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Vapor synthesis of silicon and silicon carbide powders

Wu, Huann-Der, Ph.D.
The Ohio State University, 1987

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To my wife, Mei-Ying

and

To my parents
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CHAPTER I
INTRODUCTION

As technology advances, fine homogeneous powders are needed for high performance material applications. Vapor synthesis is gaining increased attention as a preferred powder preparation technique in refractory oxides and non-oxides. Compared to traditional preparation methods (communion, element reaction, etc.), vapor phase reaction (VPR) has several advantages¹:

(1) High purity.
(2) Loose aggregation.
(3) Fine and narrow particle size distribution.

Silicon carbide (SiC) and Silicon nitride (Si₃N₄) are the candidate materials for high performance engines and gas turbines². SiC is generally accepted as the best material for use at temperatures above 1400°C because of its low density, high temperature strength, chemical inertness, refractoriness, and creep resistance. However, it is hard to fabricate due to the extremely low self-diffusion coefficients of Si and C in SiC. Desired properties and easy fabrication cannot be achieved unless
the starting powders have the following characteristics: fineness, narrow size distribution, nonagglomeration, and high purity. Therefore, preparing pure and ultrafine SiC powders is very important for high temperature applications, and attracts both industry and researchers.

Processes used for preparing fine powders fall into two distinct categories: breaking-down and building-up. Breaking-down processes, such as atomization and ball milling, are frequently used. However, it is difficult to obtain high purity and fine powders (< 1 um) using these processes, and the yields are very low. Building-up processes, including liquid-precipitation and vapor-condensation, produce highly pure ultrafine powders (<1 um) because of the homogeneous nucleation and growth processes under a high degree of supersaturation. Therefore, vapor phase reaction has great potential for preparing high quality SiC powders for applications at high temperatures. The VPR process can be further delineated as evaporation-condensation and chemical reaction-condensation. Evaporation-condensation is a physical process which needs a high energy source such as, a plasma, an arc, or a laser to evaporate materials. The very steep temperature gradients at the edge of hot flame results in nucleation and growth of powders under a high supersaturation
condition. On the other hand, chemical reaction-condensation is a chemical process in which a high temperature and a steep temperature gradient are sufficient but not necessary conditions to reach high supersaturation. Since the temperature gradient is not critical, this research used a tube furnace as a heat source to study SiC powder formation in chemical vapor reaction.

In reviewing the literature, it was concluded that SiC powder formation processes using tetramethylsilane (TMS, (CH$_3$)$_4$Si(g)), silane-methane (SiH$_4$(g)-CH$_4$(g)), and silane-ethylene (SiH$_4$(g)-C$_2$H$_4$(g)) have been misinterpreted. To attempt to better understand VPR of SiC, therefore, a processes was developed to allow better sample analysis. Based on the thermodynamic data, tetramethylsilane ((CH$_3$)$_4$Si), silane-ethylene (SiH$_4$(g)-C$_2$H$_4$(g)), and silane-ethane (SiH$_4$(g)-C$_2$H$_6$(g)) were chosen as the precursor systems of this study. The SiH$_4$(g)-C$_2$H$_6$(g) system, especially, was interesting since it is a new system and has the highest supersaturation ratio (SSR) among the systems studied.

A substantial difference between a biprecursor (SiH$_4$(g)-C$_2$H$_4$(g) etc.)$^{23,24}$ and a monoprecursor (TMS)$^{30}$ system for SiC powder preparation was the average particle
size variations versus reaction temperatures. In a biprecursor system, the SiC particle size increased with increasing the reaction temperature. However, in contrast to previous observations, it is found in this study that the SiC particle size decreased with increasing reaction temperature for the monoprecursor (TMS).

It was felt that the difference might be caused by Si particle formation or by both kinetic and thermodynamic factors of nucleation and growth. The nucleation and growth rate can be divided into either a kinetics dominant region at relatively low temperatures, or a thermodynamics dominant region at relatively high temperatures. Therefore, whether or not the particle sizes increase with increasing the reaction temperature will depend on the temperature used.

To clarify the cause of the difference, and to establish a model of powder formation, Si powders using SiH₄(g) as the starting material have also been prepared. This reaction is simple: SiH₄(g) decomposes and the Si(s) particles nucleate and grow. In addition, the decomposition temperature of SiH₄(g) (400°C) and the melting temperature of Si(s) (1410°C) are sufficiently low. Both kinetic and thermodynamic regions can be easily examined through experimentation.
Consequently, the objectives of this research were to study:

(1) the relationship between the formation of SiC and Si powders.

(2) the mechanisms of particle formation.

(3) SiC powder preparation in a flowing gas furnace to provide information pertinent to the synthesis of ultrafine and pure SiC powders.
CHAPTER II
LITERATURE REVIEW

2.1 Introduction

The chemical vapor deposition (CVD) process for synthesis of SiC was first mentioned in 1909 by Pring and Fielding\textsuperscript{6}, who used SiCl\textsubscript{4}(g)-C\textsubscript{6}H\textsubscript{6}(g) in H\textsubscript{2}(g) at 1700\textdegree C to 2000\textdegree C. Since then, various techniques and precursor systems have been applied to prepare SiC product.\textsuperscript{7,8} However, SiC powder preparation through the VPR became popular only in the early 1980s due to the need for high performance structural materials.

Presently, there is not much documentation on the synthesis of silicon-based powders using VPR, and there are few scientific and systematic studies in this field.

This review is presented in two parts. The first part is a general presentation of powder preparation using different heat sources, and the second part is a discussion of formation processes of Si based powder formation through VPR.

2.2 Powder Preparation

2.2.1 Arc Heat Source
Preparing submicron oxides, metals, and carbides using evaporation-condensation has been successful and commercially available since the 1960s. One popular heat source is the high intensity arc capable of producing temperatures as high as 7000°K in the flame edge. Materials can be evaporated using a high temperature flame, then fine powders nucleate and grow under a high degree of supersaturation achieved by supercooling. The particle sizes range between 5 and 100 nm. Most of the powders are spherical.

Y. Ando etc. designed a new arc device. In that device, a carbon rod was used as an electrode and was mounted vertically with a block of silicon at the bottom of the system. Beta-SiC powder with sizes 10 - 80 nm, was synthesized when carbon and silicon were evaporated by an electric arc.

2.2.2 Plasma Heat Source

A plasma is one of the most efficient heat sources for mass production of ultrafine (< 100 nm) oxide powders and carbides (TaC, NbC, and TiC). It is also used successfully to produce ultrafine silicon carbide powder as published in several patents. Generally, the temperatures were kept at approximately 2000°C - 3000°C. The common precursors have low free energies of reaction,
such as $\text{SiCl}_4(\text{g})$-$\text{CH}_4(\text{g})$ and $(\text{CH}_3)\text{SiCl}_3(\text{g})$ were chosen as reactants, and the final powder sizes ranged from 10 to 1000 nm.

Vogt etc.\textsuperscript{17} prepared both SiC (10-20 nm) and Si$_3$N$_4$ powders using a newly developed high temperature plasma tube that overcame the melting problem of the water-and gas-cooled quartz tubes commonly used.

Kong etc.\textsuperscript{18} also synthesized beta-SiC powder using a plasma by a reaction between methane and silicon monoxide. Particle sizes ranged from 2 to 40 nm at reaction temperatures higher than 10,000°K. The morphologies are triangular and hexagonal.

2.2.3 Laser Heat Source

The laser has been applied to the production of ultrafine SiC powder since the early 1980s. Presently, it is limited to laboratory use.

An evaporation-condensation technique using a focused laser to evaporate bulk SiC was used to produce nm sized SiC powders.\textsuperscript{10} J. S. Haggerty and co-workers,\textsuperscript{19-22} using a CO$_2$ laser, synthesized Si, SiC, and Si$_3$N$_4$ powders by a chemical reaction-condensation technique. However, SiC powder could not be obtained until a SiH$_4(\text{g})$-$\text{C}_2\text{H}_4(\text{g})$\textsuperscript{19,23,24} system was used.
2.2.4 Tube Furnace

The tube furnace has also been used to prepare a variety of fine powders (Mo2C, TiO2, ZrO2, WC, NiO, Si3N4)25-29, 40 using the chemical vapor phase reaction technique.

Kato etc. prepared beta-SiC powder using (CH3)4Si(g)-H2(g)30 and SiH4(g)-CH4(g)-H2(g)31 and has proved that SiC powder made from TMS has excellent sinterability32,33 (97%, 2050°C with a boron additive).

Recently, J. Wu etc.34 developed a 5-zone aerosol reactor using a SiH4(g)-N2(g) system to synthesize Si powder in the 100 - 200 nm size range. They further used a multi-stage reactor, along with seed and CVD techniques to prepare large particle size Si powder (10 um).

2.3 VPR Formation Processes

2.3.1 SiH4(g) System

Si powder can be obtained using a tube furnace or a laser source according to the simple reaction

\[ \text{SiH}_4(g) = \text{Si}(s) + 2\text{H}_2(g). \]  

It is believed that SiH4(g) is one of the best systems for study of the powder formation mechanism through VPR. Since the decomposition temperature of SiH4(g) (400°C) and the melting temperature of Si(s) (1410°C) are sufficiently low, both kinetic and thermodynamic regions can be easily
examined.

R. A. Marra$^{19,35}$ used a laser to study Si powder formation from SiH$_4$(g). The Si powder morphologies ranged from spherical to chained agglomerates depending on the reaction temperatures. The particle sizes ranged from 10 to 100 nm which increased with increasing laser intensity.

Transmission electron microscopy (TEM) microstructures and X-ray diffraction (XRD) patterns showed that the Si particles were not single crystalline. Rather they were polycrystalline with grain sizes of approximately 15 nm. The dense particle structure indicated that the particles were not formed by the agglomeration of individual small grains. Instead, the polycrystalline particles resulted from crystallization as they cooled from an amorphous state.

The particle size was controlled by the number of embryos which reached critical sizes and grew via vapor deposition. The narrow particle size distribution might have been caused by initially formed nuclei and fast growth. This means that there was little nucleation between the appearance of initial nuclei and final particles.

In Marra's studies, particle growth was not limited by
elapsed growth time but by the depletion of silane. This means that all the reactant was converted to Si(s) during the process.

2.3.2 (CH₃)₄Si(g)-H₂(g) System

Fine SiC powder has been prepared using a (CH₃)₄Si(g)-H₂(g) system in a tube furnace. The powder was spherical and the particle size was between 0.02 - 0.12 μm. The particle size decreased with an increase in reaction temperature, and with a decrease in (CH₃)₄Si(g) concentration. The XRD patterns indicated that all powders were amorphous SiC. It was explained by Kato that powders produced at 800°C consisted of organosilicon polymers with a structure similar to SiC. Therefore, it was concluded that the SiC powder formation was a result of organosilicon polymers forming above 700°C, then decomposing to SiC above 900°C, as shown by following equations:

\[
n(CH₃)_4Si(g) = (-Si-CH₂)_n(l or s) + CH₄(g) \quad (>700°C) \quad (2)
\]

\[
(-Si-CH₂)_n(l or s) = SiC(s) + CH₄(g) \quad (>900°C) \quad (3)
\]

Free silicon was not found in the above experiment.

In contrast, Avigal etc. proposed that the co-deposition of Si, C, and SiC occurred in the formation of chemical vapor deposition (CVD) from TMS vapor on a silicon substrate at temperatures between 960°C and 1290°C. The formation processes suggested were as follows:
\[(CH_3)_4Si(g) = Si(s) + 4CH_3(g) \quad (4)\]
\[4CH_3(g) = C(s) + 3CH_4(g) \quad (5)\]
\[Si(s) + C(s) = SiC(s) \quad (6)\]
\[(CH_3)_4Si(g) = SiC(s) + 3CH_4(g) \quad (7)\]
\[(CH_3)_4Si(g) + 2H_2(g) = Si(s) + 4CH_4(g) \quad (8)\]

In the absence of \(H_2(g)\), reactions (4), (5), (6), and (7) can occur. However, the presence of \(H_2(g)\) in the reaction system led to the preferential deposition of \(Si(s)\) due to equation (8).

S. K. Varshnery etc. synthesized \(SiC\) powder using a \((CH_3)_4Si(g)-Ar(g)\) system in a vertical tube furnace. Powder was analyzed by SEM and IR. Spherical powder with sizes from 0.1 to 4 \(\mu m\) was prepared. Powder synthesized at 800°C had both an IR absorption peak at 1260 cm\(^{-1}\), due to \(Si-CH_3\) bending, and a broad absorption band with a peak at 835 cm\(^{-1}\) due to the \(Si-C\) stretching. This was evidence that the pyrolysis of \((CH_3)_4Si(g)\) to \(SiC\) was incomplete at this temperature. The IR spectrum of powder prepared at 1100°C showed only a broad absorption peak with a maximum at 835 cm\(^{-1}\), due to \(Si-C\) stretching. In other words, the pyrolysis of \((CH_3)_4Si(g)\) to \(SiC\) was complete at this temperature.

2.3.3 \(SiH_4(g)-CH_4(g)\) System
The studies of SiC powder formation using a SiH₄(g)-CH₄(g) system have been investigated with a CO₂ laser³⁹ and a tube furnace³¹. SiC powder was not easily formed using CO₂ laser due to the fact that CH₄(g) does not absorb CO₂ laser light. Although beta-SiC powder was produced using SiH₄(g)-CH₄(g)-H₂(g) in a tube furnace, the reaction temperature had to be as high as 1400°C to obtain a high percentage SiC powder with respect to Si. The yield of powder was as low as 10 wt% - 39 wt%. Both hollow and solid powders were obtained depending on the heating rate of the reactants.

A two step process of powder formation using the SiH₄(g)-CH₄(g) system was given by Kato etc.¹,³¹ as shown below.

\[
\begin{align*}
\text{SiH}_4(g) & = \text{Si}(s) + 2\text{H}_2(g) \quad (T > 700^\circ C) \quad (9) \\
\text{Si}(s) + \text{CH}_4(g) & = \text{SiC}(s) + 2\text{H}_2(g) \quad (T > 1000^\circ C) \quad (10)
\end{align*}
\]

Hollow SiC powder was formed when the flow rate was small because the carburization of Si powder by CH₄(g) took place by the outward diffusion of Si through SiC layer formed. On the other hand, solid SiC powder was formed when the flow rate was large. The complex explanation given for this result was that rapid carburization of the Si particle induced cracks in the SiC layer, and caused the inward diffusion of CH₄(g).
Sawano used a laser to study SiC powder formation from SiH$_4$(g)-CH$_4$(g).$^{39}$ He also concluded that the SiC powder formation was a two step reaction process, in which the silicon powder was produced in the first step of the reaction. Then diffusion-controlled carburization produced hollow SiC powder.

2.3.4 SiH$_4$(g)-C$_2$H$_4$(g) System

When SiH$_4$(g)-C$_2$H$_4$-Ar(g) was heated by a laser, Suyama$^{23,24}$ successfully synthesized SiC powder along with various amounts of free Si or C depending on the reaction temperatures. The yield of SiC powder in this process was more than 90%. Particle sizes ranged between 19 to 49 nm and increased with increasing laser intensity (1100°C - 1750°C) and reactant concentration as expected in a nucleation and growth process. Boron-doped SiC powder with sizes less than 100 nm was also prepared using SiH$_4$(g)-C$_2$H$_4$(g)-B$_2$H$_6$(g)-Ar(g). Although fine and uniform beta-SiC powder was obtained, the formation mechanism was unclear. The synthesis process was given as the following reaction equations:

\[
2\text{SiH}_4(\text{g}) + \text{C}_2\text{H}_4(\text{g}) = 2\text{SiC}(\text{s}) + 6\text{H}_2(\text{g}) \tag{11}
\]

\[
\text{SiH}_4(\text{g}) = \text{Si}(\text{s}) + 2\text{H}_2(\text{g}) \tag{12}
\]

According to these equations, free carbon cannot be
obtained. Therefore, a questionable interpretation given was that the decomposition of SiC and the evaporation of Si at high temperature caused excess carbon to form.

A two step reaction of SiC powder formation using $\text{SiH}_4(\text{g}) - \text{C}_2\text{H}_4(\text{g})$ (laser) was given by Sawano.\textsuperscript{39} A significant amount of SiC powder was formed at a temperature as low as $1500^\circ \text{K}$. He explained that this was caused by the rapid pyrolysis of $\text{C}_2\text{H}_4(\text{g})$. However, the low diffusion coefficients of Si and C in SiC would make it improbable for the formation of SiC via two step reaction at $1500^\circ \text{K}$. 
CHAPTER III
MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 Introduction

The possible formation processes of SiC powder through VPR include the following:

\[
\text{Precursor} = \text{SiC}(g) = \text{SiC}(s) \quad (13)
\]

\[
\text{Precursor} = \text{Si}(s) + \text{Hydrocarbon}(g) = \text{SiC}(s) \quad (14)
\]

\[
\text{Precursor} = \text{Polymerization}(s) = \text{Decomposition}
\]

\[
= \text{SiC}(s) \quad (15)
\]

\[
\text{Precursor} = \text{Si}(s) + \text{C}(s) = \text{SiC}(s) \quad (16)
\]

In order to determine which one is the correct process, reaction systems were designed for this study, as given in Figure 1.

In this experiment, powders were synthesized as a function of temperature and concentration. Synthesized and heat treated powders were analyzed using X-ray diffraction (XRD), transmission electron microscopy (TEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and BET surface area analysis.

3.2 Powder Synthesis

3.2.1 Precursor Systems
Figure 1. Flow chart for synthesis of silicon and silicon carbide powders.
In order to reach a high degree of supersaturation for homogeneous nucleation and growth, the criterion for selecting all precursor systems was their large equilibrium constant.

* Silane (SiH₄(g))

Silane of semiconductor purity (Matheson Gas Co.) was used. Its boiling point is -86°C and it is an extremely flammable gas. The reaction of

\[ \text{SiH}_4(g) + 2\text{O}_2(g) = \text{SiO}_2(s) + 2\text{H}_2\text{O}(g) \] (17)

can cause a serious explosion at room temperature. Therefore, extreme caution must be used when working with silane.

Both the vapor pressure and the supersaturation ratio (SSR) of Si (see Appendix A for details) are shown in Figure 2 and Figure 3, according to the following assumed equilibrium reaction equations:

\[ \text{SiH}_4(g) = 2\text{H}_2(g) + \text{Si}(g) \]
\[ \text{Si}_{eq}(g) = \text{Si}(s) \]
\[ \text{SSR} = \frac{P_{Si}(g)}{P_{Si_{eq}}(g)} \] (20)

* Tetramethysilane (TMS, (CH₃)₄Si(g))

The TMS is NMR grade (Morton Thiokol. Inc.) with purity at least 99.9%. The boiling point is 26.5°C and the
Figure 2. Equilibrium partial pressure of silicon vapor over pure silicon and in the silane system.
Figure 3. Supersaturation ratio of silicon vapor in silane system.
specific gravity is 0.651 at 20°C. It is stable in air at room temperature. The decomposition temperature is approximately 700°C in an inert atmosphere.

Both the vapor pressure and the supersaturation ratio of SiC (see Appendix A for details) are shown in Figure 4 and Figure 5, according to the following assumed equilibrium reaction equations:

\[
(\text{CH}_3)_4\text{Si}(g) = 3\text{CH}_4(g) + \text{SiC}(g) \quad \Delta G^\circ_{\text{f21}} \quad (21)
\]

\[
\text{SiC}_{\text{eq}}(g) = \text{SiC}(s) \quad \Delta G^\circ_{\text{f22}} \quad (22)
\]

\[
\text{SSR} = \frac{p_{\text{SiC}}(g)}{p_{\text{SiC}}(g)} \quad (23)
\]

* Silane(SiH\textsubscript{4}(g))-ethane(C\textsubscript{2}H\textsubscript{6}(g))\textsuperscript{42}

The property of silane is the same as (a). The purity of C\textsubscript{2}H\textsubscript{6}(g) (Matheson Gas Co.) is at least 99.99%.

Both the vapor pressure and supersaturation ratio of beta-SiC (see Appendix A for details) are shown in Figure 6 and Figure 7, according to the following assumed equilibrium reaction equations:

\[
2\text{SiH}_4(g) + \text{C}_2\text{H}_6(g) = 7\text{H}_2(g) + 2\text{SiC}(g) \quad \Delta G^\circ_{\text{f24}} \quad (24)
\]

\[
\text{SiC}_{\text{eq}}(g) = \text{SiC}(s) \quad \Delta G^\circ_{\text{f25}} \quad (25)
\]

\[
\text{SSR} = \frac{p_{\text{SiC}}(g)}{p_{\text{SiC}}(g)} \quad (26)
\]

* Silane-ethylene (C\textsubscript{2}H\textsubscript{4}(g))\textsuperscript{41}
Figure 4. Equilibrium partial pressure of silicon carbide vapor over pure silicon carbide and in the TMS system.
Figure 5. Supersaturation ratio of silicon carbide vapor in TMS system.
Figure 6. Equilibrium partial pressure of silicon carbide vapor in pure silicon carbide and SiH$_4$-C$_2$H$_6$ systems.
Figure 7. Supersaturation ratio of silicon carbide in SiH$_4$-C$_2$H$_6$ system.
The purity of ethylene is at least 99.5% (Matheson Gas Co.). Both the vapor pressure and supersaturation ratio of beta-SiC (see Appendix A for details) are shown in Figure 8 and Figure 9, according to the following assumed equilibrium reaction equations:

\[ 2\text{SiH}_4(\text{g}) + \text{C}_2\text{H}_4(\text{g}) = 6\text{H}_2(\text{g}) + 2\text{SiC}(\text{g}) \quad \Delta G_f^{\circ} (27) \]

\[ \text{SiC}_{\text{eq}}(\text{g}) = \text{SiC}(\text{s}) \quad \Delta G_f^{\circ} (28) \]

\[ \text{SSR} = \frac{p_{\text{SiC}}(\text{g})}{p_{\text{SiC}_{\text{eq}}}(\text{g})} \quad (29) \]

3.2.2 Reactor System

The reactor system is illustrated in Fig-10. Two resistance furnaces were used as heat sources. One was a steep temperature gradient tube furnace (25°C/cm) with a narrow heating zone (10 cm, 1200°C max.). The other was a small temperature gradient tube furnace (1700°C) made by C&M Co. The gas tight reactor tube (ID=45 mm) was made of highly pure alumina (99.8%). The precursors were carried by prepurified Ar (O₂ < 10 ppm) and combined in the mixer which contained 4 mm glass beads. There was a by-pass design in the system to keep input concentrations of the precursors steady. The powders synthesized were collected at the end of the furnace tube and in a flask by natural sedimentation. The gas products were burned by a natural gas flame.

3.2.3 Parameters of Reaction
Figure 8. Equilibrium partial pressure of silicon carbide vapor in pure silicon carbide and SiH₄-C₂H₄ systems.
Figure 9. Supersaturation ratio of silicon carbide vapor in SiH$_4$-C$_2$H$_4$ system.
Figure 10. Schematic of experimental apparatus for synthesis of silicon and silicon carbide powders.
* Concentration

The gas precursor concentrations were controlled by the carrier gas flow rate. They ranged from $10^{-3}$ to $10^{-1}$ atm.

Since TMS is a liquid, the concentration of TMS was measured before the experiment. If it was assumed that the TMS vapor is an ideal gas, then the flow rate and concentration of TMS was calculated from the total liquid volume of TMS consumed in a given time:

$$f_{\text{TMS}} = \frac{\rho vRT}{tM} \quad (30)$$

- $\rho$: specific weight of TMS
- $v$: volume of TMS
- $R$: gas constant
- $T$: absolute temperature
- $t$: reaction time
- $M$: molecular weight of TMS

$$C_{\text{TMS}} = \frac{f_{\text{TMS}}}{f_{\text{Ar}} + f_{\text{TMS}}} \quad (31)$$

- $f_{\text{Ar}}$: flow rate of Ar

* Temperature

The reaction temperatures used ranged from 600°C to 1500°C, depending on the precursor systems.

1. $\text{SiH}_4(\text{g})$ system: 600 - 1100°C
2. TMS system: 800 – 1500°C
3. SiH₄(g)–C₂H₆(g) system: 700 – 1300°C
4. SiH₄(g)–C₂H₄(g) system: 700 – 1000°C

3.3 Heat Treatment

Post deposition treatment temperature ranged from 500°C to 1500°C, depending on the powder system.

3.4 Analysis

(1) Composition and grain size by line broadening (see Appendix B for calculation) were determined by X-ray (Philips XRG-3100) diffraction patterns (XRD). The Cu Kα line was used for X-ray diffraction. Since the composition was very important for explanation of the powder formation process, all the prepared powders were examined by X-ray diffraction.

(2) Specific surface area was measured by BET (Micromeritics In. Flow Sorb II 2300). Powder was dried at 150°C using 30% N₂–70% He flow gas for 30 min and then the powder specific surface area was determined by the absorption of 30% N₂–70% He at -196°C.

(3) Particle size was calculated from specific surface area of BET, based on the equation

\[ D = \frac{6w}{\rho s} \]  

\[ D : \text{particle size} \]
\[ w : \text{weight} \]
\( \rho: \) density

\( S: \) specific area

(4) The morphology and sizes of powders were investigated by scanning transmission electron microscopy (STEM, JEOL-200CX). The image observation and electron diffraction pattern were done at an acceleration voltage of 200 KV. Powder was dispersed by ultrasonic agitation in isopropyl alcohol for 5 min. Then a 200 mesh copper grid with carbon film coating was dipped into the solution to obtain a sample for TEM analysis. The TEM micrographs were enlarged to 8" by 10" and a Zeiss Videoplan was used to measure the particle size. Approximately 130 to 500 particles were measured for each sample. The mean particle size, and standard deviation were printed. The powder microstructures provided significant evidence about powder formation mechanism, if the powder sizes were between 100 - 300 nm.

(5) The carbon content was measured by TGA (Perkin Elmer) in air, heated at a rate of 20 °C/min. from room temperature to 800°C. The oxidation of pure carbon began at 450°C and ended at 650°C, as shown in Figure 11. Therefore, the presence of free carbon could be determined by TGA. But the amount present could not be quantitatively
Figure 11. Thermogravimetric analysis of pure carbon in air.
evaluated.

(6) Crystallization temperatures and other thermal effects were determined using DTA (Perking Elmer) in N₂ with a heating rate of 20°C/min.

(7) The nucleation rate was calculated from the total weight of powder prepared in a given time and the particle size:

\[ n = \frac{6W}{\pi \rho D^3 t} \quad (33) \]

- \( D \): particle size
- \( W \): total weight
- \( \rho \): density
- \( t \): time
4.1 \( \text{SiH}_4(g) \) System

Si powder was synthesized by decomposition, nucleation, and growth according to the following equations:

\[
\text{SiH}_4(g) = \text{Si}(g) + 2\text{H}_2(g) = \text{Si}(s) + 2\text{H}_2(g) \quad (34)
\]

Generally, silicon powders prepared using VPR were red-brown to yellow-brown depending on reaction temperatures. The yield of the powder increased with increasing temperature between 600\(^\circ\)C and 700\(^\circ\)C. Beyond 700\(^\circ\)C, they became nearly constant at approximately 75\%, as shown in Figure 12. In the following, data are presented as functions of reaction temperatures and silane concentrations to interpret the powder formation mechanism.

4.1.1 Physical Properties

* \( P_{\text{SiH}_4(g)} = 7.5 \times 10^{-2} \text{ atm} \)

The transmission electron micrographs and diffraction patterns of Si powders are shown in Figures 13-18. The particles were nearly spherical at reaction temperatures below 800\(^\circ\)C and became a chained structure above 900\(^\circ\)C.
Figure 12. The yields of silicon powder in silane system under various concentrations.
Figure 13. TEM micrograph and electron diffraction pattern of Si powder synthesized at 600°C under $P_{\text{silane}} = 7.5 \times 10^{-2}$ atm.
Figure 14. TEM micrograph and electron diffraction pattern of Si powder synthesized at 700°C under $P_{\text{silane}}=7.5\times10^{-2}$ atm.
Figure 15. TEM micrograph and electron diffraction pattern of Si powder synthesized at 800°C under $P_{\text{silane}}=7.5 \times 10^{-2}$ atm.
Figure 16. TEM micrograph and electron diffraction pattern of Si powder synthesized at 900°C under $P_{\text{silane}} = 7.5 \times 10^{-2}$ atm.
Figure 17. TEM micrograph and electron diffraction pattern of Si powder synthesized at 1000°C under $P_{\text{silane}}=7.5\times10^{-2}$ atm.
Figure 18. TEM micrograph and electron diffraction pattern of Si powder synthesized at 1100°C under $P_{\text{silane}}=7.5 \times 10^{-2}$ atm.
The electron diffraction patterns show that the powder was amorphous when prepared below 700°C and crystalline above 800°C. Obviously, the particle sizes decreased with increasing reaction temperatures between 600°C and 800°C, then increased with increasing reaction temperatures above 800°C.

The specific surface areas measured by BET vary slightly with temperature, increasing with increasing reaction temperatures from 600°C to 800°C, and decreasing with increasing temperatures between 800°C and 1100°C, as shown in Figure 19. The particle sizes calculated from the specific surface areas are shown in Figure 20. The BET measured particle sizes versus reaction temperatures agree with the results obtained by TEM.

The XRD patterns shown in Figure 21, also confirmed that powders were amorphous below 700°C and crystalline above 800°C. The grain sizes (assuming amorphous Si was microcrystalline) calculated from X-ray line broadening increased very little with increasing reaction temperature from 600°C to 700°C. However, there was a jump between 700°C and 800°C; beyond 800°C, grain sizes increased with increasing reaction temperature, as shown in Figure 20.

The nucleation rates were dependent on reaction temperatures, as shown in Figure 20. At temperatures below
Figure 19. BET surface area of silicon powder prepared under various concentrations.
Figure 20. The particle size, nucleation rate, and grain size of silicon powder prepared at various temperatures under $P_{\text{silane}}=7.5\times10^{-2}$ atm.
Figure 21. The comparison of X-ray diffraction patterns of silicon powder prepared at various temperatures.
800°C, the nucleation rate increased with increasing reaction temperature, then decreased with increasing reaction temperature above 800°C.

* $P_{SiH_4(g)} = 2.3 \times 10^{-2}$ atm

Generally, the characteristics of Si powders were the same when the silane concentration was decreased from $7.5 \times 10^{-2}$ atm to $2.3 \times 10^{-2}$ atm. The TEM micrographs are shown in Figures 22-26. Also, the particle size decreased with increasing reaction temperature between 600°C - 730°C. The surface areas increased with increasing reaction temperature below 730°C and decreased with increasing temperature above 730°C, as shown in Figure 19. The particle sizes, grain sizes, and nucleation rates versus reaction temperatures curves are given in Figure 27. Obviously, the particle size was dependent on the nucleation rate, and both of them were a function of the reaction temperature.

* $P_{SiH_4(g)} = 3.3 \times 10^{-3}$ atm

The TEM images shown in Figures 28-32, indicate that the powders were uniform and fine. The BET surface area decreased with increasing reaction temperature, as shown in Figure 14. The particle sizes, grain sizes, and nucleation rate versus reaction temperature curves are shown in Figure
Figure 22. TEM micrograph and electron diffraction pattern of silicon powder synthesized at 600°C under $P_{\text{silane}}=2.3\times10^{-2}$ atm.
Figure 23. TEM micrograph and electron diffraction pattern of silicon powder synthesized at 730°C under $P_{\text{silane}}=2.3\times10^{-2}$ atm.
Figure 24. TEM micrograph and electron diffraction pattern of silicon powder synthesized at 800°C under $P_{\text{silane}} = 2.3 \times 10^{-2}$ atm.
Figure 25. TEM micrograph and electron diffraction pattern of silicon powder synthesized at 900°C under $P_{\text{silane}}=2.3 \times 10^{-2}$ atm.
Figure 26. TEM micrograph and electron diffraction pattern of silicon powder synthesized at 1000°C under $P_{\text{silane}}=2.3 \times 10^{-2}$ atm.
Figure 27. The particle size, nucleation rate, and grain size of silicon powder prepared at various temperatures under $P_{\text{silane}}=2.3\times10^{-2}\text{ atm}$.
Figure 28. TEM micrograph of silicon powder synthesized at 600°C under $P_{\text{silane}} = 3.3 \times 10^{-3}$ atm.
Figure 29. TEM micrograph of silicon powder synthesized at 700°C under $P_{\text{silane}}=3.3\times10^{-3}$ atm.
Figure 30. TEM micrograph of silicon powder synthesized at 800°C under $P_{\text{silane}}=3.3\times10^{-3}$ atm.
Figure 31. TEM micrograph of silicon powder synthesized at 900°C under $P_{\text{silane}}=3.3\times10^{-3}$ atm.
Figure 32. TEM micrograph of silicon powder synthesized at 1000°C under $P_{\text{silane}} = 3.3 \times 10^{-3}$ atm.
Similarly, the profile of the nucleation rate versus reaction temperature was bell-shaped. The particle size distribution versus reaction temperature, however, was not U-shaped as were previous profiles.

4.1.2 Crystalline Properties

The degree of crystallization was strongly dependent on temperature and concentration. Powders prepared above 800°C were crystalline. The grain size increased with increasing reaction temperature, as shown in Figures 20, 27, and 33. When the reaction temperatures were at or below 700°C, powders were amorphous, and could transform to a crystalline phase by heating above 600°C. The crystallization temperatures of amorphous Si were between 650°C - 750°C depending on the preparation conditions. The typical DTA curves with an exothermic peak are given in Figures 34-35. The crystallization temperature decreased with increasing reaction temperature and concentration, as shown in Figure 36. Also, the crystallization temperature decreased with increasing heat treatment time at 600°C, as shown in Figure 37.

4.2 C₂H₆(g) System

Carbon powders could not be obtained below 900°C from C₂H₆(g) with a concentration of 3X10⁻² atm. However, there were some oil-like materials in the cool end of the
Figure 33. The particle size, nucleation rate, and grain size of silicon powder prepared at various temperatures under $P_{\text{silane}}=3.3\times10^{-3}$ atm.
Figure 34. DTA heating curve of amorphous silicon powder prepared at 600°C.
Figure 35. DTA heating curve of amorphous silicon powder prepared at 700°C.
Figure 36. The crystallization temperature of amorphous silicon powder prepared under various concentrations.
Figure 37. The crystallization temperature of amorphous silicon powder annealed at 600°C for different heat treatment times.
furnace. When ethane was decomposed above 1000°C, spherical and nearly monosized (200 nm) carbon powders could be obtained as shown in Figures 38-40.

4.3 TMS System

Ultrafine SiC powders of narrow particle distribution could be produced using TMS with the carrier gas, Ar, in a steep temperature gradient tube furnace. The powder morphologies are shown in Figures 41-45 and Figures 46-49. The particles were nearly spherical. The particle sizes ranged from 10 nm to 200 nm, measured by Videoplan. The typical particle size distribution obtained from the Videoplan is shown in Figure 50. The others are given in Appendix C. The particle sizes decreased with increasing reaction temperature from 850°C to 1100°C, and increased with increasing TMS concentration, as shown in Figure 51. The XRD patterns show that all powders were amorphous SiC which could be heat treated, becoming crystalline at temperatures above 1100°C, as shown in Figure 52. The DTA analysis also indicated that the crystallization temperature of amorphous SiC was approximately 1100°C with heating rate 20°C/min., as shown in Figure 53.

The purpose of this research is to understand SiC powder formation mechanism using the VPR process. However,
Figure 38. TEM micrograph of carbon powder synthesized at 1000°C under $P_{\text{ethane}}=3 \times 10^{-2}$ atm.
Figure 39. TEM micrograph of carbon powder synthesized at 1100°C under $P_{\text{ethane}}=3\times10^{-2}$ atm.
Figure 40. TEM micrograph of carbon powder synthesized at 1200°C under $P_{\text{ethane}} = 3 \times 10^{-2}$ atm.
Figure 41. TEM micrograph of SiC powder synthesized at 850°C under $F_{TMS} = 2.5 \times 10^{-2}$ atm.
Figure 42: TEM micrograph of SiC powder synthesized at 900°C under $P_{\text{TMS}}=2.5\times10^{-2}$ atm.
Figure 43. TEM micrograph of SiC powder synthesized at 1000°C under $P_{\text{TMS}} = 2.5 \times 10^{-2}$ atm.
Figure 44. TEM micrograph of SiC powder synthesized at 1100°C under $P_{TMS}=2.5 \times 10^{-2}\ \text{atm.}$
Figure 45. TEM micrograph of SiC powder synthesized at 1200°C under $P_{\text{TMS}}=2.5\times10^{-2}$ atm.
Figure 46. TEM micrograph of SiC powder synthesized at 850°C under $P_{\text{TMS}}=5.0\times10^{-3}$ atm.
Figure 47. TEM micrograph of SiC powder synthesized at 900°C under $P_{\text{TMS}}=5.0\times10^{-3}$ atm.
Figure 48. TEM micrograph of SiC powder synthesized at 1000°C under $P_{TMS}=5.0 \times 10^{-3}$ atm.
Figure 49. TEM micrograph of SiC powder synthesized at 1100°C under $P_{\text{TMS}}=5.0\times10^{-3}$ atm.
Figure 50. The particle size distribution of SiC powder synthesized at 1000°C under $P_{\text{TMS}}=5.0\times10^{-3}$ atm.
Figure 51. The average particle size of SiC powder prepared at various temperatures.
Figure 52. The comparison of X-ray diffraction patterns of SiC powder before and after heat treatment.
Figure 53. DTA heating curve of SiC powder prepared at 1000°C under $P_{TMS}=1.8 \times 10^{-1}$ atm.
the above mentioned powders were too small to analyze. Improved powders, therefore, were prepared in a low temperature gradient furnace to amplify factors of powder formation, allowing for greater accuracy in determining the mechanism of powder formation.

The XRD patterns of as prepared powders from TMS with a concentration of $1.8 \times 10^{-1}$ atm and a flow rate of 1000 CC/min. between 850°C to 1500°C, are shown in Figure 54. The dwell time of the gas was approximately 4 seconds in the hot zone. These patterns give evidence that SiC powders were obtained at temperatures above 850°C. At temperatures below 1100°C, the powders were amorphous; above 1300°C, crystalline SiC powders were formed. The carbon peaks (0002) appeared at temperatures above 1100°C and the intensity increased with increasing reaction temperature.

The TEM images of those powders are shown in Figures 55-59. These powders have a "core-shell" structure at reaction temperatures of 850°C, 1100°C, 1300°C, and 1500°C. At these temperatures, according to XRD patterns, the particle cores were beta-SiC. At 1300°C and 1500°C, due to the existence of extra carbon peaks, the shells of powders are probably carbon. In contrast, at 850°C, the shells were organosilicon polymers, since no extra peaks were
Figure 54. The comparison of X-ray diffraction patterns of as-prepared SiC powder at various temperatures.
Figure 55. TEM micrograph of SiC powder prepared at 850°C under $P_{\text{TMS}}=1.8 \times 10^{-1} \text{ atm.}$
Figure 56. TEM micrograph of SiC powder prepared at 1000°C under $P_{\text{TMS}}=1.8\times10^{-1}$ atm.
Figure 57. TEM micrograph of SiC powder prepared at 1100°C under $P_{TMS} = 1.8 \times 10^{-1}$ atm.
Figure 58. TEM micrograph of SiC powder prepared at 1300°C under $P_{TMS}=1.8 \times 10^{-1}$ atm.
Figure 59. TEM micrograph of SiC powder prepared at 1500°C under $P_{\text{TMS}}=1.8\times10^{-1}$ atm.
shown in XRD patterns.

The variation of weight percent during TGA tests in air are shown in Figure 60. The powders prepared at 850°C had significant weight gain at temperatures below 500°C. This indicates that the shell of 850°C powder was not carbon. However, powders prepared at 1100°C, 1300°C, and 1500°C had no weight gain below 500°C. Instead, there was significant weight loss beyond 500°C which corresponds to the temperature of carbon oxidation. The free carbon contents based on TGA weight loss increased with increasing reaction temperature, as shown in Figure 61. The TEM microstructure of 1300°C powder after TGA test is shown in Figure 62. The shell had been eliminated from the powder. Also, the carbon peak in the XRD pattern of TGA tested powder could not be found, as shown in Figure 63. This information strongly reconfirms that the shell materials of 1300°C and 1500°C powders were carbon.

The TEM image of powders prepared at 1300°C and heat treated at 1400°C in an Ar atmosphere is shown in Figure 64. The shells were amorphous carbon and the cores were crystalline beta-SiC. The carbon peak of XRD pattern still existed, as shown in Figure 63. On the other hand, the microstructure of powders formed at 850°C and heat treated
Figure 60. The comparison of TGA curves for pure C and SiC powder synthesized at different temperatures.
Figure 61. The free carbon content in SiC powder prepared at various temperatures under $P_{TMS}=1.8 \times 10^{-1}$ atm.
Figure 62. TEM micrographs of SiC powder, (a) as-prepared at 1300°C and (b) after TGA heating up to 800°C.
Figure 63. The comparison of X-ray diffraction patterns of SiC powder under different conditions.
Figure 64: TEM micrograph of SiC powder synthesized at 1300°C and then heat treated at 1400°C.
at 1400°C in Ar did not show the core and shell structures, as shown in Figure 65. There were uniform beta-SiC crystalline powders because the shell of the organosilicon polymers decomposed, becoming beta-SiC, the same as the beta-SiC of the core structure.

4.4 Si(A)-C(A) System

Amorphous Si powders prepared from SiH$_4$(g) and amorphous C powders prepared from C$_2$H$_6$(g), were mixed in a 1:1 molar ratio. Then they were heat treated from 800°C to 1300°C in an Ar atmosphere for 1 hr. The XRD Patterns of the reacted powders are shown in Figure 66. The amorphous Si became highly crystalline above 800°C, and SiC did not appear at temperatures below 1200°C.

4.5 Si(A)-C$_2$H$_6$(g) System

Shown in Figure 67 are the carburization results of amorphous Si (made at 700°C) with C$_2$H$_6$(g) at 800°C and 1100°C for 1 hour in an Ar atmosphere. Neither carbon nor silicon carbide could be obtained at 800°C. At 1100°C, large amounts of crystalline silicon and amorphous carbon were formed, along with small amounts of beta-SiC.

4.6 SiH$_4$(g)-C$_2$H$_6$(g) System

The results of synthesized powders using SiH$_4$(g)-C$_2$H$_6$(g) with 1:1 ratio between 700°C and 1200°C in an Ar atmosphere are shown in Table 1. These powders were
Figure 65. TEM micrograph of SiC powder synthesized at 850°C and then heat treated at 1400°C.
Figure 66. The X-ray diffraction patterns of the products from the reaction of Si and C at different temperatures.
Figure 67. The X-ray diffraction patterns of the products from the reaction of Si and C$_2$H$_6$ at different temperatures.
amorphous, and the particle sizes were determined to be approximately 20 nm by TEM analysis, as shown in Figures 68-73. The yields of powders increased with increasing reaction temperature.

Table 1. Results of synthesized powders in SiH₄-C₂H₆-Ar system.**

<table>
<thead>
<tr>
<th>SiH₄:C₂H₆:Ar (cc/m)</th>
<th>Temp. (°C)</th>
<th>Products</th>
<th>Particle size (nm)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700</td>
<td>Si(A) Si(A)</td>
<td></td>
<td>42.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>?(A) ?(A)</td>
<td>20</td>
<td>68.0</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>?(A) ?(A)</td>
<td>20</td>
<td>82.6</td>
</tr>
<tr>
<td>15:15:970</td>
<td>1000</td>
<td>?(A) ?(A)</td>
<td>20</td>
<td>85.3</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>SiC(A) SiC(A)</td>
<td>20</td>
<td>90.2</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>SiC(A) SiC(A)</td>
<td>20</td>
<td>94.5</td>
</tr>
</tbody>
</table>

** Notes: A stands for amorphous. Yield was based on Si source.

Figure 174 shows the XRD patterns of as prepared powders. The SiC powders could be formed at temperatures above 1100°C. At reaction temperatures between 800°C and 1000°C, amorphous powders were obtained. The 2θ peaks
Figure 68. TEM micrograph and electron diffraction pattern of Si powder synthesized at 700°C under $P_{\text{silane}} = P_{\text{ethane}} = 1.5 \times 10^{-2}$ atm.
Figure 69. TEM micrograph and electron diffraction pattern of Si$_x$C$_y$ powder synthesized at 800°C under $P_{\text{silane}}=P_{\text{ethane}}=1.5\times10^{-2}$ atm.
Figure 70. TEM micrograph and electron diffraction pattern of Si_xC_y powder synthesized at 900°C under P_{silane}=P_{ethane}=1.5\times10^{-2} atm.
Figure 71. TEM micrograph and electron diffraction pattern of Si$_x$C$_y$ powder synthesized at 1000°C under $P_{\text{silane}}$=$P_{\text{ethane}}$=$1.5\times10^{-2}$ atm.
Figure 72. TEM micrograph and electron diffraction pattern of SiC powder synthesized at 1100°C under $P_{\text{silane}} = P_{\text{ethane}} = 1.5 \times 10^{-2}$ atm.
Figure 73. TEM micrograph and electron diffraction pattern of SiC powder synthesized at 1200°C under $P_{\text{silane}}=P_{\text{ethane}}=1.5 \times 10^{-2}$ atm.
Figure 74. The comparison XRD patterns of powder prepared at various temperatures in SiH₄-C₂H₆ system.
fell between 28.7° (Si(111)) and 35.8° (SiC(111)), with peaks shifting toward beta-SiC phase as the reaction temperature increases. At temperatures below 700°C, only amorphous Si could be obtained.

The SiC powders made above 1100°C, could be crystallized without excess free silicon by heat treatment above 1300°C as shown in Figure 75. However, the products synthesized between 800°C and 1000°C, could be heat treated (T>900°C), becoming Si and SiC, as shown in Figures 76. The 700°C prepared powders crystallized easily at 800°C for 1 hr. in Ar.

Figures 77-79 shows the DTA data of 20°C/m heating. The peak of 700°C powders appeared at 710°C which is close to the transition temperature of pure Si from amorphous to crystalline. However, the powders made above 800°C, had a crystallization temperature at approximately 960°C. There was no crystallization temperature of the 1200°C powders.

The powders prepared at temperatures above 1000°C contained free carbon based on TGA weight loss, which increased with increasing reaction temperature, as shown in Figure 80. The TEM image of powder prepared at 1300°C indicates carbon shell, as shown in Figure 81.

Figure 82 shows the XRD pattern of SiH₄(g):C₂H₆(g) with 2:1 ratio at temperature 1100°C. Excess Si was
As-prepared 1100°C
Heat Treated 1300°C

Figure 75. The XRD pattern of SiC powder prepared at 1100°C and then heat treated at 1300°C.
Figure 76. The comparison of XRD pattern of powder as-prepared at 900°C and heat treated.
Figure 77. DTA heating curve of powder prepared at 700°C in SiH₄-C₂H₆ system.
Figure 78. DTA heating curve of powder prepared at 900°C in SiH₄-C₂H₆ system.
Figure 79. DTA heating curve of powder prepared at 1200°C in SiH₄-C₂H₆ system.
Figure 80. The free carbon content of SiC powder prepared at different temperatures in SiH₄-C₂H₆ system.
Figure 81. TEM micrograph of SiC powder prepared at 1300°C in SiH$_4$-C$_2$H$_6$ system.
Figure 82. The XRD patterns of powders prepared at 1100°C under SiH₄:C₂H₆ = 2:1.
observed. In contrast, pure SiC was obtained at 1100°C for a 1:1 ratio.

4.7 SiH₄(g)-C₂H₄(g) System

The results of powder synthesis using the SiH₄(g)-C₂H₄(g) system were quite similar to those of SiH₄(g)-C₂H₆(g) system.

Figure 83 shows the XRD patterns of as-prepared powders using SiH₄(g)-C₂H₄(g) with 1:1 ratio. Crystalline SiC powder could not be obtained at temperatures below 1000°C. However, amorphous powders could be obtained. The 2θ peaks of powders fell between 28.7° (Si(111)) and 35.8° (beta-SiC(111)) with peaks shifting towards beta-SiC(111) as the reaction temperature increases. These powders can be heat treated, becoming Si and SiC, as shown in Figure 84.

The DTA curves are shown in Figures 85-87. The crystallization temperatures were approximately 960°C.
Figure 83. The comparison of XRD patterns of powder prepared at different temperatures in $\text{SiH}_4-\text{C}_2\text{H}_4$ system.
Figure 84. The comparison of XRD patterns of powder as-prepared at 700°C and heat treated at 1100°C in SiH₄-C₂H₄ system.
Figure 85. DTA heating curve of powder prepared at 800°C in SiH₄-C₂H₄ system.
Figure 86. DTA heating curve of powder prepared at 900°C in SiH$_4$-C$_2$H$_4$ system.
Figure 87. DTA heating curve of powder prepared at 1000°C in SiH$_4$-C$_2$H$_4$ system.
CHAPTER V
DISCUSSION

5.1 General Discussion of Vapor Phase Reaction of Powder Formation

The purpose of this research was to evaluate a flowing gas system for the preparation of nonoxide ceramic powders. The formation of both Si and SiC powders was investigated. In both cases, the powder formation mechanism appears to be that of homogeneous nucleation in the gas phase followed by particle growth. Due to the fact that gas concentrations are changing in the reactor because of the reaction, there is a strong interaction between nucleation rates, growth rates, and the overall composition and morphology of the resultant powder particles. No attempt was made to control agglomeration of the powders. In all cases, significant agglomeration occurred with necks formed between many of the particles. These necks doubtlessly resulted from the continued deposition of SiC or Si in the hot zone of the furnace rather than by sintering of touching particles.

5.2 Preparation of Silicon Powder by Decomposing SiH$_4$
5.2.1 Nucleation Rates

Once particles exceed a critical nucleus size\textsuperscript{44,45}, \( r_c \), given by:

\[ r_c = \frac{2\sigma}{\rho R T \ln S} \] \hspace{1cm} (35)

where \( \sigma \) = surface energy,
\( \rho \) = density,
\( S \) = supersaturation,
\( R \) = gas constant,
\( T \) = absolute temperature

the particles are stable and can grow. The rate of nucleation is given by\textsuperscript{46}:

\[ n = A \exp\left(-\frac{B}{T^3 \ln^2 S}\right) \] \hspace{1cm} (36)

where \( n \) = nucleation rate
\( A, B \) = constants.

In these experiments, the nucleation rate was determined from the number of nuclei, \( N \), in a given weight of powder product, \( W \), and the particle diameter, \( d \), from:

\[ N = \frac{6W}{\pi \rho d^3} \] \hspace{1cm} (37)

Knowing the flow rate and length of the furnace hot zone, the nucleation rates plotted in Figures 20, 27, and 33, were calculated.

The nucleation rate shows a strong temperature dependence, low at low temperatures, increasing to a maximum, and then decreasing again. At elevated temperatures, the decrease in the nucleation rate is simply due to the decrease in the supersaturation. Below about
800°C, the nucleation rate decreases with temperature. This is clearly related to the kinetics of decomposition of silane to form silicon. Whether the silane decomposes to silicon and hydrogen gases or whether the decomposition occurs on the silicon particles is not known nor is it important in this analysis. It only matters that the decomposition of silane is temperature dependent and the nucleation rate decreases as the temperature decreases.

5.2.2 Particle Sizes

In contrast to the nucleation rates, the particle size (which is equivalent to the particle growth rate) decreased from a large value at low temperatures, reached a minimum at about the maximum in the nucleation rate, and then increased again as the temperature increased and the nucleation rate fell. Clearly, the particle size and the nucleation rate are inversely related. This is not too surprising. As Figure 12 shows, most of the silane that will react thermodynamically does so when the temperature is above 700°C. Therefore, when the nucleation rate is low, the depletion of the gas concentration is low and there is ample material in the gas phase for the particles to grow large before the equilibrium gas concentration is reached. Conversely, when the nucleation rate is high, the
amount of silane left in the gas to produce particle growth is low and the particle size is small. This all occurs as the gas and the growing particles are flowing through the reactor.

The fact that the particle size is larger than the grain size suggests that the silane decomposition occurs on pre-existing nuclei for further particle growth. Further nucleation occurs on the pre-existing nuclei for particle growth rather than agglomeration of individual particles. However, as evidenced in the photomicrographs of Figures 13 and 22, there is considerable particle agglomeration as well. Nevertheless, the particle size increased as the concentration of silane increased while the nucleation rate essentially did not. This is not too surprising, since the supersaturation rate for nucleation is so high that it was essentially independent of gas concentration. As a result, as the reactant gas concentration increased, the amount of reactant available for particle growth increased leading to a larger particle size. It should be noted that the particle size distribution is not too different than that obtained using a laser heat source\textsuperscript{19,20}.

The degree of crystallinity of the as-prepared powder also depended strongly on the preparation temperature. As the temperature increased, so did the crystallite size. At
low temperatures, the silicon powders produced were essentially amorphous. However, during subsequent heat treatment, crystallization occurred at temperatures between 650 and 750°C. This is very close to the temperature at which a transition from amorphous to crystalline is observed in the as-prepared powders as well. Therefore, from these results it is difficult to determine whether the as-prepared powders were first amorphous and then crystallized or whether the deposition temperature was high enough to produce crystalline powders directly.

5.3 Preparation of SiC Powders from Tetramethylsilane, $(\text{CH}_3)_4\text{Si}$

5.3.1 Formation of the "Core-shell" Structure

There are two possible formation mechanisms of SiC powders using tetramethylsilane. The first of these is the formation of polymerized particles which then decompose into SiC. The second is the direct nucleation and growth of SiC powders from the vapor phase. Kato, et al.\textsuperscript{30} found organosilicon polymers using $(\text{CH}_3)_4\text{Si}$ below 900°C. In these experiments, x-ray diffraction data indicated the coexistence of amorphous SiC with the organosilicon polymers. Kato explained that the organosilicon polymer structure was similar to that of amorphous SiC. Therefore,
he concluded that the powder formation mechanism was the formation of a solid polymer precursor below 900°C which decomposed above 900°C. Such a mechanism would lead to a homogeneous microstructure in powders prepared below 900°C. However, results of this study clearly show that when particles prepared under similar conditions were sufficiently large for microstructural examination (100nm-300nm), they were clearly inhomogeneous. Particles consisted of a core of amorphous silicon carbide with a shell of organosilicon compounds at low temperatures. At high temperatures, the SiC core was surrounded by a carbon shell. The x-ray diffraction and weight loss data clearly indicate this.

Silicon carbide powder prepared at 1000°C showed no core-shell structure. However, powders prepared at lower temperature clearly showed the presence of an organosilicon shell which could be heat-treated to form pure silicon carbide. At temperatures of 1300°C and 1500°C, however, a shell of carbon was clearly present as shown by x-ray diffraction (Figure 54) and thermogravimetric weight loss measurements (Figure 60).

The presence of the core-shell structure can be explained as follows. The core, which is SiC, forms in the
main hot zone due to nucleation and growth from \((\text{CH}_3)\text{Si}_4\). Since the dwell time of gas is as short as 4 seconds in the hot zone, at reaction temperatures below 1000°, unreacted \((\text{CH}_3)\text{Si}_4\) partially decomposes on the SiC particles in the cooler exit zone of the furnace. At about 1000°C, most of the \((\text{CH}_3)\text{Si}_4\) is reacted to form SiC and \(\text{CH}_4\). Above 1000°C, the \(\text{CH}_4\) produced by the decomposition of \((\text{CH}_3)\text{Si}_4\) in the hotter regions of the furnace, decomposes to form carbon on the surface of SiC in the cooler exit zone of the furnace. The reactions are:

\[
(\text{CH}_3)\text{Si}_4(\text{g}) = \text{SiC}(\text{s}) + 3\text{CH}_4(\text{g}) \quad (38)
\]

and

\[
\text{CH}_4(\text{g}) = \text{C}(\text{s}) + 2\text{H}_2(\text{g}). \quad (39)
\]

As the reaction temperatures increased, the amount of carbon in the shell increased. Theoretically, if all of the methane decomposes to free carbon, the SiC-C particles should contain about 47 percent free carbon. At 1500°C, the particles contained about 39 percent free carbon which is very close to complete decomposition of the methane produced.

In addition, powders prepared at 850°C with an organosilicon shell could be heat treated to decompose the shell to SiC at temperatures as low as 800°C as shown in Figure 88. This lends support to the hypothesis that the
Figure 88. TEM micrograph of SiC powder prepared at 850°C and then heat treated at 800°C in Ar.
organosilicon shell was produced in the cool exit zone of the furnace. All the evidence suggests that the SiC does not form by condensation and crystallization of an organosilicon polymer but rather by direct formation of SiC.

5.3.2 Absence of Free Silicon

Avigal, et al. showed that codeposition of Si, C, and SiC occurred during chemical vapor deposition, CVD, from (CH₃)₄Si in helium on silicon below 1200°C. They suggested the following reaction sequence:

\[
\begin{align*}
(CH₃)₄Si(g) &= Si(s) + 4 \cdot CH₃(g) \\
4 \cdot CH₃(g) &= C(s) + 3 \cdot CH₄(g) \\
Si(s) + C(s) &= SiC(s)
\end{align*}
\]

where \( \cdot CH₃ \) is a free radical.

No free silicon in the presence of free carbon was found in these experiments by x-ray diffraction. If there were free silicon, as shown by the decomposition of silane to silicon, it should be crystalline at temperatures above 800°C and easily detected by x-ray diffraction. In the present experiments, only beta-SiC was found in the x-ray patterns. It seems highly unlikely that SiC could form by reaction of deposited carbon and silicon at these temperatures due to the low diffusion coefficients in the
SiC system. The experiments performed in this study showed that carbon and silicon did not react below 1200°C to form SiC.

Therefore, it is concluded that SiC carbide powders were formed directly by a nucleation and growth process from the decomposition of (CH₃)₄Si in Ar.

5.4 Preparation of SiC by Reaction of SiH₄(g) and C₂H₆(g)

Powder formation in this system is summarized in Table 2. Silicon powder formed from pure SiH₄(g) at temperatures below 800°C were amorphous and crystalline above 800°C. Carbon powders could not be obtained by decomposing C₂H₆(g) alone until temperatures above 1000°C were reached. Nevertheless, carbon was found in the powders produced by reacting SiH₄(g) and C₂H₆(g) at temperatures as low as 800°C. These powders were amorphous. In addition, it was shown in Figure 40, that reaction of previously prepared amorphous silicon powder with C₂H₆(g) did not occur until temperatures exceeded 1100°C. Therefore, the evidence suggests that the SiC powders produced in this reaction formed homogeneously by gas phase nucleation and growth by reaction of SiH₄(g) and C₂H₆(g) rather than by the formation of either silicon or carbon first and then subsequent further reaction with the gas phase.
Table 2. Summary of powder formation ($\text{SiH}_4:\text{C}_2\text{H}_6 = 1:1$).

<table>
<thead>
<tr>
<th>$T$(°C)</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>SiH$_4$</td>
<td>Si(A)</td>
<td>Si(A)</td>
<td>Si(K)</td>
<td>Si(K)</td>
<td>Si(K)</td>
<td>Si(K)</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_6$</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>C(A)</td>
<td>C(A)</td>
</tr>
<tr>
<td>SiH$_4$ + C$_2$H$_6$</td>
<td>-</td>
<td>Si(A)</td>
<td>$\text{Si}_x\text{C}_y$(A)</td>
<td>$\text{Si}_x\text{C}_y$(A)</td>
<td>$\text{Si}_x\text{C}_y$(A)</td>
<td>SiC(A)</td>
<td>SiC(K)</td>
</tr>
<tr>
<td>Si(A) + C$_2$H$_6$</td>
<td>-</td>
<td>-</td>
<td>Si(K)</td>
<td>-</td>
<td>-</td>
<td>Si(K)</td>
<td>+C</td>
</tr>
<tr>
<td>Si(A) + C(A)</td>
<td>-</td>
<td>-</td>
<td>Si(K)</td>
<td>Si(K)</td>
<td>Si(K)</td>
<td>Si(K)</td>
<td>+C</td>
</tr>
<tr>
<td>A: amorphous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K: crystalline</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*: the amount of SiC is very small</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Below 1000°C, powders formed by reaction of SiH₄(g) and C₂H₆(g) are amorphous as shown in Figure 74. However, as this figure shows, there is a single broad peak falling between the Si and SiC peaks shifting toward SiC with increasing reaction temperature. Two possibilities exist. The first is that there exists an intimate two-phase mixture of amorphous silicon and silicon carbide whose peaks overlap to produce the single x-ray peak. The fact that the silicon content increases as the temperature decreases is consistent with the fact that silane decomposition to silicon occurs at much lower temperatures that the decomposition of ethane to carbon. The second is that there is a homogeneous amorphous solid solution of silicon and carbon. Various attempts were made to try to determine which of the two actually occurs. The following observations were made.

When the amorphous reaction product was heated above 900°C for one hour in Ar, both crystalline Si and SiC were obtained. Temperatures lower than this would not cause crystallization. On the other hand, pure silicon powders produced by decomposition of SiH₄(g) were crystalline above 800°C. Amorphous silicon powders produced at lower temperatures by SiH₄(g) decomposition could be easily crystallized at temperatures as low as 600°C. This
suggests, that if the amorphous product were a mixture of silicon and silicon carbide, the silicon should have crystallized at much lower temperatures than those observed. The DTA results show that as the amount of SiC in the powders increases, the crystallization temperature increases. For powders prepared above 1100°C in a 1:1 SiH₄(g) to C₂H₆(g) gas mixture, only SiC was observed to form. On the other hand, in a 2:1 SiH₄(g) to C₂H₆(g) gas, a mixture of crystalline silicon and SiC was found. These data all suggest that an amorphous solid solution of silicon and carbon forms at low temperatures which can be crystallized to mixtures of silicon and silicon carbide at elevated temperatures.

At temperatures above 1000°C, free carbon was found to form a core-shell structure on the particles just as in the case of decomposition of (CH₃)₄Si discussed above. In this case, the formation of the carbon shell could be caused by decomposition of unreacted C₂H₆(g) or CH₄(g) produced as a reaction product of silane and ethane by the following reaction:

\[ \text{SiH}_4(\text{g}) + \text{C}_2\text{H}_6(\text{g}) = \text{SiC}(\text{s}) + \text{CH}_4(\text{g}) + 3\text{H}_2(\text{g}). \]  

The free energy for this reaction is more favorable than for the reaction:

\[ 2\text{SiH}_4(\text{g}) + \text{C}_2\text{H}_6(\text{g}) = 2\text{SiC}(\text{s}) + 7\text{H}_2(\text{g}) \]
which leads to higher supersaturation as shown in Figure 89.

In summary, the formation of powders in the SiH$_4$(g) - C$_2$H$_6$(g) system is as follows.

- **T < 700°C**: only silicon powder is formed
- **700°C < T < 1100°C**: an amorphous solid solution of silicon and carbon is formed which can be crystallized to a mixture of silicon and silicon carbide
- **T > 1100°C**: SiC is formed with a carbon shell.

These results are summarized in Figure 90.

### 5.5 Preparation of SiC Powder by Reaction of SiH$_4$(g) and C$_2$H$_4$(g)

Powders prepared by the reaction of SiH$_4$(g) and C$_2$H$_4$(g) were virtually identical to those prepared by the reaction of SiH$_4$(g) and C$_2$H$_6$(g). As shown in Figure 83, amorphous powders having a single peak between those of silicon and beta-silicon carbide was found. The position of the peak was closer to that of silicon as the reaction temperature decreased. Subsequent heat treatment of these powders lead to crystallization at temperatures between 950°C and 1100°C. The crystallization temperature increased as the reaction temperature increased and the amount of silicon in the powder decreased.
Figure 89. The comparison of supersaturation ratio for different reactions.
Figure 90. The mechanism of SiC powder formation in SiH$_4$–C$_2$H$_6$ system.
CHAPTER VI
CONCLUSIONS

This research was primarily an assessment of the feasibility of using a flowing tube furnace reactor for the preparation of nonoxide ceramic powders. The main results of this study are the following.

1. Powders of silicon and silicon carbide could be prepared from a variety of precursor gases.

2. These powders typically have a small particle size (ten to a few hundred nanometers in diameter), a relatively small particle size range, and are agglomerated. As a result, these powder characteristics do not differ greatly from those of powders produced by other heating techniques such as laser or plasma heating.

3. Most of the powder preparation techniques studied lead to powders formed by homogeneous nucleation and growth in the gas phase.

4. In the case of silicon powders prepared by the decomposition of silane, SiH₄(g), the nucleation rate was low at low temperatures, went through a
maximum and then decreased at elevated temperatures. The particle size showed just the opposite behavior. These results can be explained by the total amount of reactant gas available for powder formation. If the nucleation rate is high, nucleation consumes more of the reactant and less reactant is available for subsequent particle growth. The opposite occurs if the nucleation rate is low.

5. Regardless of the system studied, amorphous powders were produced at low temperatures which could then be crystallized at higher temperatures. High reaction temperatures resulted in crystalline powders directly.

6. Beta-silicon carbide powders were successfully produced by: decomposition of tetramethylsilane, (CH₃)₄Si; reaction of silane, SiH₄(g), with ethane, C₂H₆(g); and reaction of silane with ethylene, C₂H₄(g).

7. A core-shell structure was observed for powders produced by decomposition of (CH₃)₄Si. In all cases the core was beta-SiC produced at high temperatures and the shell was a post powder formation deposition in the cool end of the
furnace. At low powder formation temperatures, an organosilicon shell formed by pyrolysis or polymerization of unreacted \((\text{CH}_3)_4\text{Si}\). This layer could be heat treated to form SiC. At elevated reaction temperatures, unreacted \((\text{CH}_3)_4\text{Si}\) or CH\(_4\) reaction product produced an amorphous carbon shell. At intermediate temperatures, no core-shell structure was observed.

8. SiC powders were produced from both \(\text{SiH}_4(\text{g})-\text{C}_2\text{H}_6(\text{g})\) and \(\text{SiH}_4(\text{g})-\text{C}_2\text{H}_4(\text{g})\) precursor systems. In both cases, an amorphous phase was formed at reaction temperatures below 1100°C. This amorphous phase appears to be a solid solution of Si and C, being richer in silicon as the reaction temperature decreases. This solid solution crystallized to mixtures of silicon and SiC upon heating. The crystallization temperature increased as the amount of SiC increased. At elevated temperatures, a carbon shell was observed on the powders for similar reasons to those discussed above for tetramethylsilane decomposition. In this case, the carbon shell is produced by the decomposition of methane, CH\(_4\),
present as a reaction product or unreacted ethane or ethylene.
CHAPTER VII
FUTURE WORK

Generally, the mechanisms of nucleation and growth of ultrafine Si and SiC powders are well investigated and presented in this study. However, in order to explore the possibility of synthesizing fine SiC powders at lower temperature range, which involves economical concepts when this powder synthesis process is applied in practice, it is suggested that SiC powder could be prepared from silane-acetylene system. In addition, by using the similar technique as shown in this study, the preparation of fine powders containing both SiC and Si₃N₄ grains would be feasible, which then could be used to manufacture ceramic composite materials for special applications.

7.1 SiC powder preparation from silane (SiH₄)-acetylene (C₂H₂) system

In this study, fine SiC powders are synthesized successfully from both silane-ethane and silane-ethylene systems. Based on the revealed mechanisms of the nucleation and growth of SiC powders, it is reasonably expected that acetylene (C₂H₂) could be another candidate
precursor for preparing SiC powders. Acetylene is known as an unstable hydrocarbon gas decomposing easily at low temperature. This low decomposition temperature in turn implies that the formation of SiC powders, or a solid solution of Si and C with rich carbon, could be obtained at low temperature range in SiH₄-C₂H₂ system.

7.2 The preparation of SiC and Si₃N₄ composite powder

The same technique used in this study for preparing SiC powders could also be applicable for synthesizing powders containing both SiC and Si₃N₄ grains. A powder sample prepared from SiH₄-C₂H₄ at 900°C, with composition SiₓCᵧ, showed exothermic reactions in DTA analysis (in N₂), as illustrated in Figure 91. The peak occurring at 960°C results from the crystallization of SiC and Si; and the peak at 1350°C corresponds to the nitrogenization of Si. Thus, composite powders containing fine SiC and Si₃N₄ grains are obtained. Therefore, the composite powders could be prepared through the nitrogenization of SiₓCᵧ at 1350°C in N₂ or NH₃ for further study.
Figure 91. DTA heating curve of $\text{Si}_x\text{C}_y$ powder in $\text{N}_2$. 
APPENDIX A

Tabulated Data of Vapor Pressure and Supersaturation Ratio

In gaseous systems in which a solid is formed by vapor phase reaction, the supersaturation ratio (SSR) is defined as the ratio of partial pressure of the growth species \( p \) to the equilibrium partial pressure of the growth species \( p_0 \) at a given temperature.

\[
SSR = \frac{p}{p_0}
\]  

For a general vapor phase reaction equation \( 46 \), the supersaturation ratio (SSR) is derived in terms of the thermodynamic quantities by the following calculations:

\[
aA(g) + bB(g) = cC(g) + dD(s) \quad \Delta G_{f46}^o
\]  

The formation of a solid by a vapor phase reaction consists of two consecutive elementary processes shown by equation \( 47 \) and equation \( 48 \):

\[
aA(g) + bB(g) = cC(g) + dD(g) \quad \Delta G_{f47}^o
\]

\[
D_{eq}(g) = D(s) \quad \Delta G_{f48}^o
\]

The supersaturation ratio for the deposit of \( D(s) \) by equation \( 46 \) is the ratio of the partial pressure of \( D(g) \) \( (p_D(g)) \) derived by equation \( 47 \) to the equilibrium partial pressure given by equation \( 48 \) \( (p_{D_{eq}}(g)) \) at temperature \( T \).
SSR = \frac{P_D(g)}{P_{Deq}(g)} \quad (49)

\(P_D(g)\) is obtained by setting the equilibrium conditions for the gas phase reaction of equation 47.

\begin{align*}
K_{eq} &= \frac{(P_C(g)^d P_D(g))}{(P_A(g)^a P_B(g))} \\
&= \exp(-\Delta G^o_{f47}/RT) \quad (50)
\end{align*}

\begin{align*}
P_D(g) &= \left[\frac{(P_A(g)^a P_B(g))}{P_C(g)^c}\right] \exp(-\Delta G^o_{f47}/RT) \quad (51)
\end{align*}

\begin{align*}
P_C(g) &= \frac{C}{d} P_D(g) \quad (52)
\end{align*}

By substituting equation 52 into equation 51, it is then rearranged and \(P_D(g)\) is expressed as equation 53:

\begin{align*}
P_D(g) &= \left(\frac{d}{c}\right)^{c+d} a/c+d b/c+d \exp(-\Delta G^o_{f47}/[(c+d)RT]) \quad (53)
\end{align*}

The equilibrium condition is also assumed for equation 48 and \(P_{Deq}(g)\) is derived as follows:

\begin{align*}
P_{Deq}(g) &= \exp(\Delta G^o_{f48}/RT) \quad (54)
\end{align*}

Consequently, by substituting equation 53 and 54 into equation 49 SSR is then obtained as a general expression equation 55 for all reactions.

\begin{align*}
SSR &= \left(\frac{d}{c}\right)^{c+d} a/c+d b/c+d \exp(-1/RT)[(\Delta G^o_{f47}/c+d)\Delta G^o_{f48}] \quad (55)
\end{align*}
Table 3. Log\[p_{\text{Si}(g)}\] in SiH$_4$ system.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>log[p_{\text{Si}(g)}]$_{eq}$</th>
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<th>10$^{-4}$</th>
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Table 4. Log SSR in SiH$_4$ system.

<table>
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<th>$P_{\text{SiH}<em>4(\text{g})</em>{\text{atm}}}$</th>
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Table 5. Log PsIC(g) in TMS system.

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<th>T(°K)</th>
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Table 6. Log SSR in TMS system.

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Table 7. Log $p_{SiC(g)}$ in $SiH_4 - C_2H_6$ system.

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$P_{SiH_4} = P_{C_2H_6}( atm )$  $10^{-2}$  $10^{-4}$  $10^{-8}$  $10^{-16}$
Table 8. Log SSR in SiH$_4$ - C$_2$H$_6$ system.

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Table 10. Log SSR in SiH$_4$ - C$_2$H$_4$ system.

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APPENDIX B

X-ray Line Broadening

It has been shown that the grain size can be determined by measuring the line broadening of an x-ray diffraction peak. The line broadening resulted from both small grain size (less than 100 nm) and lattice distortion are related by:

\[(B - b)\cos\theta/(k\lambda) = 1/D + [4(\Delta a/a)(\sin\theta/k\lambda)]\]  (56)

- \(D\) = grain size
- \(\lambda\) = x-ray wavelength
- \(\Delta a/a\) = average lattice distortion
- \(k\) = shape factor equal to 0.9
- \(\theta\) = Bragg diffraction angle
- \(B\) = sample broadening
- \(b\) = instrument broadening

Table 11 summarizes the broadening from three different diffraction peaks of Si powders prepared at 900°C. The instrument broadenings were determined by the x-ray diffraction peak of a single crystalline Si. Also tabulated values of \(d\) are listed in Table 11.

A plot of \(\sin\theta/k\lambda\) versus \([(B-b)\cos\theta]/k\lambda\) (Figure 92) give a slope of 0.0037 indicates a lattice distortion of less than 0.1%. Therefore, it can be concluded that the lattice distortion had negligible effect on the line broadening. Consequently, by simplifying the above
equation the grain sizes are then calculated as follows.

\[ \text{D} = \frac{0.9 \lambda}{[(B - b) \cos \theta]} \]  

\( D \) = grain size  
\( B \) = sample broadening  
\( b \) = instrument broadening

Table 11. Diffraction line broadening from typical tube furnace synthesized Si  
\( (900^\circ \text{C}, p(\text{SiH}_4 = 2.3 \times 10^{-2} \text{ atm}) \)

<table>
<thead>
<tr>
<th>Bragg diffraction angle (degree)</th>
<th>(hkl)</th>
<th>( \frac{\sin \theta}{0.9 \lambda} ) (nm(^{-1}))</th>
<th>Sample broadening (B) (radians)</th>
<th>Instrument broadening (b) (radians)</th>
<th>( (B - b) \cos \theta ) (nm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.45 (111)</td>
<td>1.7984</td>
<td>0.01805</td>
<td>3.5718 \times 10^{-3}</td>
<td>0.1010</td>
<td></td>
</tr>
<tr>
<td>23.90 (220)</td>
<td>2.9198</td>
<td>0.01992</td>
<td>4.3639 \times 10^{-3}</td>
<td>0.1025</td>
<td></td>
</tr>
<tr>
<td>28.15 (311)</td>
<td>3.4001</td>
<td>0.02146</td>
<td>4.6191 \times 10^{-3}</td>
<td>0.1070</td>
<td></td>
</tr>
</tbody>
</table>
Figure 92. Plot of \((B-b) \cos \theta /k\lambda\) versus \(\sin \theta /k\lambda\) from line broadening results of 900°C Si sample.
APPENDIX C

Particle Size Distribution Data

Figure 93. The particle size distribution of SiC powder synthesized at 850°C under $P_{\text{TMS}}=5.0\times10^{-3}$ atm.
Figure 94. The particle size distribution of SiC powder synthesized at 900°C under $P_{TMS}=5.0 \times 10^{-3}$ atm.
Figure 95. The particle size distribution of SiC powder synthesized at 1100°C under $P_{\text{TMS}}=5.0\times10^{-3}$ atm.
Figure 96. The particle size distribution of SiC powder synthesized at 850°C under $P_{\text{TMS}}=2.5\times10^{-2}$ atm.
Figure 97. The particle size distribution of SiC powder synthesized at 900°C under $P_{\text{TMS}}=2.5\times10^{-2}$ atm.
Figure 98. The particle size distribution of SiC powder synthesized at 1000°C under P_{TMS}=2.5\times10^{-2} \text{ atm}.
REFERENCES


11. D. A. Everest, I. G. Sayce, B. Selton, "Preparation of


44. F. F. Abraham, Homogeneous Nucleation Theory, Academic
