

Thermal plasma chemical vapour deposition for SiC powders from $\text{SiCH}_3\text{Cl}_3\text{-H}_2$

HYUK-SANG PARK*, HONG-SUN SEON, SHI-WOO RHEE, KUN-HONG LEE
*Laboratory for Advanced Materials Processing, Department of Chemical Engineering,
Pohang Institute of Science and Technology, Pohang 790-600, Korea*

SUNGGI BAIK

*Department of Materials Science and Engineering, Pohang Institute of Science and
Technology, Pohang 790-600, Korea*

Ultrafine β -SiC powders were synthesized by introducing trichloromethylsilane and hydrogen into the high temperature RF thermal plasma argon gas. Powders were characterized by XRD, TEM, TGA, FT-IR and wet chemical analysis. Two different positions of reactant gas injection, i.e., upstream and downstream of the plasma flame, were compared in terms of the powder characteristics. The optimum concentration of hydrogen was found out to be about 3 to 4 mol% for the upstream injection. Amorphous SiC with free carbon was formed when the hydrogen concentration was lower than optimum and β -SiC with free silicon was formed when it was higher than the optimum. For the downstream injection, free silicon formation was not significant and free carbon formation was suppressed when the hydrogen concentration was higher than 7 mol%. Chemical reaction pathways were suggested which could explain these observations.

1. Introduction

Silicon carbide, with silicon nitride, is one of the most promising high temperature structural materials. Silicon carbide has been commercially produced by the Acheson process in an arc furnace from silicon dioxide and carbon. Recently, gas phase synthesis of ceramic materials has attracted much attention because it is easier to grow ultrafine and high purity ceramic powders. Most of the gas phase reactions for the production of ceramic powders have to be performed at high temperatures because their equilibrium constants are usually low. Thermal plasma synthesis is suitable for this purpose because much higher temperatures can be obtained compared to other conventional methods.

Silicon carbide powders have been synthesized with thermal plasmas by many researchers, from silicon dioxide and methane [1], silane and methane [2], silicon tetrachloride and methane [3], silicon and carbon [4], silicon and methane [5, 6], and trichloromethylsilane and hydrogen [7]. Chemical compositions as well as other characteristics of the powders were found to be strongly dependent on the chemical composition of the reactant mixture and the reaction temperature. In this research, silicon carbide powders were synthesized with a high temperature RF thermal plasma reaction system from SiCH_3Cl_3 and H_2 . In this case, the Si to C ratio in the reactant gas mixture is fixed at 1. The effect of the operating variables on the properties of the powders was experimentally identified. By comparing two modes of reactant gas injection,

possible chemical reaction pathways of the Si-C-H-Cl system in the different plasma reaction zone were proposed which could explain the chemical composition of the powders.

2. Experimental procedure

The plasma chemical reaction system used in our experiment is shown in Fig. 1. An induction coil of three turns around the double walled and water cooled quartz tube is connected to a 4 MHz, 25 kW RF generator. A plasma flame is generated with argon gas which flows through the torch. The flow rate of the total argon gas was fixed at 50 l min^{-1} . Hydrogen and trichloromethylsilane are introduced either into the upstream (A in Fig. 1) or the downstream of the plasma flame (B in Fig. 1). For the upstream injection, trichloromethylsilane flows through the high temperature plasma flame and for the downstream injection, it flows into the tail of the plasma flame. A bubbler with trichloromethylsilane liquid is heated in a water bath and the vapour is transported into the reactor with argon gas. Trichloromethylsilane was introduced at a rate of 1 g min^{-1} and the flow rate of hydrogen was varied between 0 to 6 l min^{-1} (0 to about 11 mol%). For the upstream injection, the plasma temperature becomes lower with the introduction of hydrogen and the flame becomes unstable. To maintain the stable plasma flame about the same size and brightness, the electric power was increased from 6 to

* Present address: SKC (Ltd) Research Center

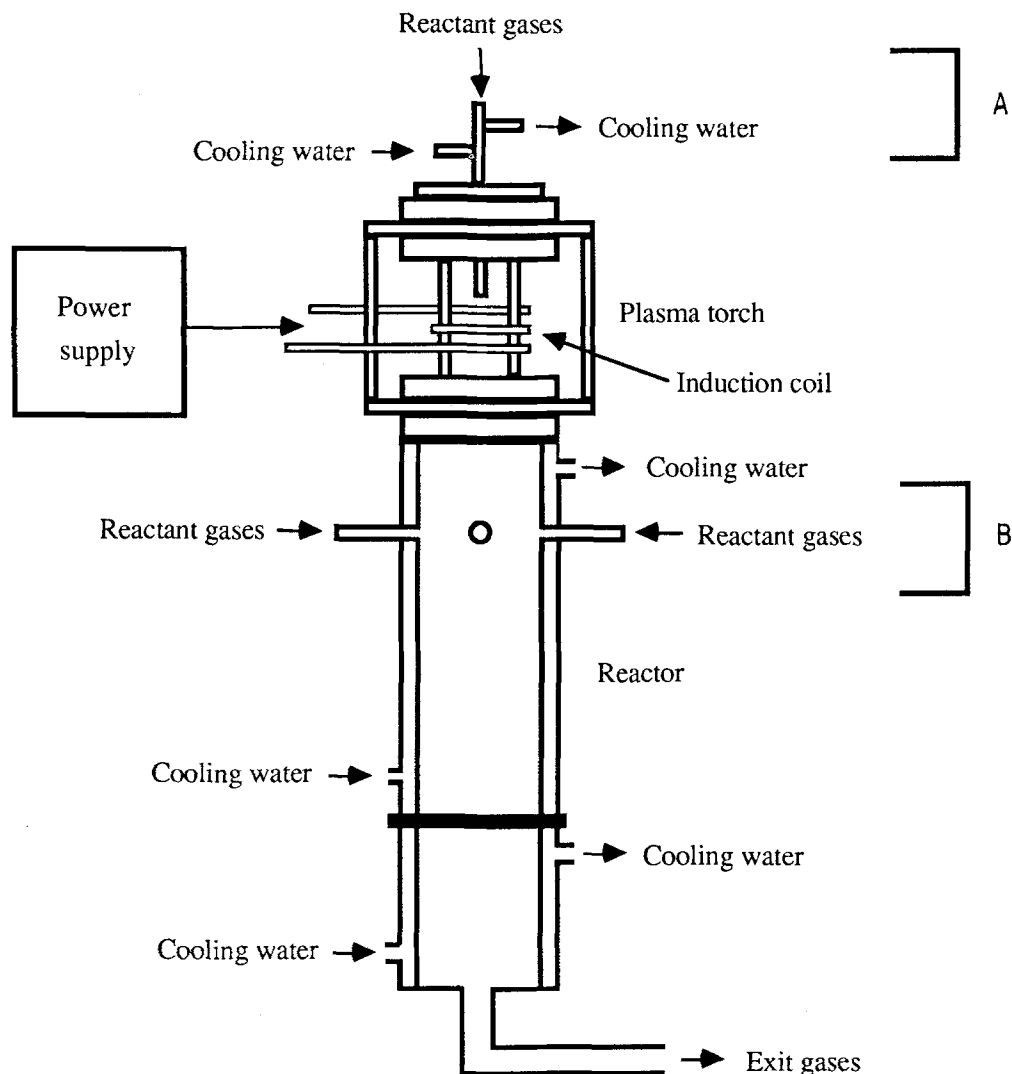


Figure 1 Thermal plasma chemical reactor with (a) upstream injection and (b) downstream injection of reactant gases.

17 kW when the hydrogen gas flow rate was increased from 0 to about 3 l min^{-1} for the upstream injection. For the downstream injection, electric power was maintained at 6 kW. The reaction chamber connected to the plasma torch is 15 cm in diameter and 1 m in height. Reactant gases mixed with the high temperature plasma gas flow into the reactor and SiC powders are formed in the gas phase and quenched in the reactor. The reaction was carried out for about an hour and most of the powders produced were recovered from the side wall of the reactor. Some of the powders were recovered from the torch wall for the upstream injection. Shape and size of the powders, their crystallinity and chemical compositions were analysed with transmission electron microscope (TEM), thermogravimetric analyser (TGA), X-ray diffractometer (XRD), and Fourier transform-infrared spectroscopy (FT-IR).

3. Results and discussion

3.1. Crystallinity

Fig. 2 shows the X-ray diffraction pattern of silicon carbide powders synthesized with various amount of hydrogen for the upstream injection.

Amorphous powders were formed when no hydrogen was introduced. In fact, most of the powders were amorphous when the hydrogen concentration was less than 3%. It was also confirmed that free silicon was formed when the hydrogen concentration was higher than 4%. Optimum hydrogen concentration is about 3 to 4% and most of the powders are in β phase. Fig. 3 shows the X-ray diffraction pattern of SiC powders recovered from the torch wall and the reactor for the upstream injection of SiCH_3Cl_3 with 4% of hydrogen.

Those powders recovered from the torch wall contain a large fraction of free silicon, while the powders recovered from the reactor do not. Powders recovered from several different locations inside the reactor do not show any differences in crystallinity and chemical composition. The amount of powders recovered from the torch wall is usually less than 5% of the total powders formed. Fig. 3 suggests that when trichloromethylsilane flows through the plasma flame where the temperature is presumably higher than $10\,000^\circ\text{C}$, atomic silicon is formed and condenses onto the torch wall without having enough time to be carbonized.

Fig. 4 shows the XRD pattern of those powders produced with the downstream injection of trichloromethylsilane and hydrogen.

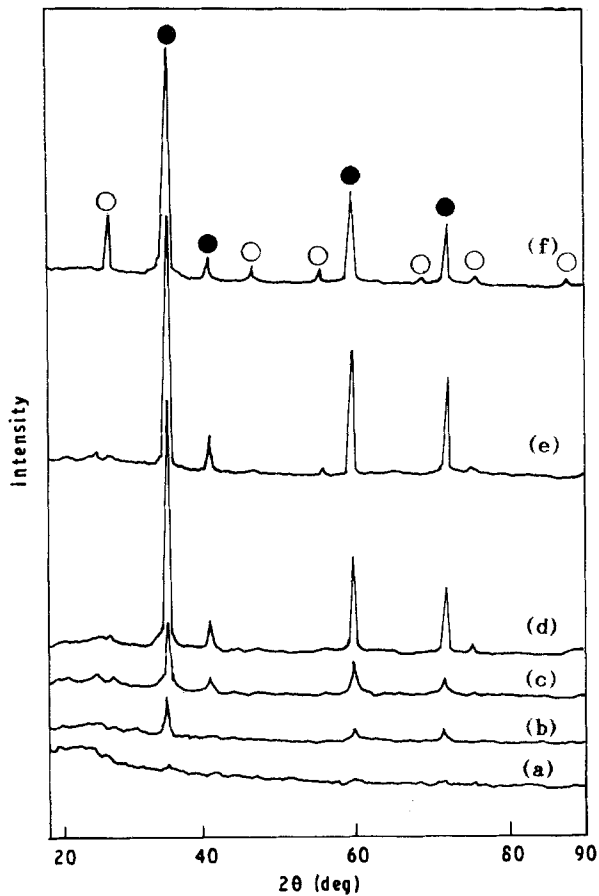


Figure 2 X-ray diffraction pattern of silicon carbide powders (● β -SiC, ○ Si) synthesized with (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5% hydrogen and upstream injection.

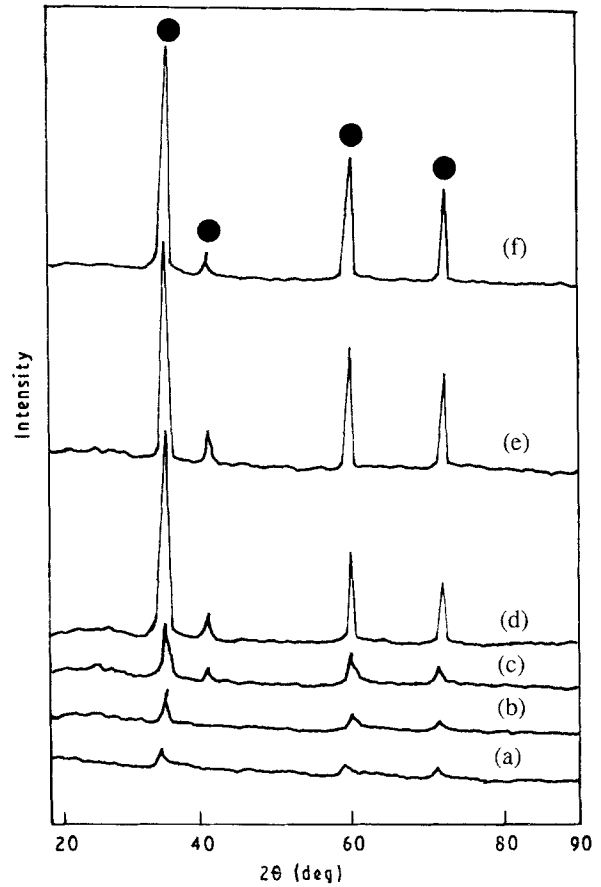


Figure 4 X-ray diffraction pattern of silicon carbide powders (● β -SiC) synthesized with (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5% hydrogen and downstream injection.

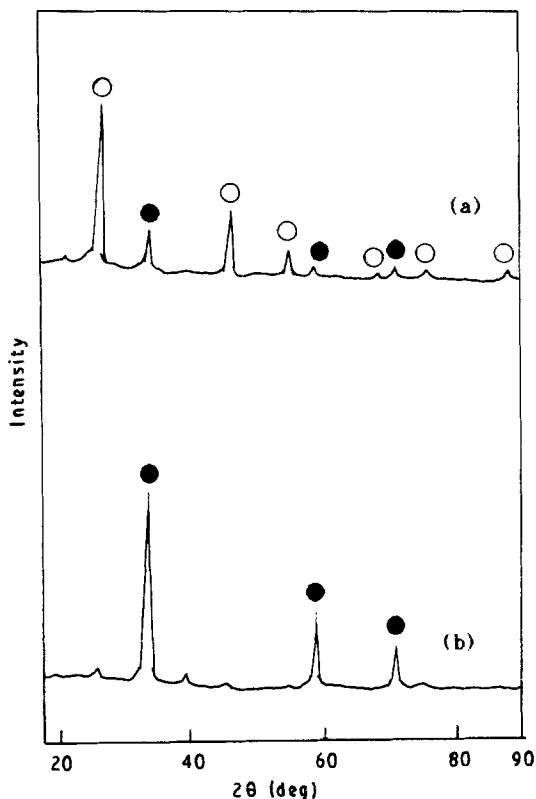


Figure 3 X-ray diffraction pattern of silicon carbide powders (● β -SiC, ○ Si) formed (a) in the torch and (b) in the reactor with 4% hydrogen and upstream injection.

For the downstream injection, free silicon was not detected from XRD analysis and the crystallinity improves as the hydrogen concentration was increased.

3.2. TGA and chemical analysis

Fig. 5 shows the thermogravimetric analysis of silicon carbide powders synthesized with various amount of hydrogen and with the upstream injection of reactants. The temperature was raised from 100 to 1200 °C at a rate of 10 °C min⁻¹ in the oxygen atmosphere.

The weight loss beginning around 350 °C was due to the oxidation of free carbon and the weight gain beginning around 800 °C was due to the oxidation of free silicon and silicon carbide as already pointed out by Kong *et al.* [1]. When the hydrogen concentration in the reactant gas mixture is less than 3%, a considerable amount of amorphous free carbon is formed. This free carbon suppresses the formation of crystalline silicon carbide as already confirmed in the XRD analysis.

When the hydrogen concentration is higher than 2%, the formation of free carbon is negligible and the powders are crystalline as confirmed in the XRD analysis. TGA analysis of those powders synthesized with 5% hydrogen showed higher rate of weight gain, which is due to the additional oxidation of free silicon.

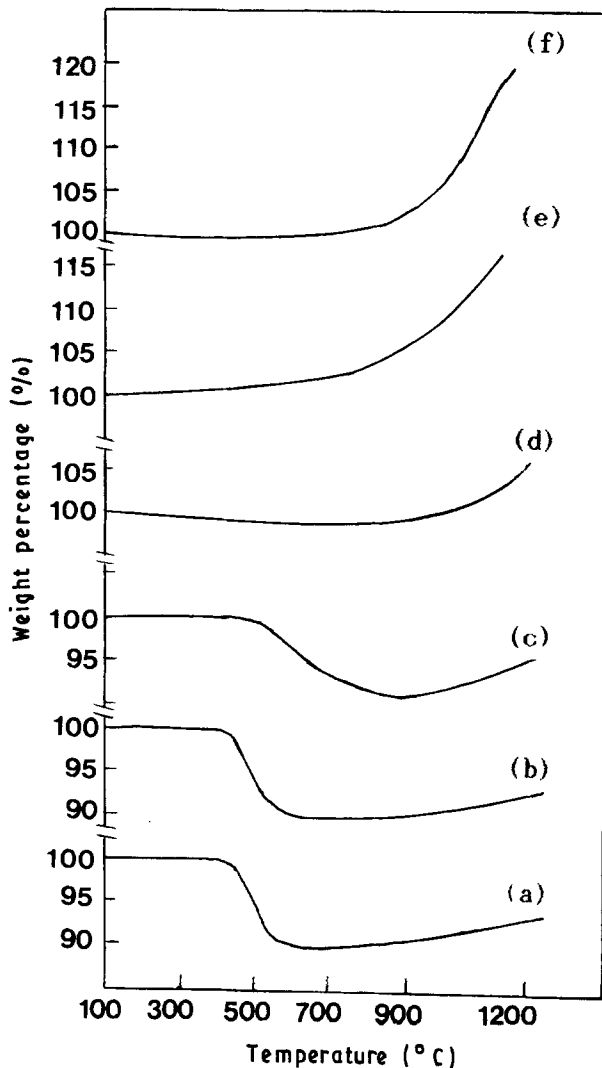


Figure 5 Thermogravimetric analysis of silicon carbide powders synthesized with (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5% hydrogen and upstream injection.

This confirms the XRD results which showed that when the hydrogen concentration increased above 4%, free silicon was formed for the upstream injection. The formation of crystalline silicon does not seem to interfere with the formation of crystalline SiC. The TGA analysis of those powders synthesized with the downstream injection of reactants also showed loss of free carbon. The amount of free carbon loss decreased with increasing concentration of hydrogen, which also leads to the improved crystallinity. A higher rate of weight gain at high temperatures was not observed in this case which suggests that free silicon formation is minimal.

Free carbon content of the SiC powders synthesized with the downstream injection was obtained from wet chemical analysis and is shown in Fig. 6.

The amount of free carbon was negligible when the hydrogen concentration was higher than 7%. The formation of free silicon is minimal regardless of the hydrogen concentration. This can be compared with the thermodynamic equilibrium calculation done by Kingon *et al.* [8]. When the reaction temperature is around 2000 K, no free silicon is formed according to their calculations. The amount of free carbon formed

as a function of hydrogen concentration is comparable to our experimental data.

3.3. FT-IR analysis

Silicon-carbon and other chemical bonds in the powders can be detected by FT-IR analysis as shown in Fig. 7. This figure is for the upstream injection. According to the spectrum, Si-C bond appears at about 800 cm^{-1} , Si-O about 1200 cm^{-1} , C-H about 1700 cm^{-1} and O-H about 3400 cm^{-1} . When the hydrogen concentration in the reactant gases was

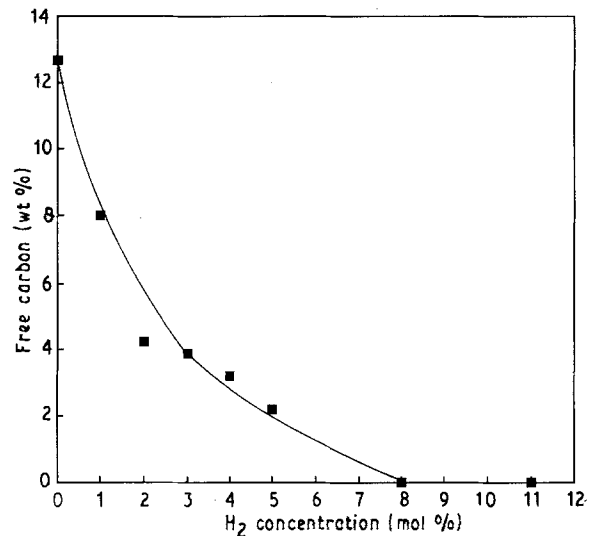


Figure 6 The amount of free carbon formed as a function of the hydrogen concentration for downstream injection.

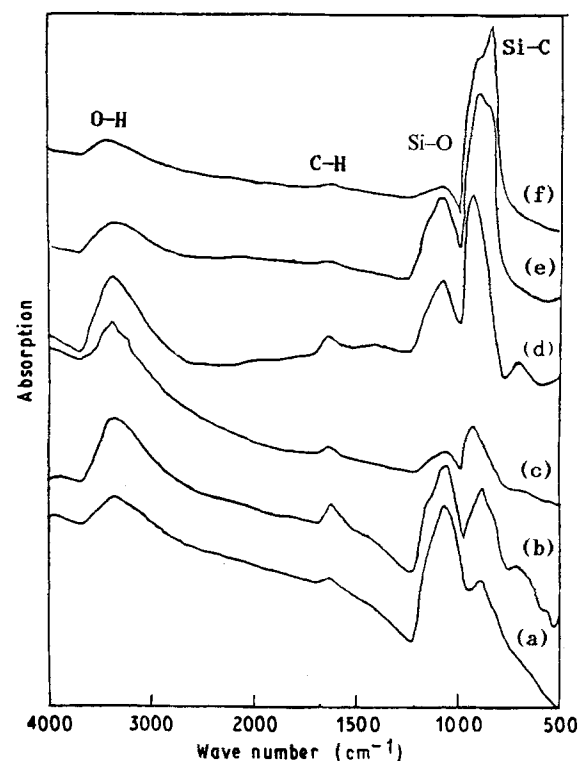


Figure 7 Infrared spectra of silicon carbide powders synthesized with (a) 0, (b) 1, (c) 2, (e) 4, (f) 5% hydrogen and upstream injection.

0–2%, Si–O bond appears relatively stronger than Si–C bond while Si–C bond appears stronger when it was higher than 2%. Si–O bond is probably due to the oxidation of the powder surfaces while C–H bond is due to the unreacted carbon and O–H bond due to the absorption of moisture. IR spectra of those powders synthesized with the downstream injection showed a similar trend.

Chen *et al.* [9] and Pai *et al.* [10] prepared SiC powders with an electric furnace from $\text{SiH}_4\text{--H}_2\text{--CH}_4$ and observed two split absorption peaks at about 940 and 810 cm^{-1} especially with those powders synthesized below 1623 K. It was believed that these particles consisted of a $\beta\text{-SiC}$ shell and a silicon core. They also found that the intensity of the peak at 940 cm^{-1} decreased as the reaction temperature was increased up to 1673 K because single phase $\beta\text{-SiC}$ powders were obtained at this temperature. In the thermal plasma synthesis, it is believed that single phase $\beta\text{-SiC}$ is obtained because the reaction temperature is much higher than conventional methods.

3.4. Transmission electron microscope analysis

Fig. 8 shows the transmission electron micrograph of SiC powders synthesized with various amounts of hydrogen and with the upstream injection of reactants.

Fig. 8a, b, c show TEM micrographs of those powders synthesized with 0, 1, and 2% of hydrogen, respectively. The agglomerate of powders is mainly a mixture of amorphous SiC and free carbon. Fig. 8d, f, g is a TEM micrograph of those powders synthesized with 3, 4, and 5% of hydrogen, respectively, and powders are mainly crystalline SiC with various shapes, i.e., hexagons and triangles. Fig. 8e shows a selective area diffraction pattern in the $\beta\text{-SiC}$ [0 1 1] plane of a powder synthesized with 4% hydrogen and most of the powders seem to be monocrystalline.

Fig. 8h shows a selective area diffraction pattern of a powder synthesized with 5% hydrogen. The pattern shows a diamond structure of free silicon in [0 1 3] plane. This confirms the result of XRD analysis where crystalline free silicon was detected. In the thermal plasma synthesis, silicon carbide and free silicon crystals are formed into independent powders while in the electric furnace reaction system, powders in the form of silicon core covered with $\beta\text{-SiC}$ shell were formed [9, 10]. In the electric furnace reaction system, it was believed that two step reactions, i.e. formation of silicon melt and carbonization of the melt were involved. In the thermal plasma chemical vapour deposition reaction, a two step reaction mechanism does not seem to play an important role because the reaction temperature is much higher. This is especially true when silicon source and carbon source gases are injected near the plasma flame at the same time. Two step reactions were reported in the plasma reactor by injecting silicon source gas into the plasma flame and carbon source gas into the second chamber at the downstream of the plasma [11].

Fig. 9 shows the TEM micrograph of SiC powders

synthesized with various amount of hydrogen and with the downstream injection of reactants.

Fig. 9a, c, d and e is for those powders synthesized with 0, 1, 2, and 3% of hydrogen, respectively. When the hydrogen concentration is not high enough, powders formed are mixtures of amorphous carbon, amorphous SiC and crystalline SiC. Fig. 9b shows the selective area diffraction pattern of powders synthesized without hydrogen gas and it shows a small amount of crystalline SiC. For the upstream injection, most of the powders were amorphous when the hydrogen concentration was low, presumably because powders were formed by rapid quenching of highly saturated reactant gases at high temperatures. Fig. 9f shows a selective area diffraction pattern of powders formed with 3% hydrogen and it clearly identifies $\beta\text{-SiC}$ single crystals. Fig. 9g and h is for those powders formed with 5 and 11% of hydrogen, respectively. The size of the powders is greater than those powders synthesized with the upstream injection of the reactants and shapes are more regular. It seems that for the upstream injection, the number of nuclei formed in the gas phase and the quenching rate are much higher than the downstream injection because the reaction temperature is much higher for the upstream injection. Then the particle size becomes smaller and the particle shape becomes more irregular in this case. Size distribution and the average size of the powders were analyzed by image analysis of TEM micrographs. Fig. 10 shows the size distribution of the powders synthesized with 4% hydrogen and the upstream injection of reactant gases.

The particle size ranges between 10 to 70 nm and the average size is around 40 nm. Fig. 11 shows the average size of the powders as a function of the hydrogen concentration in the reactant gas mixture.

The average particle size decreases as the hydrogen concentration is increased. Hydrogen suppresses the formation of free carbon powders and this might enhance the nucleation rate of silicon carbide. Also the quenching rate of the reactant gas mixture increases with increased amount of hydrogen. Both effects tend to reduce the size of the SiC powders.

3.5. Reaction mechanism

The plasma flame temperature has been measured with optical emission spectroscopy by many investigators and believed to be higher than $10000\text{ }^\circ\text{C}$ [12, 13]. For the plasma generation, a large volume of argon gas is usually used. Both facts mean that the reaction rate is very fast and the residence time of the reactant gases in the reactor is very short. Furthermore, the reaction mechanism is usually very complicated at high temperatures when it is nearly impossible to find out the reaction pathways of the plasma chemical reaction.

It seems that hydrogen plays an important role in the plasma chemical reaction and also in determining the chemical composition of powders. For the downstream injection, the reaction temperature is much lower than the upstream injection which could make a difference in chemical reaction pathways. For the

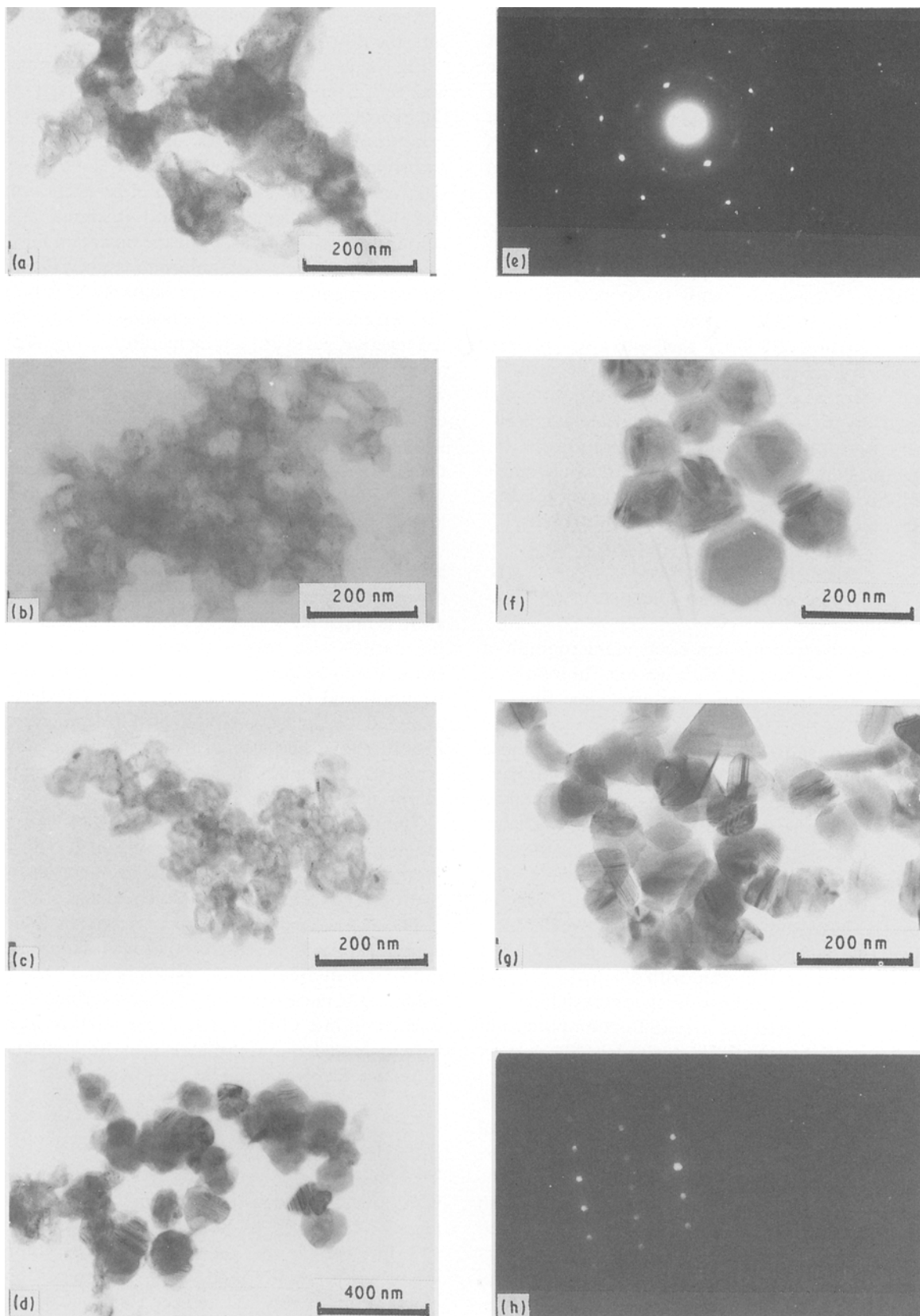
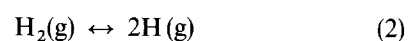
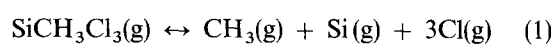


Figure 8 Transmission electron micrograph of silicon carbide powders synthesized with various amount of hydrogen and upstream injection. (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) selective area diffraction pattern of (d), SiC [011] plane, (f) 4%, (g) 5%, (h) selective area diffraction pattern of (g), Si[013] plane.

upstream injection, those powders recovered from the torch wall contain a large fraction of free silicon. High temperature reactions seem to favour the formation of atomic silicon, which is the case for the upstream injection.

Here we suggest a set of qualitative reaction pathways from our experimental observation.



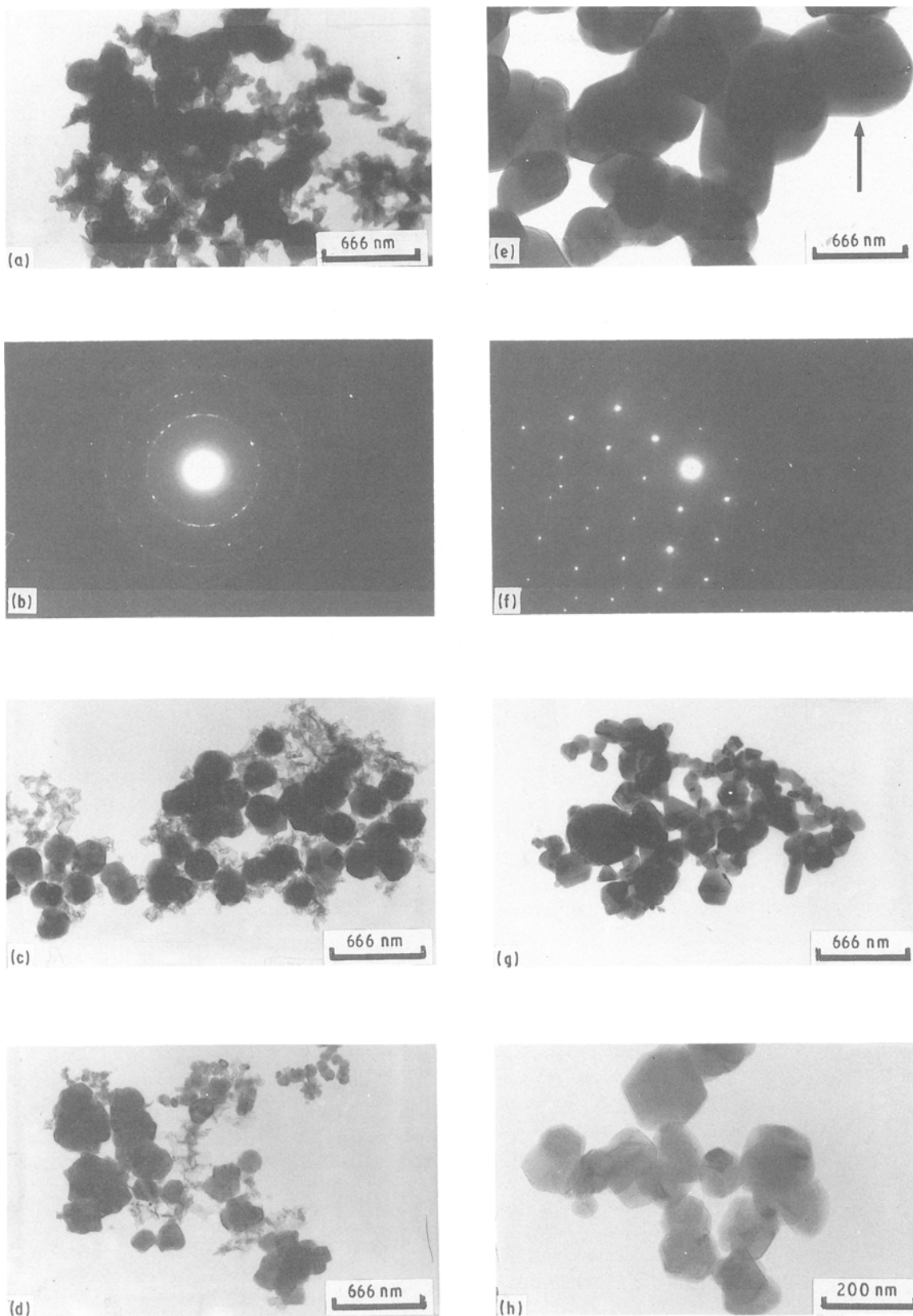
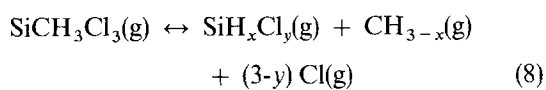
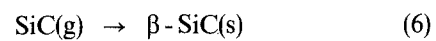
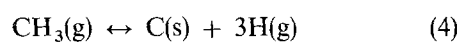


Figure 9 Transmission electron micrograph of silicon carbide powders synthesized with various amount of hydrogen and downstream injection. (a) 0%, (b) selective area diffraction pattern of (a), (c) 1%, (d) 2%, (e) 3%, (f) selective area diffraction pattern of (e) indicated by an arrow, β -SiC [011] plane, (g) 5%, (h) 11%.



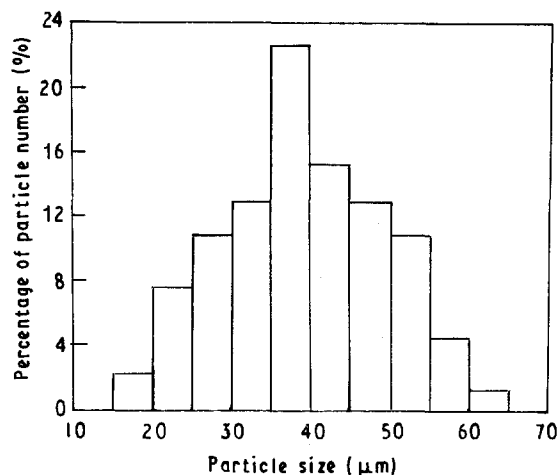


Figure 10. Size distribution of the silicon carbide powders synthesized with 4% hydrogen and upstream injection.

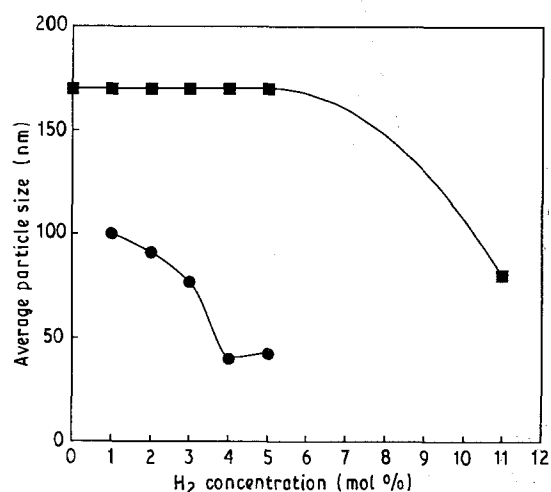


Figure 11 Average size of the powders as a function of the hydrogen concentration for upstream (●) and downstream (■) injection of reactants.

Reactions 1, 2, 3, 4, 5 and 8 are reversible reactions occurring in the high temperature reaction zone and reactions 6 and 7 are irreversible reactions occurring in the quenching reaction zone. A higher concentration of hydrogen favours the reverse reactions of 3 and 4, which enhances the formation of free silicon while suppressing the formation of free carbon. For the downstream injection, on the other hand, the silicon sub-hydrochloride radicals, SiH_xCl_y ($x + y < 4$) may be formed as in reaction 8, instead of atomic silicon as in reaction 1, because the reaction temperature is much lower than the upstream injection. This prevents the condensation of atomic silicon and the silicon formation is negligible for the downstream injection. As we increase the hydrogen concentration, we could suppress the formation of free carbon but for the upstream injection, this could lead to the formation of free silicon. The two-step reaction mechanism, where silicon melt is formed first and then carbonized from the surface, does not seem to play an important role in the plasma chemical reaction. Silicon carbide, free silicon and free carbon all seem to deposit independently from the gas phase.

4. Conclusions

β -SiC powders were synthesized by plasma chemical vapour deposition of $\text{SiCH}_3\text{Cl}_3\text{-H}_2$ system with reactants injected at the upstream or the downstream of the plasma flame. The structure and properties of the powders were studied and the following results were obtained.

1. For the upstream injection, 3 to 4% of hydrogen in the reactant gas mixture was optimum for the monocrystalline β -SiC production. Below the optimum concentration, amorphous free carbon was formed and free silicon was formed above the optimum concentration.

2. For the downstream injection, free silicon formation is negligible and free carbon formation can be suppressed when the hydrogen concentration was higher than 7%. Powder size is bigger and the shape is more regular compared to the upstream injection.

3. When there was no free carbon formation, single crystal β -SiC was formed with various shapes, i.e., triangular and hexagonal. Average size of the powders decreased when the hydrogen concentration was increased.

4. Qualitative reaction pathways were suggested which could explain the chemical composition of the powder.

Acknowledgement

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