

Preparation of SiC hollow particles by gas-phase reaction in the SiH₄-CH₄-H₂ system

C. H. PAI, K. KOUMOTO, S. TAKEDA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

H. YANAGIDA

Research Centre for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153, Japan

The formation of SiC hollow particles by gas-phase reaction in the silane-methane-hydrogen system was studied at temperatures from 1200 to 1400°C. Synthesized powders were analysed by means of the thermogravimetry, X-ray diffraction, transmission electron microscopy, infrared irradiation, etc. The powders synthesized at 1200 to 1300°C consisted of β -SiC and silicon phases, but they became almost hollow β -SiC particles at 1400°C. The composition, particle size, and shell thickness of the synthesized particles were dependent on the reaction conditions. From lattice parameter measurements, a certain amount of excess silicon was verified to be incorporated into the β -SiC lattice. On the other hand, excess carbon existed, for the most part, as an amorphous phase not forming solid solutions with β -SiC. Transmission electron microscopy observations and infrared absorption measurements have shown that excess carbon is contained within the shells of hollow particles, while unreacted excess silicon exists as a crystalline phase mostly in the cores of the particles.

1. Introduction

Silicon carbide is a promising material for high-temperature structural application because of its extreme hardness, excellent thermal and mechanical properties, and high thermal shock resistance. Furthermore, silicon carbide is considered to be a potentially useful material for high-temperature electronic devices as its band gap is large compared to silicon [1]. Its high thermal conductivity and good electrical insulation when sintered with a small amount of BeO have made high-quality integrated circuit (IC) substrates [2].

Recently porous ceramics of silicon carbide have been found to show high figures of merit for thermoelectric energy conversion [3]. We have pointed out that microstructural inhomogeneities would have significant effects on thermoelectric properties and microstructure control would become an inevitable point in materials development for thermoelectric energy conversion. For this purpose, it was attempted in this study to synthesize hollow β -SiC particles as a precursor material for controlling the microstructure of porous SiC ceramics.

Ultrafine SiC powders have been synthesized by various methods such as gas-phase reactions in conventional furnace tubes [4], plasma CVD [5, 6], laser-driven CVD [7, 8], and gas evaporation [9, 10], etc. In this paper, the silane-methane-hydrogen system was employed as a gas-phase reaction source and SiC synthesis was carried out under the temperature gradient of the electric furnace.

The formation of hollow β -SiC particles from the silane-methane-hydrogen system was first reported by Okabe *et al.* [4]. This report focuses on the formation mechanism of hollow SiC particles and the effects of the gas composition, flow rate, and reaction temperature on the powder composition, particle size (outer radius) and shell thickness.

2. Experimental procedure

2.1. Synthesis of SiC particles by gas-phase reaction

Conventional gas-phase reaction apparatus was used with metal valves in the portions having contact with silane, methane, hydrogen and the reaction products. The reaction vessel was a recrystallized alumina tube 60 cm long and 2 cm diameter. A Pyrex flask was connected to the vessel to collect the reaction products.

Special grade silane, methane and hydrogen were purchased from Takachiho Trading Co. Ltd, Tokyo, and the impurities were 0.1 to 20 p.p.m. oxygen, nitrogen, carbon monoxide, carbon dioxide, etc. The system was initially pumped down through a vacuum pump. The reactant gases having a prescribed composition were introduced into the reaction vessel whose highest temperature was 1200 to 1400°C. Gas flow rates were calculated from calibrated flowmeter readings.

2.2. Characterization of the particles

Thermogravimetric (TG) analyses were carried out to estimate the compositions of the synthesized powders.

The sample was put in a platinum pan, and temperature was increased at $5^{\circ}\text{C min}^{-1}$ in air and held at 1400°C for 0.5 h until the weight change became negligible. The composition was calculated from the weight change based on the assumption that silicon was oxidized to SiO_2 and carbon was eliminated as oxide gas. X-ray diffraction (XRD) analysis was performed to examine the phases present in the powder and precise lattice parameters of $\beta\text{-SiC}$ were measured using $\text{CuK}\alpha$ radiation with a nickel filter and high-purity silicon as an internal standard. Transmission electron microscope (TEM) observations were carried out to examine the shape and size of the particles and also the phase distributions. The infrared absorption spectra of the synthesized powders were obtained to examine further the phase distributions, the specimens being dispersed in KBr powder and pressed into pellets.

3. Results

3.1. Dependence of the powder composition on the reaction conditions

The composition of the synthesized powder, $\text{Si}/(\text{Si} + \text{C})$ (molar ratio), for the fixed ratio of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4) = 0.3$ (molar ratio) in the gas phase as a function of hydrogen flow rate is shown in Fig. 1. As the flow rate of hydrogen and the reaction temperature were increased, the $\text{Si}/(\text{Si} + \text{C})$ ratio decreased and the composition of the powder shifted to the carbon-rich side. When $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) \geq 50$ at 1400°C , the formation of pure $\beta\text{-SiC}$ was confirmed by XRD (Fig. 2). However, for the powders synthesized at 1200 to 1300°C , diffraction peaks corresponding to silicon were found in spite of the high hydrogen flow rate at $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) = 70$, which indicates that the reaction had not proceeded completely at these temperatures.

Fig. 3 shows the composition, $\text{Si}/(\text{Si} + \text{C})$, for the fixed ratio of $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) = 50$ as a function of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4)$ ratio. It is seen that the change in $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4)$ ratio exerted little influence upon the powder composition, except for the results obtained at 1200°C . It should be noted that as the reaction temperature increased, the powder composition shifted to the carbon-rich side as was also the case in Fig. 1. Fig. 4 shows the change in powder composition with the gas composition at 1400°C for a fixed total flow rate of 850 ml min^{-1} . On the whole, the powder composition and the lattice parameter of $\beta\text{-SiC}$ were little changed when the total flow rate was fixed.

From Figs 1, 3 and 4, it is immediately clear that the total flow rate and the concentration of hydrogen introduced as a carrier gas have great effects upon the powder composition. Temperature is also a significant factor for the reaction and 1200 to 1300°C does not appear to be high enough to complete the gas-phase reaction in the present system.

3.2. Lattice parameter of $\beta\text{-SiC}$

The lattice parameter of the $\beta\text{-SiC}$ phase in the synthesized powders is shown in Fig. 5 as a function of the $\text{H}_2/(\text{SiH}_4 + \text{CH}_4)$ ratio for the fixed ratio of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4) = 0.3$. The open symbols in the figure

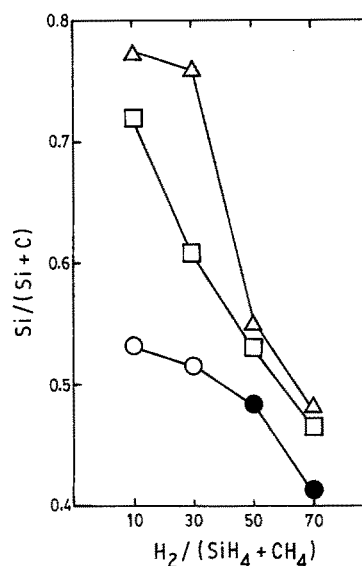


Figure 1 Effects of H_2 flow rate and temperature on the powder composition, $\text{Si}/(\text{Si} + \text{C})$ (molar ratio), for the $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4)$ ratio fixed at 0.3. (Δ) 1200°C , (\square) 1300°C , (\circ) 1400°C , (\bullet) XRD patterns only from $\beta\text{-SiC}$ phases.

indicate that the XRD patterns revealed diffraction peaks corresponding to crystalline silicon and solid symbols are from XRD patterns only showing the $\beta\text{-SiC}$ phase present.

The lattice parameters 0.43594 and 0.43591 nm (\bullet) for the $\text{H}_2/(\text{SiH}_4 + \text{CH}_4)$ ratios of 50 ($\text{Si}/(\text{Si} + \text{C}) = 0.49$) and 70 ($\text{Si}/(\text{Si} + \text{C}) = 0.41$), respectively, nearly agree with the standard value [11] of 0.43596 nm, within experimental error. This result supports the suggestion that the $\beta\text{-SiC}$ formed has a composition very close to stoichiometry and the excess carbon exists, for the most part, as a separated amorphous phase not forming solid solutions with SiC .

The powders obtained at 1200 and 1300°C under the conditions of $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) = 70$ also showed large lattice parameters (Fig. 5), although the $\text{Si}/(\text{Si} + \text{C})$ ratios were smaller than 0.5 (carbon-rich

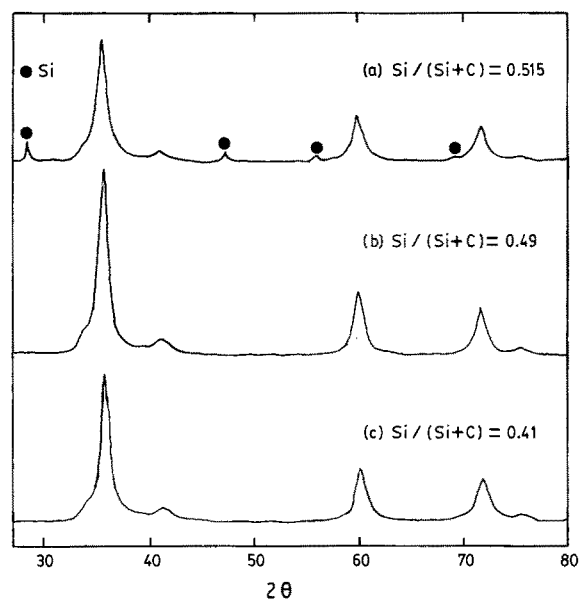


Figure 2 X-ray diffraction patterns of the powders synthesized under the conditions of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4) = 0.3$, 1400°C , and $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) =$ (a) 10, (b) 50, (c) 70.

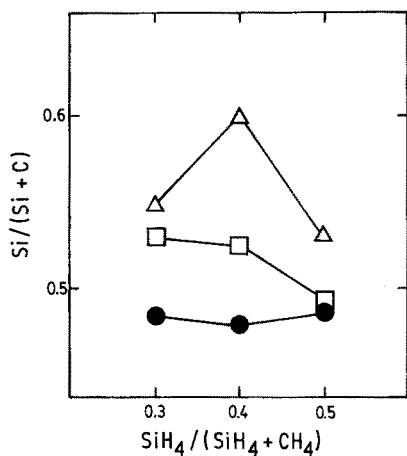


Figure 3 Effect of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4)$ ratio on the powder composition for the $\text{H}_2/(\text{SiH}_4 + \text{CH}_4)$ ratio fixed at 50. (Δ) 1200°C, (\square) 1300°C, (\circ) 1400°C, (\bullet) X-ray patterns only from β -SiC phases.

compositions). This result would lead one to suppose that the reaction was incomplete and still in the intermediate stage, possibly due to a low reaction temperature and a high flow rate of hydrogen. Another point of view is that excess carbon may have been incorporated into the interstitial sites of the β -SiC lattice. On the other hand, the lattice parameters of β -SiC for the powders containing excess free silicon are all larger than the standard value, which clearly indicates that a certain amount of excess silicon can be incorporated into the β -SiC lattice.

Nonstoichiometry in SiC was also reported by other workers. In their investigation on the stability of SiC structure, Ryan *et al.* [12] indicated that the observed alpha forms were nonstoichiometric and to a greater degree than β -SiC. By contrast, Shaffer [13] indicated Si/C ratios of 1.049 and 1.032 for high-purity beta(C) and alpha(6H) single crystals, respectively. Whether excess silicon atoms occupy interstitial sites or carbon sites substitutionally could not be determined from lattice parameter measurements alone, because both defect models would increase the lattice parameter as the covalent radius of silicon (0.117 nm) is larger than that of carbon (0.077 nm) [14].

3.3. TEM observations

TEM observations revealed that the synthesized powders were mostly composed of chained networks of hollow particles as shown in Fig. 6a.

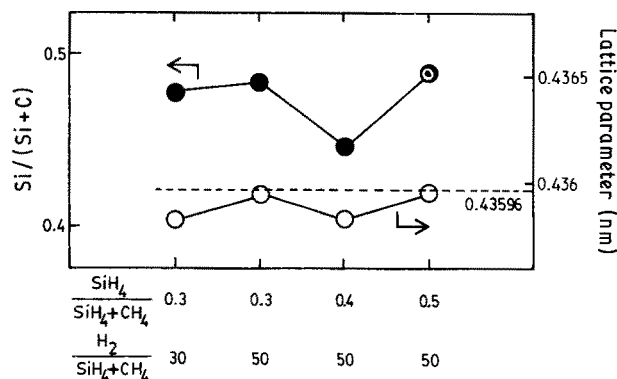


Figure 4 Effect of total flow rate on the powder composition, $\text{Si}/(\text{Si} + \text{C})$, at 1400°C.

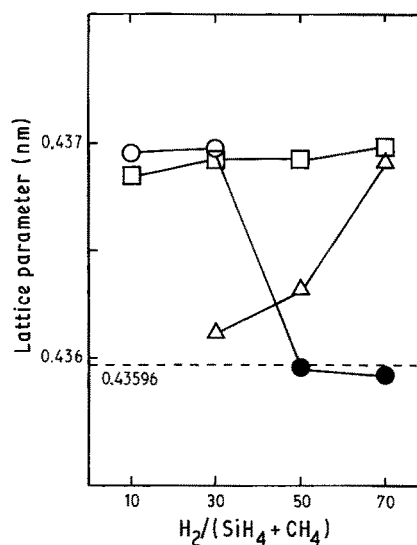


Figure 5 Lattice parameters of β -SiC phases in the powders. (Δ) 1200°C, (\square) 1300°C, (\circ) 1400°C, (\bullet) XRD patterns only from β -SiC phases.

In the case of carbon-rich powder, the electron diffraction pattern corresponds solely to that of β -SiC (Fig. 6b) and a dark-field image taken for the diffused electrons with an objective aperture off the diffracted electron beams from β -SiC phases (Fig. 6c) shows that excess carbon is distributed as an amorphous phase. This finding agrees well with the results obtained by XRD measurements (Fig. 2). A dark-field image taken for the diffracted electron beams from β -SiC (111) planes clearly indicates that an individual particle is polycrystalline and composed of much smaller crystallites (Fig. 6d). Comparison of Figs 6c and d clearly shows that excess carbon should be contained within the shells of hollow β -SiC particles.

The electron diffraction pattern of the silicon-rich powder (Fig. 6f) shows β -SiC and free silicon phases are present. Dark-field image observations using electron beams diffracted from silicon were attempted to make clear where free silicon existed, but were unsuccessful. However, it can be seen in Fig. 6g, a dark-field image taken for the diffused electrons with an objective aperture off the diffracted electron beams from silicon phases, that amorphous carbon exists on the outer surfaces of the particles. Fig. 7 shows average particle size (outer diameter of a hollow particle) and shell thickness (outer radius minus inner radius) as functions of the $\text{H}_2/(\text{SiH}_4 + \text{CH}_4)$ ratio. Both particle size and shell thickness increased with increasing $\text{H}_2/(\text{SiH}_4 + \text{CH}_4)$ ratio up to 50 and decreased at 70.

3.4. IR absorption spectra

Infrared absorption measurements were carried out to characterize further the synthesized particles. It is well known [15] that IR absorption of fine particles is closely related to their size and shape. IR absorption spectra of SiC fine particles were first calculated theoretically by Chen *et al.* [16]. According to their theory, the IR spectrum of hollow particles dispersed in KBr shows a shoulder in the higher frequency region on a principal absorption band centred at $\sim 830 \text{ cm}^{-1}$, while two separated peaks at ~ 810 and

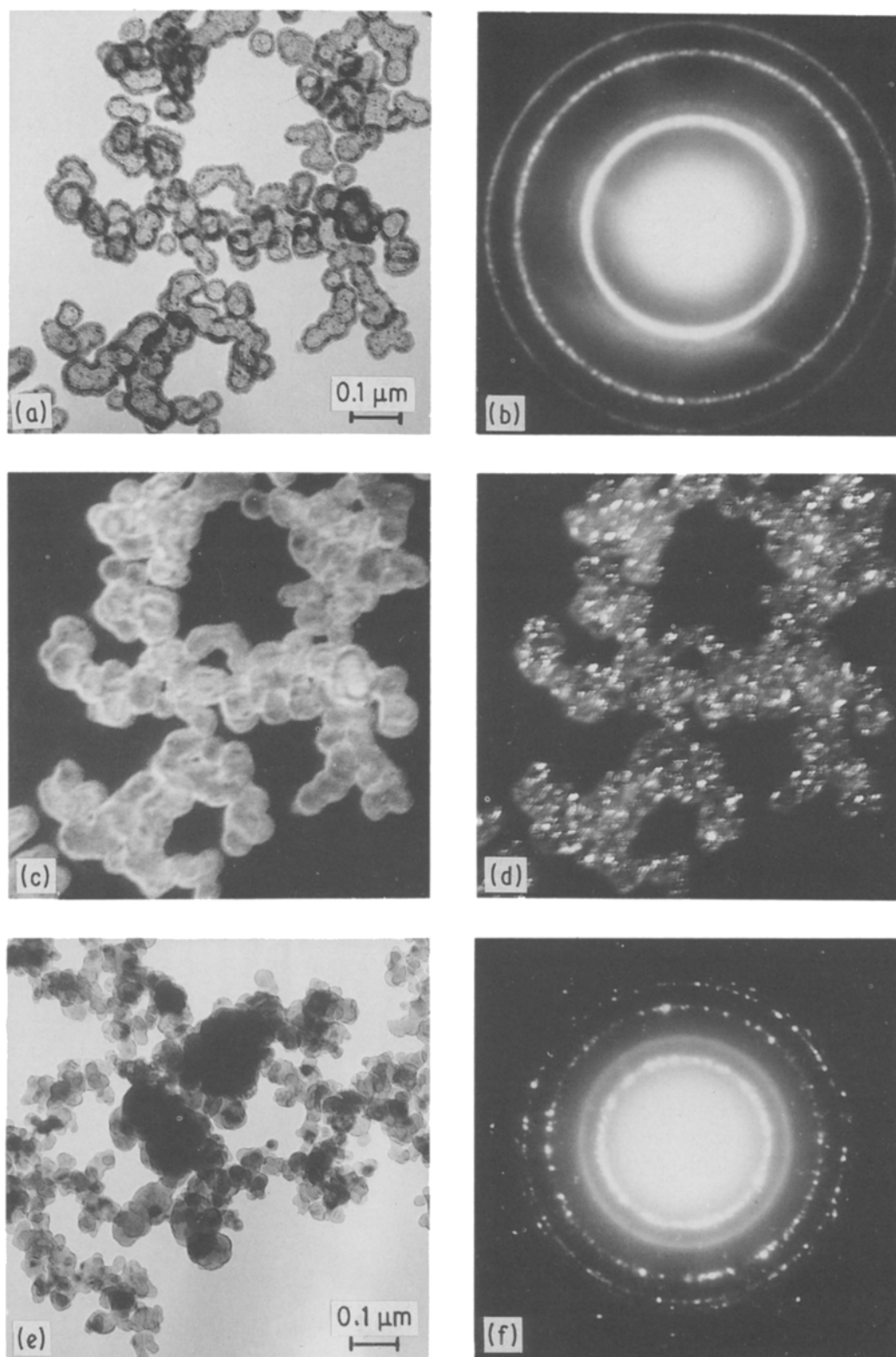


Figure 6 Transmission electron micrographs of the powders: (a) powder ($\text{Si}/(\text{Si} + \text{C}) = 0.44$) obtained under conditions of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4) = 0.4$, $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) = 50$, 1400°C ; (b) electron diffraction pattern of (a); (c) a dark-field image of (a) taken for the diffused electrons with an objective aperture off the diffracted electron beams from β -SiC phase; (d) β -SiC (1 1 1) dark-field image of (a); (e) powder ($\text{Si}/(\text{Si} + \text{C}) = 0.77$) obtained under the conditions of $\text{SiH}_4/(\text{SiH}_4 + \text{CH}_4) = 0.3$, $\text{H}_2/(\text{SiH}_4 + \text{CH}_4) = 10$, 1400°C ; (f) electron diffraction pattern of (e); (g) a dark-field image of (e) taken for the diffused electrons with an objective aperture off the diffracted electron beams from the silicon phase.

$\sim 940\text{ cm}^{-1}$ appear in the spectrum of particles with unreacted silicon left within the cores.

IR spectra of the synthesized powders with different carbon compositions are shown in Fig. 8. Spectra of silicon-rich and near-stoichiometric powders are in accordance with Chen *et al.*'s calculations, and it was ascertained

that free silicon in the heavily silicon-rich powder existed in the cores of SiC particles, although TEM observations could not reveal its location. Carbon-rich composition was not taken into consideration in Chen *et al.*'s calculations, so that the IR spectrum of the carbon-rich powder in Fig. 8 showing a rather

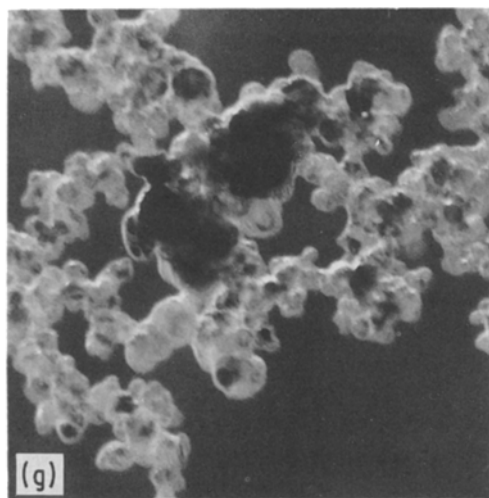


Figure 6 Continued.

sharp absorption peak at a $\sim 960\text{ cm}^{-1}$ remains to be analysed theoretically, although it must be associated with the presence of amorphous carbon.

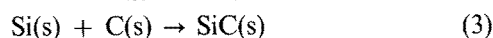
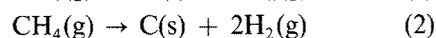
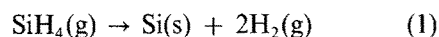
4. Discussion

4.1. Mechanism of hollow particle formation

Because chemical equilibrium describes what can be expected for a yield in an ideal state, thermodynamic considerations would become significant to elucidate the gas-phase reaction. Equilibrium partial pressures of the possible gaseous species in the $\text{SiH}_4\text{-CH}_4$ system were thus calculated and are shown in Fig. 9. The gaseous species considered in this study were SiH_4 , SiH , Si , CH_4 , CH_3 , C_2H_4 , C_2H_2 , C_2H and H_2 . Most of the thermodynamic data necessary to calculate equilibrium constants were taken from JANAF tables [17].

It can be seen in Fig. 9 that CH_4 is the most stable gaseous species at low temperatures, but as temperature increases, its equilibrium partial pressure decreases, indicating the condensation of excess carbon out of the gas phase takes place. As the equilibrium partial pressures of SiH_4 and SiH are very low, solid silicon is also expected to precipitate out of the gas phase. It was experimentally confirmed that decomposition of SiH_4 in hydrogen took place above about 700°C to yield solid silicon (particles or otherwise whiskers and films on the inner surface of the reaction tube), while

solid carbon could not be detected when CH_4 and hydrogen mixture was passed into a reaction tube, possibly because too small a quantity of solid carbon was formed. Solid silicon would be combined with solid carbon and/or CH_4 molecules to form SiC in the present temperature range, and the following reactions can be considered.



It seems that the main reactions of SiC formation are Reactions 1 and 4 at lower temperatures and 1, 2 and 3 at higher temperatures.

Based on the above discussion, the mechanism of hollow SiC particle formation can be considered as follows. First, silicon particles are formed by thermal decomposition of SiH_4 at about 700°C , and subsequently these silicon particles are carburized by CH_4 and a certain amount of solid carbon. As these particles are transported to a higher temperature region accompanied by further attack by CH_4 and/or C_2H_2 and solid carbon, the SiC formation reaction would proceed via the predominating outward diffusion of silicon atoms through the SiC layer, resulting in the consumption of inner solid silicon and hence leading to the formation of hollow SiC particles.

The predominating outward diffusion of silicon atoms through the SiC layer was first postulated by Kato and Okabe [18]. On the other hand, the self-diffusion coefficients of silicon and carbon in single crystals of both α - and β -type SiC have been reported by several workers [19–24] and the relation $D_{\text{C}} > D_{\text{Si}}$ has been confirmed for β - SiC so far. However, as the synthesized hollow SiC particles are polycrystalline individually and grain boundaries would significantly affect the atomistic diffusion, the possibility of predominant silicon diffusion along grain boundaries and/or surfaces of SiC still remains to be clarified.

4.2. Relationship between outer diameter and shell thickness of a hollow particle with carbon-rich composition

If the mechanism of SiC hollow particle formation mentioned in the previous Section 4.1 is to be correct,

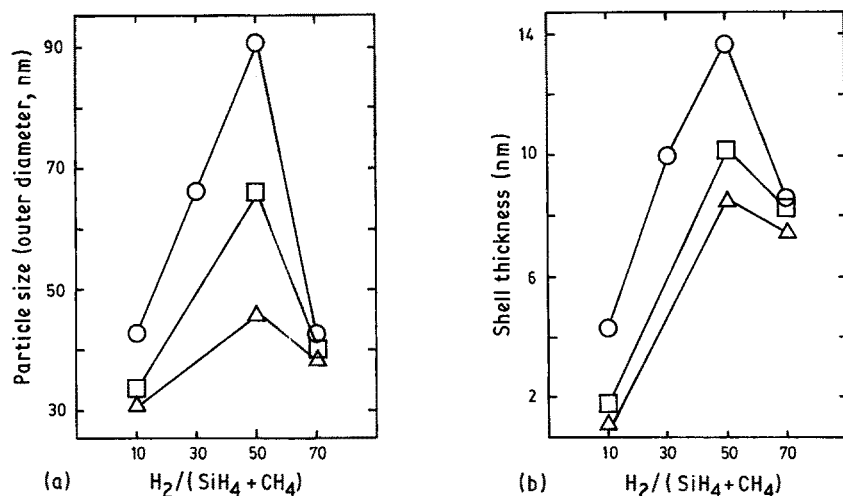


Figure 7 The relationships between $\text{H}_2/(\text{SiH}_4 + \text{CH}_4)$ ratio and (a) particle size and (b) shell thickness. (Δ) 1200°C , (\square) 1300°C , (\circ) 1400°C .

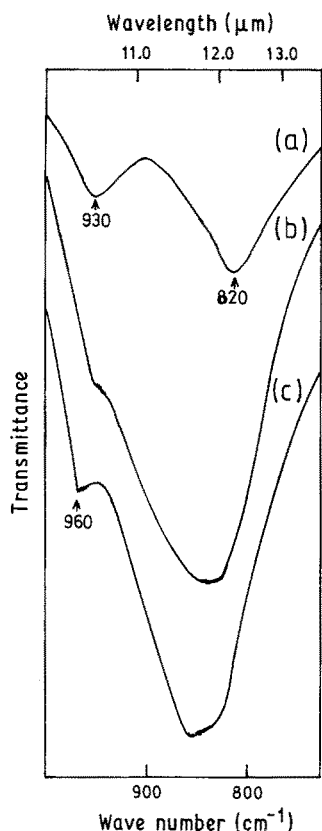


Figure 8 Infrared absorption spectra of synthesized powders: Si/(Si + C) ratios of powders (a), (b) and (c) are 0.77, 0.49 and 0.44, respectively.

the diameter of a silicon particle first formed by thermal decomposition of SiH_4 would be equal to the inner diameter of an SiC hollow particle. This was verified by Kato *et al.*'s elegant experiments [25], in which silicon whiskers were reacted with the CH_4 and H_2 gas mixture, followed by further heat treatment for solid state reaction to form hollow SiC tubes. The inner diameter of a hollow tube was found to be exactly the same as the outer diameter of a silicon whisker. Based on these findings the relationship between outer radius and shell thickness of a hollow particle could be derived as follows.

Because the powders synthesized in the present study had compositions deviating from stoichiometry,

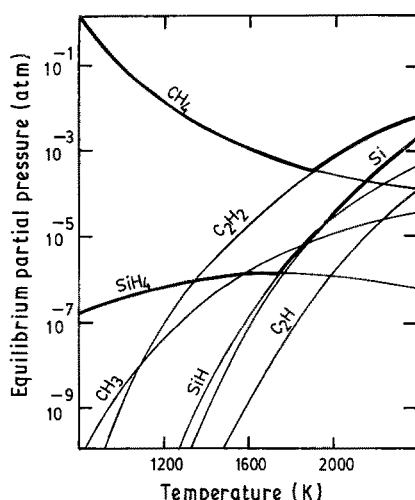


Figure 9 Calculated equilibrium partial pressures as a function of temperature of the SiH_4 - CH_4 system at 1 atm.

the manner of existence for excess carbon or silicon should be taken into consideration. Putting $\text{Si}/(\text{Si} + \text{C}) = m$, for $m < 0.5$ excess carbon in the carbon-rich powder was assumed to be dispersed as an amorphous phase (as confirmed by XRD measurements and TEM observations) within the shell of a hollow particle. Then, the weight of silicon, W_{Si} , contained within the shell which is supposed to be 100% dense can be expressed by the following equation

$$W_{\text{Si}} = \frac{4}{3}\pi(r_0^3 - r_i^3) d_{\text{SiC}} \frac{M_{\text{Si}}}{M_{\text{SiC}}} \times \left[1 + \frac{(0.5 - m)M_{\text{SiC}}d_{\text{SiC}}}{mM_{\text{C}}d_{\text{C}}} \right] \quad (5)$$

where r_0 and r_i are outer radius and inner radius of a hollow particle, d is the density of the subscript substance, and M is the atomic weight of the molecular weight of the subscript substance, respectively. Here, the weight of silicon in a β -SiC particle can be assumed to be equal to that of a silicon particle first formed by thermal decomposition of SiH_4 as expressed by

$$W_{\text{Si}} = \frac{4}{3}\pi r_i^3 d_{\text{Si}} \quad (6)$$

Consequently, the relationship between inner radius, r_i , and outer radius, r_0 , of a hollow SiC particles, combining Equations 5 and 6, can be written for $m < 0.5$ as

$$\left(\frac{r_0}{r_i}\right)^3 = 1 + \frac{M_{\text{SiC}}d_{\text{Si}}}{M_{\text{Si}}d_{\text{SiC}}} \left[1 + \frac{(0.5 - m)M_{\text{SiC}}d_{\text{SiC}}}{mM_{\text{C}}d_{\text{C}}} \right] \quad (7)$$

For $m = 0.5$ (stoichiometric β -SiC), Equation 7 gives the following relation

$$\left(\frac{r_0}{r_i}\right)^3 = 1 + \frac{M_{\text{SiC}}d_{\text{Si}}}{M_{\text{Si}}d_{\text{SiC}}} \simeq 2.04 \quad (\text{for } 100\% \text{ dense SiC}) \quad (8)$$

For $m > 0.5$, i.e. silicon-rich composition, because it was not possible to evaluate the amount of unreacted silicon left within the core of a particle, a relation similar to Equation 7 could not be derived.

Figure 10 shows the composition dependence of $(r_0/r_i)^3$ calculated from the observed particle sizes

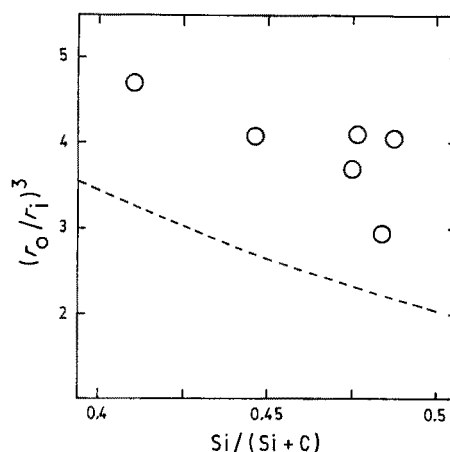


Figure 10 The composition dependence of $(r_0/r_i)^3$ calculated from the observed particle sizes and shell thicknesses, where r_0 is the particle size (outer radius), r_i is the inner radius of a hollow particle. (---) Calculated using Equation 7. See text for discussion.

and shell thicknesses. The $(r_0/r_i)^3$ calculated using Equation 7 by assuming $d_{\text{SiC}} = 3.21 \text{ g cm}^{-3}$ [26], $d_{\text{Si}} = 2.33 \text{ g cm}^{-3}$ [27], and $d_{\text{C}} = 2.0 \text{ g cm}^{-3}$, is also shown for comparison as a dotted line in the figure. The density of amorphous carbon, d_{C} , is usually smaller than 2.0 g cm^{-3} [28], but could not be estimated precisely. Comparison between the observed and calculated $(r_0/r_i)^3$ values would indicate that excess carbon should be contained in the shells of hollow SiC particles in the powders having carbon-rich compositions as supported by TEM observations. However, large differences in them would lead us to suppose from Equation 7 that the density of SiC might have been overestimated, that is, crystallites are not packed 100% dense in the shells of hollow particles. If the density of SiC crystallite and amorphous carbon packing is estimated to be smaller, the dotted line would move upward in the figure and agree with the observed values.

These results are considered to support further, though semiquantitatively, the mechanism of hollow SiC particle formation proposed in Section 4.1.

5. Conclusions

The following conclusions can be drawn from the present study on the gas phase reaction in the $\text{SiH}_4\text{-CH}_4\text{-H}_2$ system.

1. The reaction conditions, particularly the concentration of hydrogen introduced as a carrier gas, had a great influence upon the composition, particle size, and shell thickness of hollow particles.

2. A certain amount of excess silicon was incorporated into the β -SiC lattice, while excess carbon existed as an amorphous phase not forming solid solutions with SiC.

3. Excess carbon was contained within the shells of hollow particles, while unreacted excess silicon existed as a crystalline phase mostly in the cores of the particles.

4. The mechanism of hollow SiC particle formation was discussed from a thermodynamic point of view, and considerations of the mass balance for the formation process verified semiquantitatively the proposed mechanism.

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