations in both oxygen and carbon are obtained for a carrier gas flow rate of 2 SLPM whatever is the $SiCl_4$ feeding rate. In the remaining tests, the carrier gas was kept constant.

3.3. Influence of $SiCl_4$ feeding rate

The feeding rate of $SiCl_4$ and the proportion of CH_4 and H_2 gas have a marked influence on the composition of the powders obtained. Thus a high feeding rate of 11.0 $g\,min^{-1}$ results in sharp variation in composition as shown in Fig. 2c and d. For a fixed C/Si molar ratio of 1.3 and a $SiCl_4$ feeding rate of 7.8 $g\,min^{-1}$, a H_2/C molar ratio of 10 gives powders having lower oxygen and free carbon concentrations and higher proportions of bonded carbon than a H_2/C molar ratio of 5. On the other hand when a higher $SiCl_4$ feeding rate of 11.0 $g\,min^{-1}$ is used a low H_2/C molar ratio is preferable. These results point out that there exists a close relationship between the $SiCl_4$ feeding rate and the H_2/C molar ratio.

The main factors that influence the powder composition seem to be the $SiCl_4$ feeding rate, the pressure inside the reactor and the reactant molar ratios (C/Si and H_2/C). Considering that the oxygen content in the as-produced powders could depend mainly on oxygen take off during powder handling and storage, the above mentioned process parameters will rather be

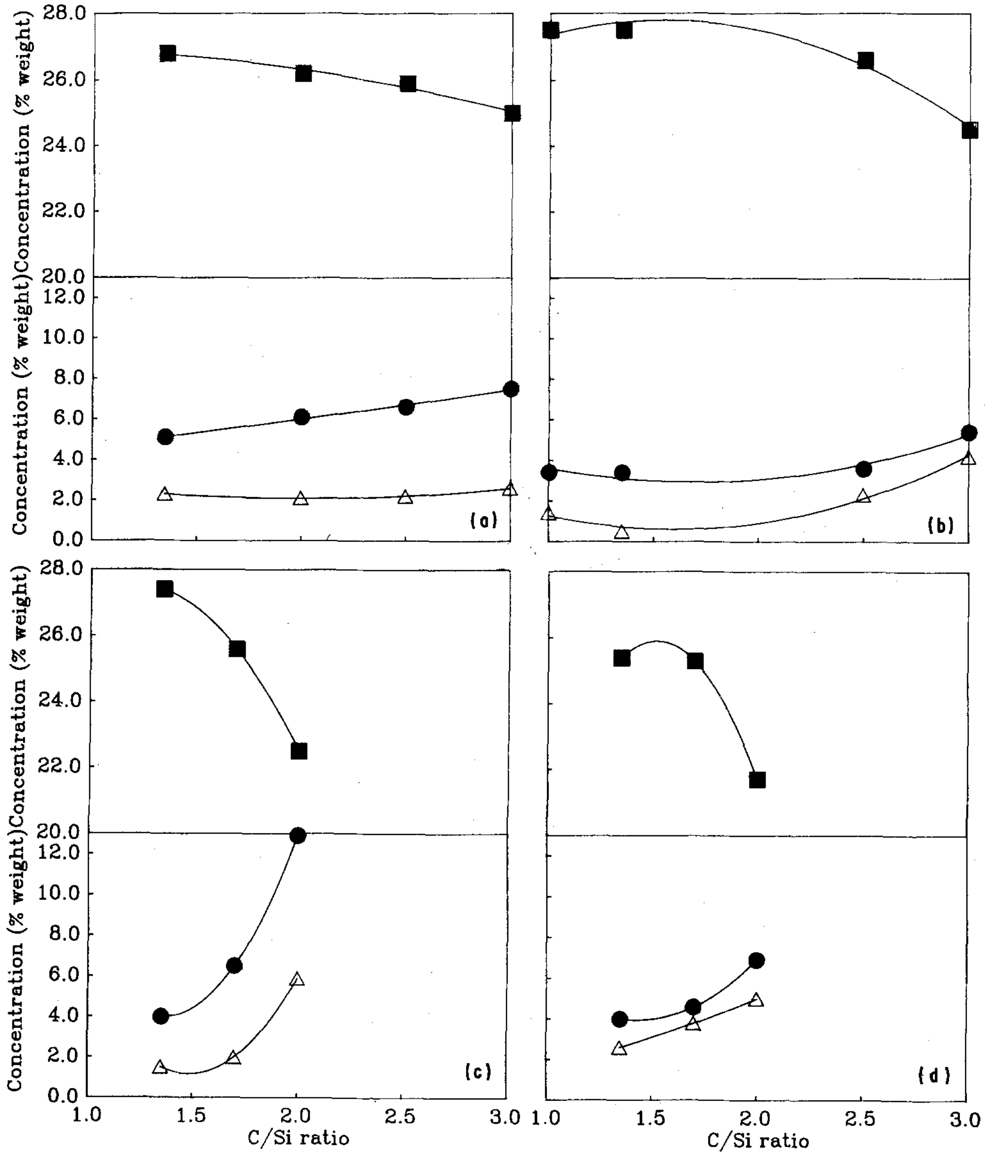

Figure 2 Variation of the oxygen, free and bonded carbon concentrations as a function of the C/Si molar ratio. Fixed parameters: Ar carrier 2 SLPM. (a) $SiCl_4$ feeding rate: 7.8 g min^{-1}, H_2/C molar ratio: 5; (b) $SiCl_4$ feeding rate: 7.8 g min^{-1}, H_2/C molar ratio: 10; (c) $SiCl_4$ feeding rate: 11.0 g min^{-1}, H_2/C molar ratio: 5; and (d) $SiCl_4$ feeding rate: 11.0 g min^{-1}, H_2/C molar ratio: 10. △, oxygen; ●, free carbon; ■, bonded carbon.

related to the carbon concentration within the powders for simplicity.

3.4. Relation between the $SiCl_4$ feeding rate and the H_2/C molar ratio

The influence of the H_2/C molar ratio on the free and bonded carbon concentrations for different $SiCl_4$ feeding rates (7.8, 11.0 and 15.0 g min^{-1}) is presented in Fig. 4 for a fixed C/Si molar ratio of 1.3 and an internal pressure comprised between 20 and 35 kPa (Note: the internal pressure is the positive differential pressure between the interior and the exterior of the reactor, the pressure outside the reactor being the atmospheric pressure).

From this figure it is quite obvious that as the $SiCl_4$ feeding rate increases, the H_2/C molar ratio must decrease to keep minimum the free carbon concentration and maximum the bonded carbon concentration. Optimum values are obtained for H_2/C molar ratios of 14.5, 10.2 and 8, corresponding to $SiCl_4$ feeding rates of 7.8, 11.0, and 15.0 g min^{-1}, respectively. This type of relationship clearly indicates that there is a narrow range of conditions, where the reaction occurs more successfully. Out of this range, the bonded carbon concentration decreases as the free carbon concentration increases. This narrow domain would correspond to a temperature zone where the synthesis occurs. Unfortunately it was not possible to measure the temperature in this zone because of the geometry of the reactor. Powders of similar size and purity can be produced at a different rate, the only limitation being the plasma saturation. The reaction takes place as long as silicon tetrachloride and methane are properly decomposed in the tail flame of the plasma.

This is obviously exemplified when the $SiCl_4$ feeding rate is multiplied by the corresponding H_2/C molar ratio. Indeed values of 113, 112 and 120 are obtained for $SiCl_4$ feeding rates of 7.8, 11.0 and 15.0 g min^{-1}, respectively. The fact that there is a constant (of about 115) demonstrates the existence of a relationship between the $SiCl_4$ feeding rate and the

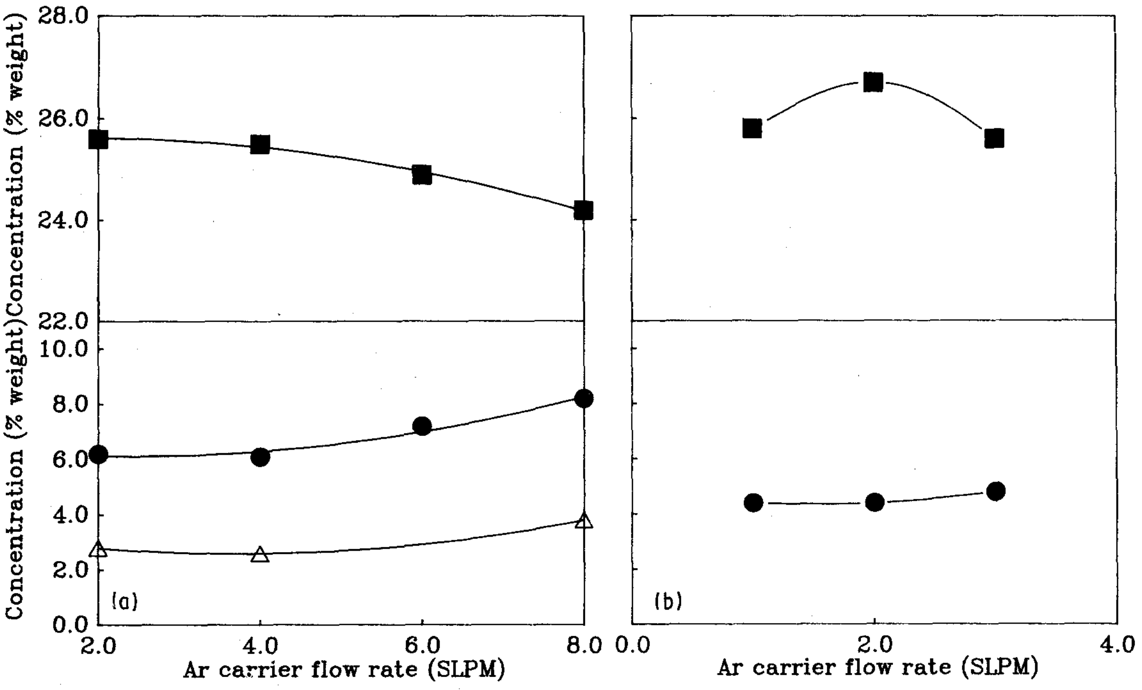

Figure 3 Variation of the oxygen (△), free (●) and bonded (■) carbon concentrations as a function of the Ar carrier gas flow rate. Fixed parameters: C/Si: 1.3, H_2/C: 10. (a) $SiCl_4$ feeding rate: 7.8 g min^{-1} and (b) $SiCl_4$ feeding rate: 11.0 g min^{-1}.

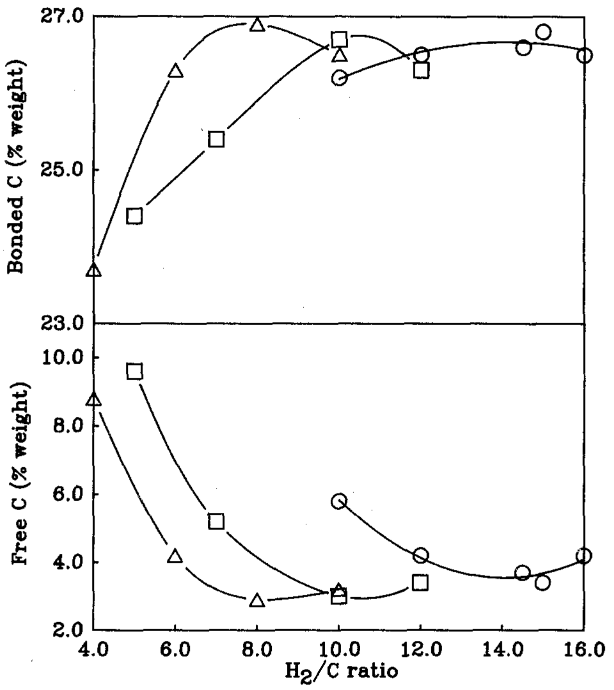

Figure 4 Variation of the free and bonded carbon concentrations as a function of the H_2/C molar ratio. Fixed parameters: Internal pressure range: 20 to 30 kPa, C/Si molar ratio: 1.3. $SiCl_4$ feeding rate: (○) 7.8, (□) 11.0 and (△) 15.0 g min^{-1}.

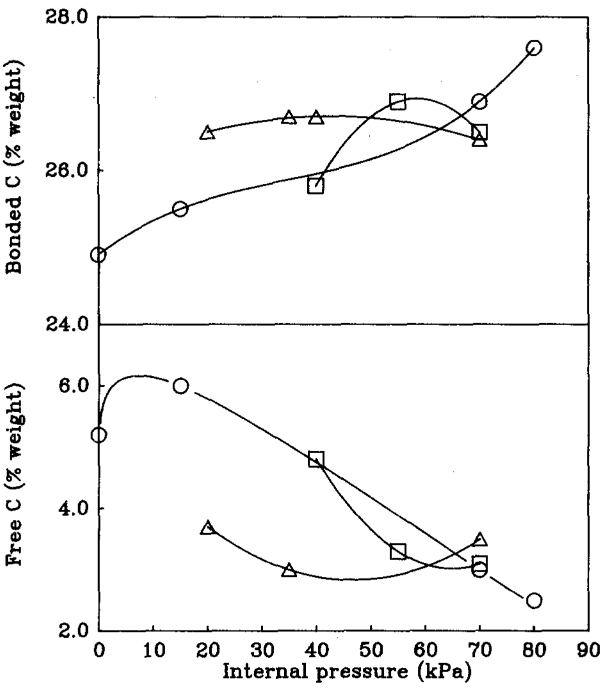

Figure 5 Variation of the free and bonded carbon concentrations as a function of the internal pressure. Fixed parameters: $SiCl_4$, feeding rate: 11.0 g min^{-1}, H_2/C molar ratio: 10. C/Si ratio: (○) 1.0, (□) 1.15 and (△) 1.3.

H_2/C molar ratio. Because of that relation, the optimum hydrogen flow rate is 21 SLPM and is not dependent on the $SiCl_4$ feeding rate. It allows, for fixed C/Si molar ratio and pressure, the determination of the optimum H_2/C molar ratio corresponding to a given $SiCl_4$ feeding rate. Then a 5.8 H_2/C molar ratio is found for a feeding rate of 20.0 g min^{-1}. For a given reactor this extrapolation is valid as long as the plasma is not saturated. However as shown in Fig. 4, an increase in the $SiCl_4$ feeding rate results in a smaller range where the stoichiometry can be controlled.

3.5. Relationship between the C/Si molar ratio and the pressure in the reactor

A lack in reproducibility results most of the time from the absence of control of the pressure inside the reactor. This has not been discussed by previous workers even though it stands to reason that pressure can modify the constant of equilibrium between reactants and products. The pressure inside the reactor can probably modify not only the chemistry but also the form of the products. Fig. 5 shows the variation in carbon concentration for a determined $SiCl_4$ feeding rate (11.0 g/min) and H_2/C molar ratio (10). As shown the C/Si molar ratio is pressure dependent. Even if the C/Si molar ratio is fixed, the internal pressure variation will alter the reproducibility and the properties of the powders produced. Then, it follows that there is an optimal C/Si molar ratio for each pressure value. As it can be observed in Fig. 5 for each C/Si molar ratio the best powder composition is obtained at a precise pressure. It corresponds to 45, 60 and >75 kPa for C/Si molar ratio of 1.3, 1.15 and 1.0. A pressure increase inside the reactor shortens the plasma tail flame resulting in a more confined zone restricting the reaction volume and the temperature increases. The plasma voltage increases and then the plasma power. A temperature increase would promote a more complete decomposition of the methane in the plasma and favours the carbon-carbon recombination. By lowering the C/Si ratio the carbon-carbon recombination is less probable.

3.6. Physical characterization

The physical characteristics of powders are influenced by the synthesis parameters. Fig. 6 shows the infrared absorbance spectrum of a silicon carbide sample between 400 and 1400 cm^{-1} with a low silica content. There is only one absorption at 880 cm^{-1} assigned to Si–C vibration modes. Since the concentration of silica in that sample is low, the absorptions between 1000 and 1200 cm^{-1} assigned to silica vibration modes are very weak. No distinct band can be observed, only a slight variation in the baseline.

The as-produced SiC powders have generally an oxygen content comprised between 1.8 and 2.5% when no special care is taken to prevent contact with oxygen and moisture. That oxygen concentration can be easily reduced to less than 1% by avoiding contact of powders with the ambient atmosphere manipulating them under nitrogen. However after exposing them to oxygen they react to produce silica as it was detected by infrared spectroscopy.

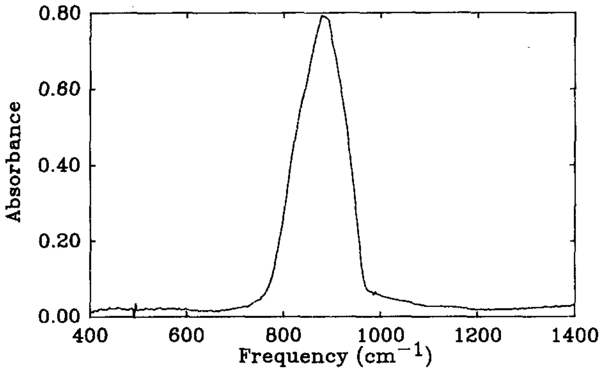

Figure 6 Infrared absorbance spectrum of silicon carbide.

Whatever are the synthesis parameters used, β-SiC is the only crystallographic form observed. Fig. 7 presents a typical X-ray diffraction pattern of these powders. α-SiC was not detected by the analysis technique used in this study.

However, the size of SiC powders depends on the reaction variables. Fig. 8 shows SEM photographs of SiC powders obtained (b) with a negligible pressure inside the reactor and (a) with an internal pressure of 70 kPa. These pictures reveal that all the SiC particles are spherical in shape but different in size.

The SiC particles obtained at higher pressure are bigger (mean diameter comprised between 0.1 and 0.2 micrometer) and less uniform in size. Hard agglomerates of fine particles can be easily seen. On the

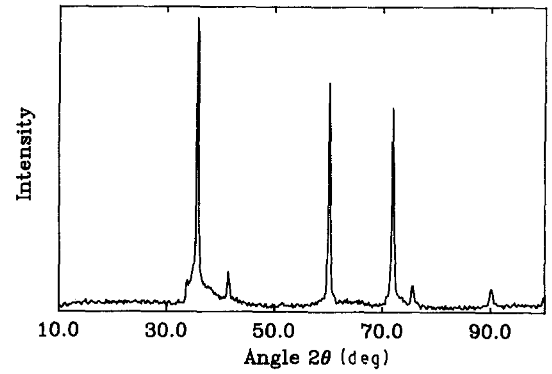

Figure 7 X-ray diffraction pattern of SiC produced powders.

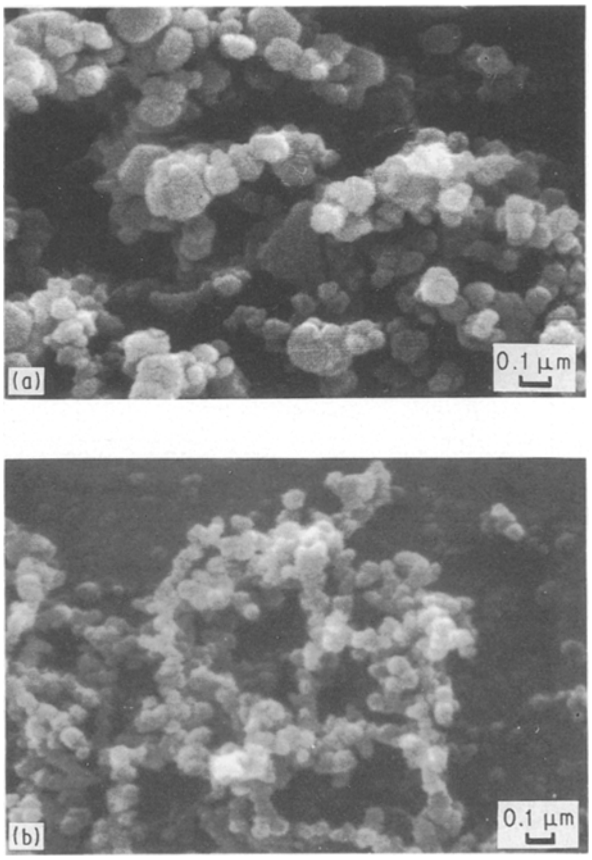

Figure 8 SEM photographs of SiC powder. (a) $SiCl_4$ feeding rate: 11.0 g min^{-1}, C/Si and H_2/C molar ratio: 1.0 and 10, internal pressure: 70 kPa. (b) $SiCl_4$ feeding rate: 11.0 g min^{-1}, C/Si and H_2/C molar ratio: 1.3 and 10, internal pressure: 0 kPa.

TABLE I Process variables and powder composition

Run	$SiCl_4$ (g min^{-1})	C/Si	CH_4 SLPM	H_2/C	H_2 SLPM	Power (kW)	P^a (kPa)	Powder C/Si	C-bonded (% wt)	C-free (% wt)
8	7.8	1.30	1.50	15.0	22	10.4	35	1.04	26.8	3.4
62	7.8	1.30	1.40	14.5	21	10.8	55	1.03	26.4	3.9
9	11.0	1.30	2.00	10.0	20	10.4	35	1.02	26.7	3.0
23	11.0	1.00	1.60	10.0	16	11.6	75	1.04	27.6	2.5
46	11.0	1.15	1.80	10.2	18	11.3	70	1.05	26.9	3.2
28B	11.0	1.20	1.90	10.0	19	9.9	0	1.03	26.3	3.6
14	15.0	1.30	2.80	8.0	22	11.3	25	1.04	26.9	2.9
29	15.0	1.15	2.50	8.0	20	11.0	70	1.03	26.5	3.2

[a] P: Internal pressure

other hand the SiC particles obtained at lower pressure (a zero pressure level) are smaller (particle size comprised between 0.06 and 0.1 μm) and more uniform in size. Agglomerates seem also to be loosely packed. SiC particles obtained between 0 and 70 kPa have morphologies comprised between those observed in Fig. 8. However small particles contain more oxygen than bigger ones and are more prone to oxidation when exposed to atmospheric conditions as confirmed by the chemical analysis. Smaller particles have higher surface area than bigger ones.

The as-produced SiC powders without special handling technique should be composed of about 90–92% by weight of pure SiC, 1.8 to 2.5% by weight of oxygen and 3 to 4% by weight of free carbon, the remaining element being silicon mainly as SiO_2 and some free Si (not detected by X-ray diffraction) could also be present. With adequate handling technique the SiO_2 level can be lowered below 1% by weight. The free carbon can be removed by a subsequent heat treatment.

3.7. Combined effect of process variables

As mentioned before some process variables ($SiCl_4$ flow rate and H_2/C molar ratio) are linked together. This could mean that different process variables, as those shown in Table I can produce powders of the same quality. In Table I, eight different runs are reproduced to show how they can give SiC powders roughly having the same product C/Si atomic ratio. However this C/Si atomic ratio is not the only parameter that serves to characterize the SiC powders. The amount of carbon actually within the lattice as well as the oxygen content and the particle size must be specified.

4. Conclusion

Near stoichiometric SiC powders with a particle size (around 0.1 μm) and having a narrow particle size distribution were produced. The powder containing β-SiC can be more or less agglomerated depending on the operating conditions. Close relationships between the $SiCl_4$ feeding rate and the H_2/C molar ratio and also between the internal pressure and the C/Si molar ratio were found. Production rate of 150 to 200 g h^{-1} are easily achieved with the present apparatus. Higher yield can be achieved by increasing the $SiCl_4$ feeding rate and using metallic filter with smaller pores.

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