Preparation of Nano-Sized Silicon Carbide Powder Using Thermal Plasma

Seung-Min Oh, Mark. Cappelli* and Dong-Wha Park†

Department of Chemical Engineering, Inha University, 253 Yonghyun-Dong, Nam-Gu, Inchon 402-751, Korea
*Department of Mechanical Engineering, Stanford University, Stanford, CA 94305-3032, USA

Abstract−Nano-sized silicon carbide (SiC) powder was prepared by thermal plasma process using silicon tetrachloride ($SiCl_4$) and methane (CH_4). The synthesized powder was characterized by X-ray diffraction pattern, scanning electron microscopy, transmission electron microscopy, FT-IR spectroscopy and particle size analyzer. The powder was dominated by β-SiC including some of α-SiC and free carbon species. The quality of the powder was varied with process conditions such as the molar ratio of H/Si and C/Si, and collecting positions. It was known that the conversion to SiC was mainly affected by the addition of hydrogen gas because it promoted the decomposition and reduction of $SiCl_4$. CH_4 was easily decomposed to carbon species for the formation of SiC as well as removal of impure oxygen, but excessive carbon suppressed the formation of crystalline SiC and resulted in the solid carbon contamination. The optimum ratio of H/Si was approx. 26 and that of C/Si was 1.1. For collecting positions, the powder collected at the vessel and filter was preferable to that at the reaction tube. The average size of the powder synthesized was estimated to be below 100 nm and uniform in distribution.

Key words: Thermal Plasma, Nano-sized Powder, Silicon Carbide, Preparation, Process

INTRODUCTION

Silicon carbide is used in a wide range of industrial applications such as turbine blades, diesel engine parts, and nuclear reactor materials due to its excellent high temperature hardness, wear resistance, low thermal expansion coefficient, high thermal conductivity, as well as strong corrosion resistance. The majority of this material in use today is produced by the Acheson process, which is based on carbothermic reduction [Pickles et al., 1995]. Recently, various processes have been proposed to improve the carbothermic reduction process [Chen et al., 2000; Koc et al., 2001]. Some disadvantages of this process are that it is a batch process, the silicon carbide crystals produced are large and impure, and the waste gases are not efficiently utilized.

A thermal plasma process is an excellent process for the preparation of high quality ceramic nanopowders due to its unique characteristics such as high temperature (>10,000 K), high chemical activity, and rapid quenching (10^{6-7} K/s) [Bolous et al., 1994; Pfender, 1999; Oh and Park, 2000]. Recently, the plasma process has been used in different ways for preparing high quality SiC particles. Both dc. and rf induction plasma have been used to prepare SiC powders [Hollabaugh et al., 1983; Park and Rhee, 1990; Kameyama et al., 1990; Zhu et al., 1993; Guo et al., 1997]. Even though the rf plasma system provides a very clean process for preparation of pure and fine powders, the low energy utilization efficiency and the instability of the plasma have proven difficult to the wide and rapid applications.

In the present work, we have developed a dc. thermal plasma system for preparation of nano-sized SiC powder from $SiCl_4$ and CH_4. The characteristics of the powder were investigated for oper-ating variables such as H/Si ratio, C/Si ratio, and collecting position. The conditions required for the production of high quality SiC nanopowder were determined.

EXPERIMENTAL

A schematic diagram of experimental apparatus is shown in Fig. 1. The system mainly consisted of a plasma torch, raw material feeding system, water-cooled reaction tube and vessel, metal filter and
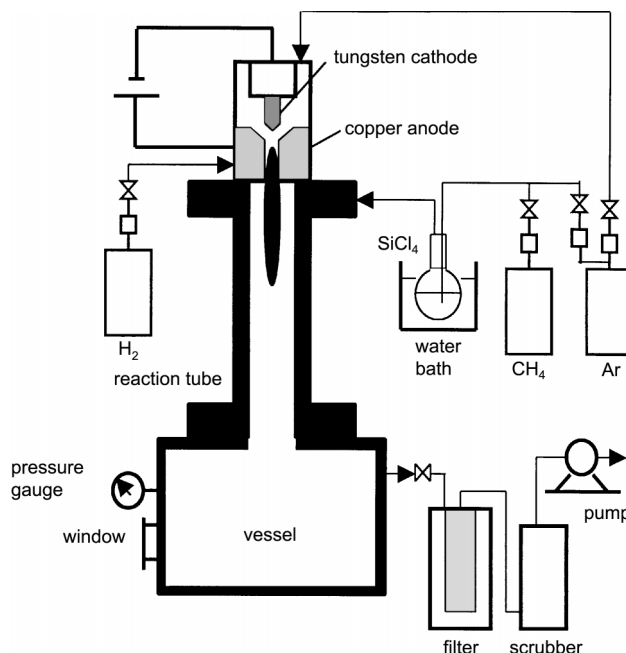

Fig. 1. Schematic diagram of a thermal plasma system for preparation of nano-sized SiC powder.

†To whom correspondence should be addressed.
E-mail: dwpark@inha.ac.kr

Table 1. Experimental conditions for plasma synthesis of nano-sized silicon carbide

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Input power	8-12 kW
Plasma gas flow rate	Ar: 15 l/min, H_2: 1.5 l/min
Reaction tube dimension	I.D.-45 mm, L-200 mm
$SiCl_4$ feeding rate	0.3-0.9 ml/min (3.5×10^{-3}-8.5×10^{-3} mol)
Ar-carrier gas	2.5 l/min
CH_4 flow rate	50-200 ml/min (2.2×10^{-3}-8.9×10^{-3} mol)
H_2 flow rate	1-5 l/min

scrubber. The plasma torch was typically run at 8 to 12 kW input power with the flow rate of 15 l/min of Ar gas. As source material, silicon tetrachloride ($SiCl_4$, 99.9% purity, Aldrich Co.) was injected below the plasma torch nozzle. The flow rate of $SiCl_4$ was controlled by water bath temperature. The feeding line was heated to prevent condensation of $SiCl_4$ vapor. Ar-carrier gas was adjusted at the flow rate of 2.5 l/min and reactant CH_4 gas was added through the feeding line of $SiCl_4$. Raw materials were rapidly decomposed and dissociated to various species in a plasma flame, and these species reacted with each other or recombined to the raw materials in a short time. Gaseous products and by-products were solidified out of the plasma flame by rapid quenching, thus they resulted in nano-sized powder. After in-flight reaction, the gases containing product powders passed through a filter assembly and scrubber by vacuum pump. Experiments were performed by changing the flow rate of silicon tetrachloride, methane and hydrogen. The experimental conditions are summarized in Table 1. The product powder was collected at the reaction tube, vessel and filter assembly.

The powders were characterized by an X-ray diffractometer (Model PW 1710, Philips Co.), SEM (scanning electron microscopy, Model S-4300, Hitachi), and light scattering particle size analyzer (Model SYS 4700, Malvern Instrument Co.), FT-IR Spectrometer (Model MB 104, Bomem Co.), and TEM/EDS(transmission electron microscopy, Model CM 200, Philips Co.).

RESULTS AND DISCUSSION

Chemical equilibrium composition was calculated by software program based on the Gibbs' free energy minimization [Chemsage version 3.2, 1996; Oh and Park, 2001]. Chemical equilibrium calculations are not practical in the low temperature region. However, they are useful for assessing the reaction system in the thermal plasma processing due to its excellent high temperature and rapid chemical reaction. Fig. 2 shows the chemical equilibrium compositions calculated for the system of CH_4/$SiCl_4$ and CH_4/$SiCl_4$/H_2. Silicon tetrachloride ($SiCl_4$) and methane (CH_4) were easily decomposed to $SiCl_x$(g), Si(g), Cl(g), C_xH_y(g), C_x(g), and H(g) at the region over 3,000 K. With decreasing temperature, gaseous species were recombined or reacted to various products, and instantaneously solidified by rapid quenching.

For the CH_4/$SiCl_4$ system, the temperature of SiC formation was in a range from 900 K to 2,300 K. The formation yield was no more than 40% of full conversion because Si(g) species was easily recombined to $SiCl_4$(g) through $SiCl_x$(g) at below 3,000 K. For the
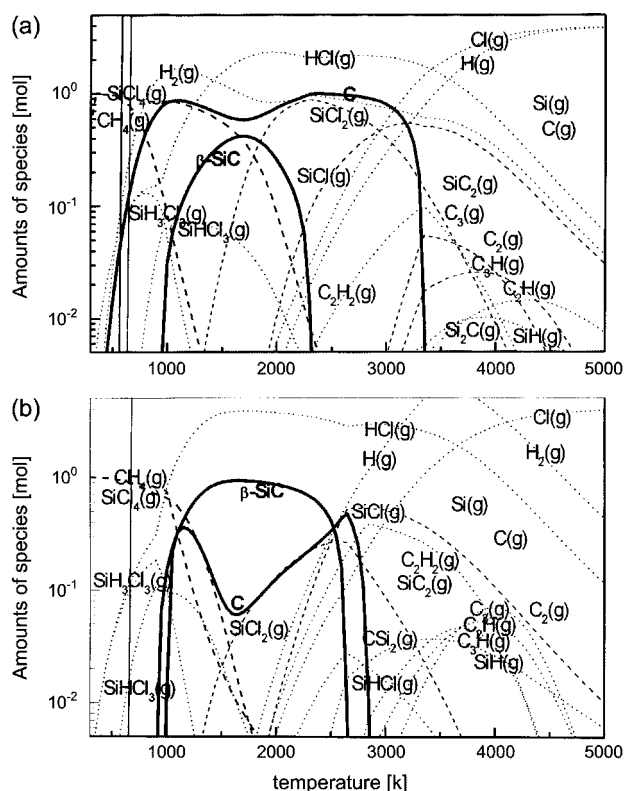
Fig. 2. Chemical equilibrium compositions calculated in different systems as a function of temperature.
(a) in the system of CH_4/$SiCl_4$=1/1, (b) in the system of CH_4/$SiCl_4$/H_2=1/1/10

CH_4/$SiCl_4$/H_2 system, the addition of H_2(g) increased the amount of SiC(s) species and the temperature range of SiC formation to be from 900 K to 2,700 K. Also, it was observed that hydrogen molecules were easily dissociated to hydrogen atoms at over 2,000 K, and solid carbon species significantly decreased at below 2,700 K due to the formation of SiC as well as increase of CH_4 gas.

From these equilibrium calculations, it was proposed that the formation of SiC depends on the prior inhibition of recombination of Si(g) species to $SiCl_4$(g). Hydrogen gas promoted the dissociation of $SiCl_x$(g) and decreased the solid carbon content, thus increased the conversion to SiC.

Fig. 3 shows the X-ray diffraction patterns of the powder synthesized in different molar ratios for the CH_4/$SiCl_4$ system, for which the ratio of C/Si was varied from 0.5 to 2.6. No peak corresponding to SiC was detected, even higher molar ratio of C/Si in the CH_4/$SiCl_4$ system. The broad peaks appearing in Fig. 3(b) and (c) corresponded to that of graphite due to higher ratio of C/Si. It was also known that the powders contained higher percentage of amorphous silicon oxide, which was identified by FT-IR spectra. These results indicated that Si species was easily recombined to $SiCl_4$ in the CH_4/$SiCl_4$ system as shown in Fig. 2(a), thus resulting in the formation of amorphous SiO_2 by ambient oxygen.

The effect of H_2 addition was presented in Fig. 4, where the powder was synthesized at the condition of C/Si=1/1 and collected in the reaction tube. The peak corresponding to SiC was observed when the molar ratio of H/Si was over 10, and it sharpened at the ratio of H/Si=26 as shown in (c). The hydrogen apparently promoted the
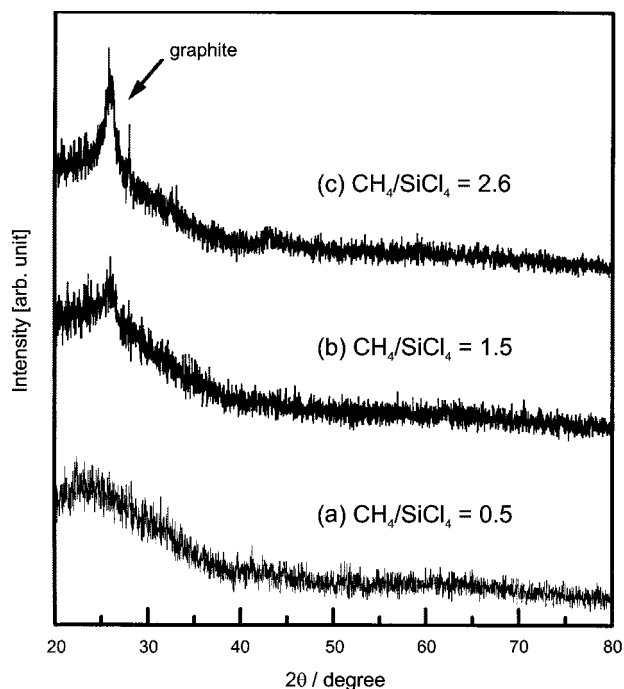
Fig. 3. X-ray diffraction patterns of the powder synthesized in different molar ratio of C/Si (without H_2 addition).
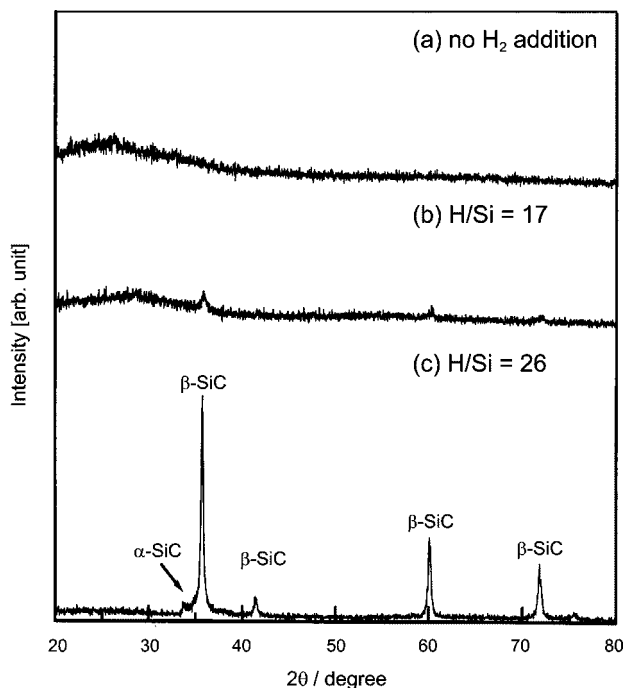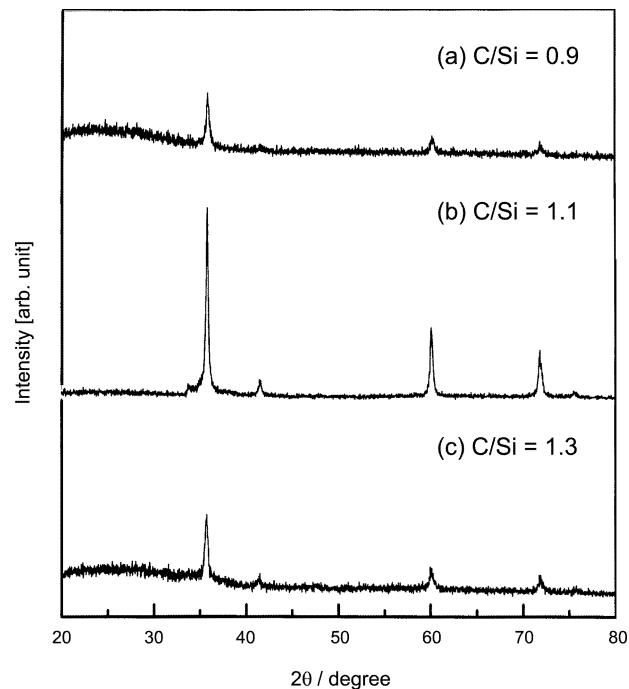(a) C/S=2.6, (b) C/Si=1.5, (c) C/Si=0.5

Fig. 5. X-ray diffraction patterns of the powder synthesized in different molar ratio of C/Si (H/Si=26).
(a) C/Si=0.9, (b) C/Si=1.1, (c) C/Si=1.3

thesized in the $CH_4/SiCl_4/H_2$ system, for which the ratio of H/Si= 26. The conversion to SiC increased with the flow rate of CH_4 because it was easily decomposed to carbon species and reacted to SiC as well as removed some impurity oxygen. However, at the higher molar ratio of C/Si over 1.1, the peak corresponding to SiC
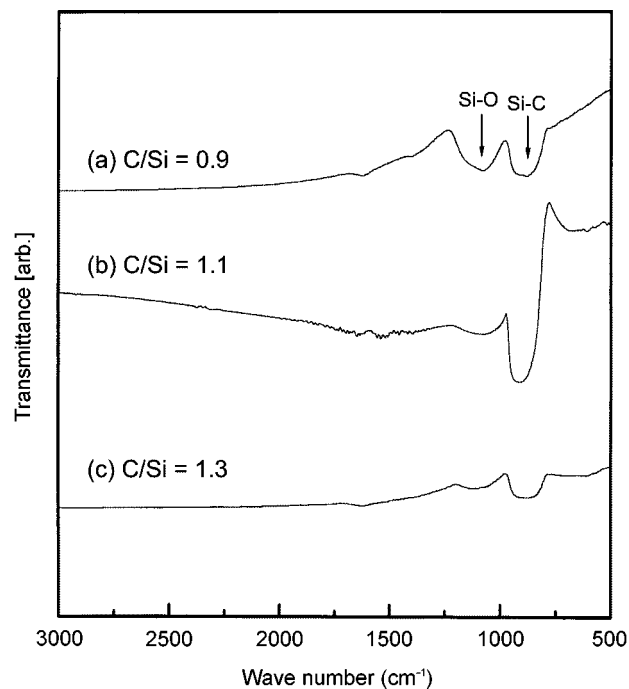

Fig. 4. X-ray diffraction patterns of the powder synthesized in different molar ratio of H/Si (C/Si=1.1).
(a) H/Si=0, (b) H/Si=17, (c) H/Si=26

decomposition and reduction of $SiCl_x(g)$. Silicon species from the decomposition of $SiCl_x(g)$ reacted rapidly with the carbon species from the decomposition of CH_4. The powder produced at the higher H_2 ratio was mostly β-SiC including some of α-SiC.

Fig. 5 shows the X-ray diffraction patterns of the powder syn-

Fig. 6. FT-IR absorption spectra of the powder collected at the vessel (H/Si=26).
(a) C/Si=0.9, (b) C/Si=1.1, (c) C/Si=1.3

decreased due to amorphous carbon derived from excessive carbon species. It was also observed by FT-IR spectra as shown in Fig. 6. The absorption peaks corresponding to Si-C bond can be seen at 810, 874, 930 and 940 cm^{-1} [Chen et al., 1989]. At the lower ratio of C/Si, the peak shown at around 900 and 1,100 cm^{-1} corresponded to Si-C and Si-O bond. The Si-O bond probably resulted from oxidation of SiCl$_x$(g) by impure oxygen or ambient oxygen. Si-O bond decreased with increase of the ratio of C/Si, because carbon species promoted formation of SiC and removal of existent oxygen impurity. At the ratio of C/Si=1.1, Si-O bond significantly decreased and Si-C bond was strongest. However, the peak intensity of Si-C decreased at the higher ratio of C/Si as shown in (c) because excessive amorphous carbon suppressed the formation of crystalline SiC [Park et al., 1991] and resulted in solid carbon contamination.

The synthesized powder was collected at the reaction tube, vessel, and filter assembly, respectively. Fig. 7 shows the X-ray diffraction pattern of the powder synthesized at the ratio of C/Si=0.9 and H/Si=26. The powder was more crystallized at the vessel and filter assembly than at the reaction tube. It was known that un-reacted Si species, which resulted from carbon deficiency, were rapidly recombined to SiCl$_x$(g) and condensed to SiCl$_4$(l) by water-cooled reaction tube wall and vessel wall. SiCl$_x$(g) and SiCl$_4$(l) reacted with impure oxygen or ambient oxygen to amorphous SiO$_2$ on the quenched collecting parts; thus the peak intensity corresponding to Si-C decreased as shown in (a) and (b). However, the peak intensity increased more at the filter due to lower quenching rate and elongated in-flight reaction in plasma flame. The diameter of the powder in Fig. 7(a), (b), and (c) was estimated to be 71 nm, 72 nm, and 78 nm, respectively by the Scherr equation [Zhu et al., 1993].

Microstructure of the powder was examined with scanning electron microscopy and transmission electron microscopy as shown
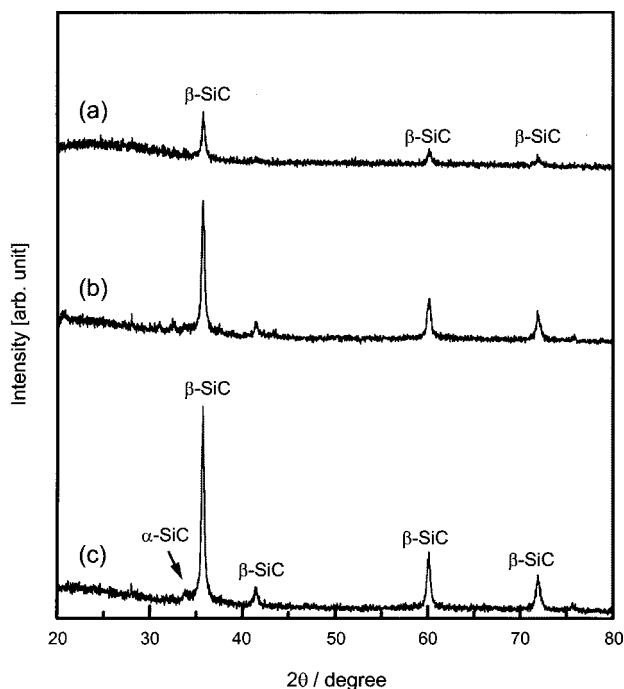

Fig. 7. X-ray diffraction patterns of the powder collected at different positions (H/Si=26, C/Si=0.9).
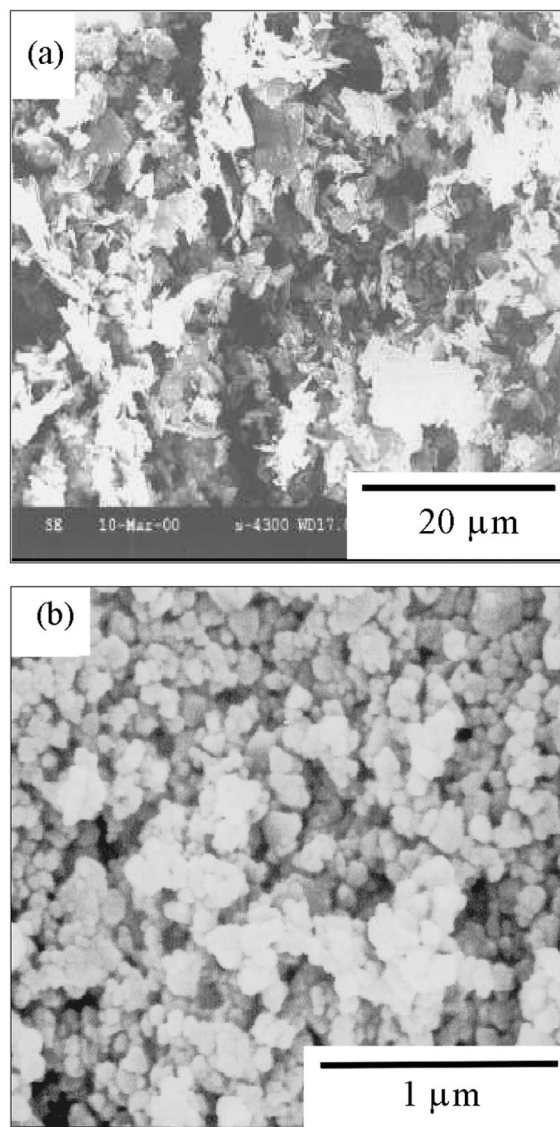(a) at the reaction tube, (b) at the vessel, (c) at the filter

Fig. 8. SEM photographs of the powder synthesized in different systems.
(a) in the CH$_4$/SiCl$_4$ system, (b) in the CH$_4$/SiCl$_4$/H$_2$ system

in Fig. 8 and Fig. 9. For the CH$_4$/SiCl$_4$ system, synthesized powder was composed of solid carbon and silicon oxide, thus random and large size particles are shown in Fig. 8(a). At the condition of higher H$_2$ addition, the powder size was below 100 nm of average diameter and uniform as shown in (b). Fig. 9 shows the TEM photographs for the powders synthesized at the conditions of H/Si=26, C/Si= 1.1. The powder collected at the reaction tube was shown to be more aggregated and partially sintered due to radiation heat by plasma jet flame. Most of the powder was observed to be hexagonal (β-SiC) including some of cubic (α-SiC) structures.

CONCLUSION

Nano-sized β-SiC powder was prepared by a dc plasma process. The characteristics of the powder were controlled by the adjustment of the process variables. The results were summarized as follows.
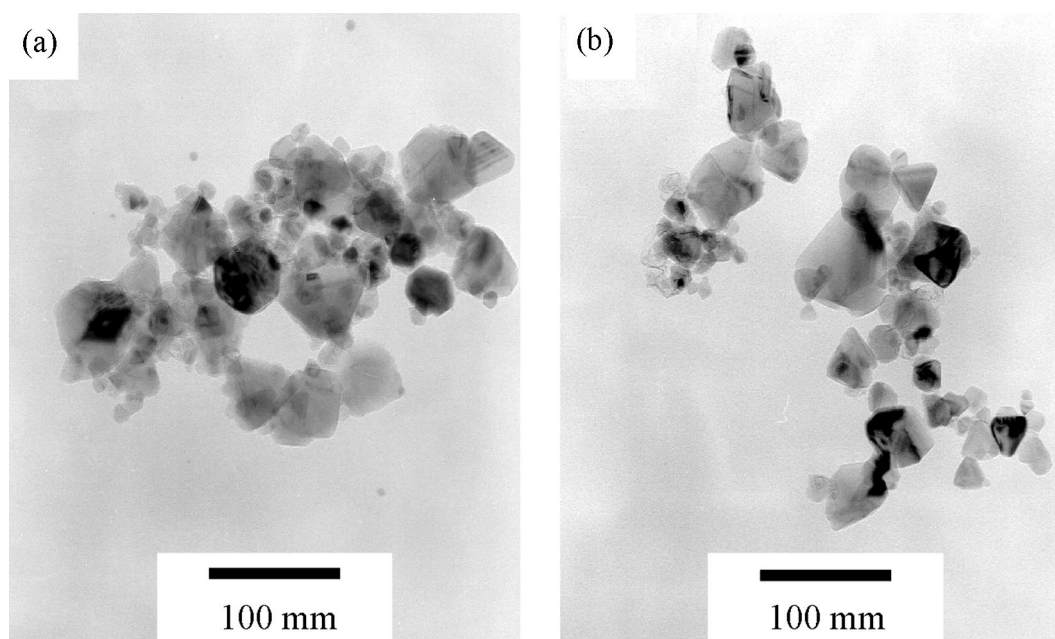
Fig. 9. TEM photographs of the powder synthesized at the condition of H/Si=26, C/Si=1.1.
(a) collected at the reaction tube, (b) collected at the vessel

1. The conversion to SiC was rapidly increased by the addition of hydrogen because the hydrogen promoted the decomposition and reduction of silicon chloride compounds. To prepare the high quality β-SiC powder, the molar ratio of H/Si was required to be over 10 and preferably to be 26.

2. The molar ratio of C/Si was required to be approximately 1.1. CH_4 was easily decomposed to carbon species for the formation of SiC as well as removal of impure oxygen. Under carbon deficient condition, Si species was easily recombined and resulted in the formation of amorphous SiO_2 by impure oxygen or ambient oxygen. Also, excess carbon species suppressed the formation of crystalline and resulted in the solid carbon contaminant in the powder.

3. For the collecting positions, the conversion was more increased at the vessel and filter due to elongated reaction time. The size of the powder was estimated to be below 100 nm and uniform in distribution.

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