

Pyrolytic Conversion of Spherical Organo-silica Powder to Silicon Nitride under Nitrogen

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Monodisperse, spherical Si_3N_4 powder composed of fine particulates was synthesized by pyrolyzing spherical organo-silica powder under nitrogen. The organo-silica powder was prepared by hydrolyzing a mixture of phenyltrimethoxysilane (PTMS) and tetraethoxysilane (TEOS) in a methanol solution of water and ammonia. The organo-silica powder consisted of 81.3 at.% silicon units derived from PTMS and 18.7 at.% silicon units derived from TEOS. During the pyrolysis under nitrogen, the organo-silica powder decomposed to a mixture of free carbon and silica, with an increase of the surface area, at $500^\circ\text{--}600^\circ\text{C}$, followed by the formation of $\alpha\text{-Si}_3\text{N}_4$, with $\beta\text{-Si}_3\text{N}_4$ as a minor phase, at 1450° and 1500°C and $\beta\text{-SiC}$ at 1550°C . The pyrolyzed powders, which retained the spherical shape and monodispersity of the organo-silica powders, with a reduction in mean particle diameter, were composed of fine particulates that were ~ 40 nm in size.

I. Introduction

SYNTHESIS of ceramic materials via pyrolysis of preceramic polymers has recently received increased interest, because of highly attractive shaping properties and low fabrication temperatures.^{1–3} Preceramic polymers have been shown to be effective as binders for pressureless sintering and injection molding,⁴ precursors for oxidation-resistant coating,⁵ adhesives in ceramic–ceramic joining applications,⁶ a matrix for continuous-fiber-reinforced composites,^{7,8} and precursors for powder synthesis.^{9–11}

Many ceramic materials, including SiC, Si_3N_4 , BN, and AlN, have been produced from preceramic polymers.¹ A single class of preceramic polymer—polysilazane—has been shown to convert to either pure Si_3N_4 or a combination of Si_3N_4 and SiC, depending on the chemistry of the polymer and the pyrolysis conditions.^{1,2,12–15} Polysilazane consists of an alternating Si–N backbone that may or may not contain organic substituents. Minimizing the amount of carbon in the polymer will result in a ceramic with a stoichiometry closer to that of Si_3N_4 . Recently, conversion of a polysilazane precursor to carbon-free Si_3N_4 has been reported by Arai *et al.*¹⁶ and Schwab *et al.*¹⁷

On the other hand, several researchers have synthesized nitrogen ceramics, including Si_3N_4 via the pyrolysis of nitrogen-

free preceramic polymers with the use of ammonia as an external nitrogen source. Burns *et al.*¹⁸ and Schmidt *et al.*¹⁹ obtained amorphous or partially crystalline Si_3N_4 via the pyrolysis of polycarbosilanes and polysilanes under an ammonia atmosphere at temperatures of $<1000^\circ\text{C}$. Crystalline Si_3N_4 was produced by additional heating above a temperature of 1400°C . Nitrogen was not contained in the polycarbosilanes and the polysilanes initially; however, nitrogen was incorporated into the pyrolyzed products from ammonia during the pyrolysis. However, the incorporation mechanism was unclear. Some authors have investigated the nitridation of alkoxy-derived gels under an ammonia atmosphere, which is called ammonolysis, to synthesize nitride glasses at a relatively low temperature ($<1000^\circ\text{C}$).^{20,21} Ammonia could be incorporated into alkoxy-derived gels during the ammonolysis. Organo-silica gels, which are gels with SiCH₃ or SiH groups, were more effective at the nitrogen incorporation level than just a silica gel.^{20,21}

Recently, several researchers (including us) have synthesized spherical organo-silica powders whose molecular structures were similar to the structure of polysiloxane polymer and obtained spherical SiC powders via the pyrolysis of the organo-silica powders under an argon atmosphere.^{10,11} It was shown that the shape, size, and size distribution of the SiC powder could be controlled effectively in this process. After the pyrolysis, the organo-silica powders derived from the phenyltriethoxysilane–tetraethoxysilane (PTES–TEOS)¹⁰ and phenyltrimethoxysilane–tetraethoxysilane (PTMS–TEOS) systems,¹¹ which retained the initial spherical shape, had a powder form in the pyrolyzed products; however, the powders derived from the PTMS system changed to a shiny black solid, as has been observed in the pyrolysis of many preceramic polymers. It can be assumed that the characteristics of the polymers are critical in maintaining the initial particle shape through the pyrolysis step. Therefore, the role of the structure of the polymers on the shape of pyrolyzed products is under investigation.

Based on our previous study,¹¹ we have synthesized spherical organo-silica powder using the sol–gel process. Because the organo-silica powder, as a preceramic polymer, did not contain nitrogen, we have used nitrogen (not ammonia) gas as an external nitrogen source to obtain Si_3N_4 . In this work, we describe the pyrolytic conversion of the organo-silica to Si_3N_4 under a nitrogen atmosphere and the characteristics of the resulting Si_3N_4 powder.

II. Experimental Procedure

(1) Preparation of Organo-silica Powder

Preparation of the organo-silica powder followed the method used in our previous work.¹¹ Reagent-grade PTMS (EP grade, Shin-Etsu Chemical Co., Tokyo, Japan), TEOS (EP grade, Shin-Etsu Chemical Co.), NH_4OH (EP grade, Kanto Chemical Co., Tokyo, Japan), and CH_3OH (absolute grade, J. T. Baker

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Chemical Co., Phillipsburg, NJ) were used as starting materials. Each of the reagents were used as-received, without further purification. The distilled and deionized water had a resistance of $>10 \text{ M}\Omega\cdot\text{cm}$.

CH_3OH , water, and NH_4OH were mixed in a 2000 mL beaker. After this methanol solution was prepared, a mixture of 60 mol% PTMS and 40 mol% TEOS was poured into the methanol solution with stirring at 600 rpm; this combination resulted in a solution with a concentration of 0.25 mol/L SiH_4 , 32.0 mol/L water, and 1.0 mol/L NH_3 . The reaction volume was 1000 mL. The time required after pouring for the solution to become turbid was ~ 70 s. Stirring continued for 10 min, after which time the solution was aged for 2 h without stirring. The reaction and aging both were performed at 25°C . The resulting powder was separated from the solution via centrifugal sedimentation at 10000 rpm and dried under vacuum at a temperature of 100°C for 10 h.

(2) Heat Treatment of Organo-silica Powder

Three grams of organo-silica powders were placed on a graphite foil sheet and loaded into a horizontal alumina tube furnace. Those samples were heated at $10^\circ\text{C}/\text{min}$ to various temperatures (1400° , 1450° , 1500° , and 1550°C) and held for 8 h at each temperature in a constant flow ($\sim 300 \text{ mL}/\text{min}$) of nitrogen gas (99.99%).

(3) Characterization

The chemical structure of the organo-silica powder was analyzed by solid-state magic angle spinning (MAS) ^{29}Si and cross polarization/magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Model AM300, Bruker Instruments, Billerica, MA) at room temperature. The solid-state MAS ^{29}Si spectra were obtained at a spinning speed of 4000 Hz, a delay of 30 s between pulses, and a 90° pulse. For the solid-state CP/MAS ^{13}C spectra, a T^1 of 1.4 s, a 1.75 s delay between pulses, a 90° pulse, and a contact time of 3.0 ms were used during the data acquisition, and the spinning speed was 4000 Hz. Thermogravimetric analysis (TGA) was performed on the samples, up to a temperature of 1500°C , at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (flow rate of $\sim 80 \text{ mL}/\text{min}$). X-ray diffractometry (XRD) measurements were used to determine the crystalline phase of the pyrolyzed powders. The XRD patterns were collected using a scan rate of $4^\circ/2\theta/\text{min}$ over a 2θ range of 10° – 80° for $\text{CuK}\alpha$ radiation. The particle size and morphology of the samples were analyzed by using scanning electron microscopy (SEM) and transmission

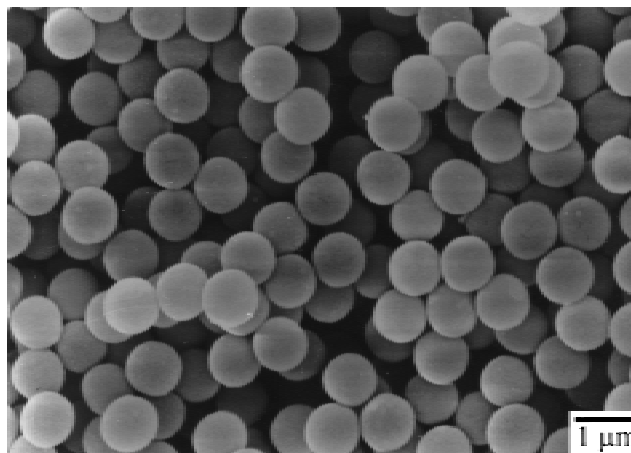


Fig. 1. SEM micrograph of the as-synthesized organo-silica powder.

electron microscopy (TEM). In addition, the Brunauer–Emmett–Teller (BET) surface area was determined, and an elemental analysis of the organo-silica and pyrolyzed powders was also conducted.

III. Results and Discussion

(1) Preparation of Organo-silica Powder

An SEM micrograph of the organo-silica powder obtained by hydrolyzing a mixture of PTMS and TEOS is shown in Fig. 1. The powder is monodisperse and spherical, with a mean particle diameter of $0.91 \mu\text{m}$. Solid-state MAS ^{29}Si and CP/MAS ^{13}C NMR spectra of the powder are shown in Fig. 2. The ^{29}Si NMR spectrum (Fig. 2(A)) exhibits two silicon peaks; the “T” silicon peaks were derived from PTMS and the “Q” silicon peaks were derived from TEOS. The molar ratios of silicon units derived from PTMS and TEOS were analyzed by deconvolution and integration of the spectrum, as shown in Table I. Those results demonstrate that the PTMS and TEOS were incorporated simultaneously into the organo-silica powder during the hydrolysis and condensation reaction. The powder consisted of 81.3 at.% silicon units that were derived from PTMS and 18.7 at.% silicon units that were derived from TEOS.

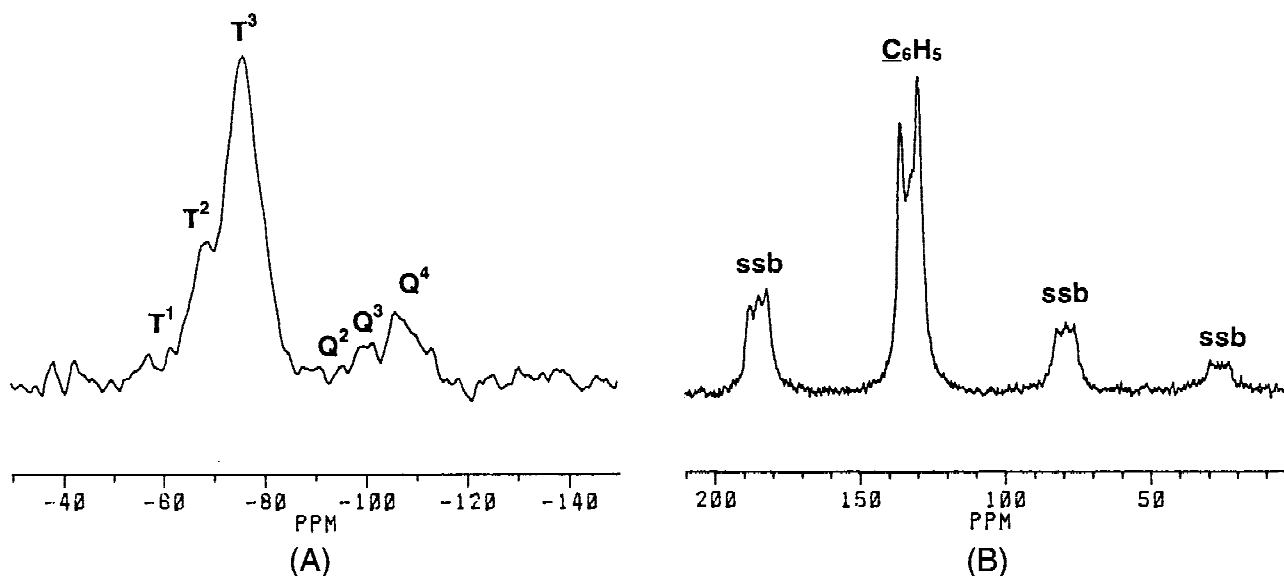


Fig. 2. (A) Solid-state MAS ^{29}Si and (B) CP/MAS ^{13}C NMR spectra of the organo-silica powder.

Table I. Relative Intensities of Different Types of Silicon Units Shown in a ^{29}Si NMR Spectrum

Molecular unit	Structure [†]	Intensity (%)
T ³	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \\ \end{array}$	70.1
T ²	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{OR} \end{array}$	9.4
T ¹	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ -\text{O}-\text{Si}-\text{OR} \\ \\ \text{OR} \end{array}$	1.8
Q ⁴	$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \\ \end{array}$	13.0
Q ³	$\begin{array}{c} \text{OR}' \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \\ \end{array}$	4.4
Q ²	$\begin{array}{c} \text{OR}' \\ \\ -\text{O}-\text{Si}-\text{OR}' \\ \\ \text{O} \\ \end{array}$	1.3

[†]The OR group denotes OCH_3 , whereas the OR' group denotes OC_2H_5 .

The ^{13}C NMR spectrum (Fig. 2(B)) shows three carbon peaks in a phenyl group in the range of 120–140 ppm and three spinning side bands. Because the R groups are nonhydrolyzable, they can remain in the molecular structure of the organo-silica powder after hydrolysis.^{22,23} In this case, the R group is

Table II. NMR and Measured Elemental Compositions of the Organo-Silica Powder

	Composition (at.%)			
	Silicon	Carbon	Oxygen	Hydrogen
NMR analysis	8.5	41.2	14.3	36.0
Measured	8.8 [†]	39.7 [‡]	15.9 [§]	35.6 [‡]

[†]Balanced. [‡]By elemental analysis. [§]By inductively coupled plasma analysis.

a phenyl group for PTMS. No carbon signal in residual methoxy (from PTMS) and ethoxy (from TEOS) groups is visible in the spectrum. These results indicate that all the methoxy groups in the PTMS and all the ethoxy groups in the TEOS were hydrolyzed, and the functional groups that remained without condensation in the T¹, T², Q², and Q³ silicon units were OH groups. Therefore, the only carbon sources in the organo-silica powder were carbons in the phenyl groups derived from the PTMS.

Table II shows the elemental compositions of the powder; one set of values have been calculated from the result of NMR analysis and the other set are measured values. The measured values are in good agreement with those calculated from the NMR analysis.

(2) Pyrolytic Conversion of Organo-silica Powder to Si_3N_4

Thermal reaction of the organo-silica powder under a nitrogen atmosphere was examined via TGA, as shown in Fig. 3. The TGA curve indicates an initial weight loss of ~15% at 500–670°C and a second weight loss that begins at 1430°C. To characterize the product that formed after the initial weight loss, the organo-silica powder was pyrolyzed at a temperature of 800°C for 4 h under a nitrogen atmosphere. The elemental composition and the BET surface area of the pyrolyzed organo-silica powder are shown in Table III. The elemental composition reveals that the pyrolyzed powder consisted of silicon, carbon, and oxygen. White *et al.*⁹ analyzed the products obtained by pyrolyzing various organo-silica powders at a temperature of 900°C under a nitrogen atmosphere to investigate the low-temperature pyrolytic behavior of the organo-silica powders, in the course of a study on the pyrolytic conversion of organo-silica powders to SiC under an argon atmosphere. According to their results, all the products consisted of a mixture of free carbon and silica. Our pyrolyzed powder can be said to be similar to the White *et al.* powder, which indicates that the product that formed after the initial weight loss is a mixture of

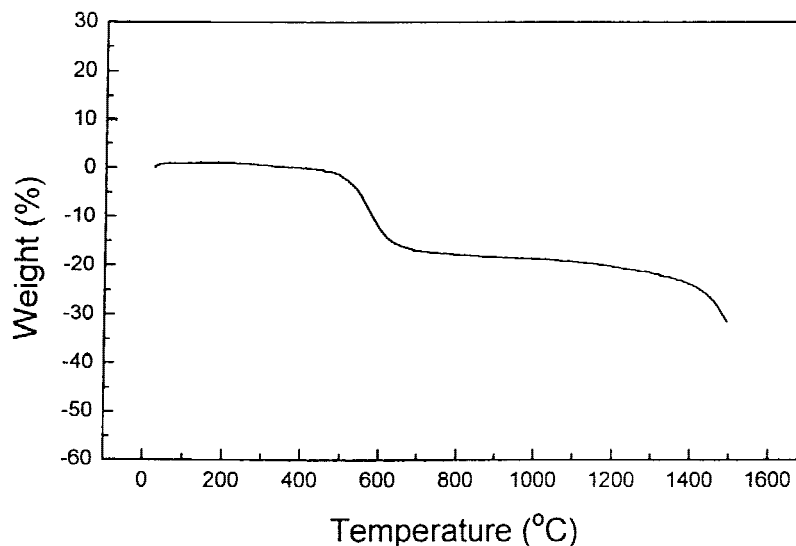


Fig. 3. TGA analysis of the organo-silica powder to 1500°C under nitrogen. Heating rate was 10°C/min.

Table III. Elemental Composition and BET Surface Area of the Organo-Silica Powder Pyrolyzed at 800°C for 4 h under Nitrogen

Elemental composition (at.%)					BET surface area (m^2/g)
Silicon	Carbon	Oxygen	Nitrogen	Carbon:silica [†]	
16.36 [‡]	48.26 [§]	35.38 [¶]	0.00	2.83	356.1

[†]Molar ratio of carbon to silica, calculated from the elemental composition. [‡]Balanced. [§]Data obtained by using a carbon analyzer. [¶]Data obtained by using an oxygen/nitrogen analyzer.

free carbon and silica. The molar ratio of carbon to silica of the pyrolyzed powder, calculated from the elemental composition, is ~ 2.83 (Table III). The BET surface area increased substantially, from $17.8 \text{ m}^2/\text{g}$ in the organo-silica powder to $356.1 \text{ m}^2/\text{g}$ in the pyrolyzed powder. Such a high BET surface area of the pyrolyzed powder can be described by not only the surface roughness of the powder but also the internal porosity. The pyrolyzed powder retained its spherical shape with a reduction of mean particle diameter. (A micrograph of the pyrolyzed powder is not shown here but can be predicted from micro-

graphs of the powder formed after the second weight loss (Figs. 5–7).) The reduction of the mean particle diameter and also the initial weight loss can be attributed to the loss of volatile oligomers and the organic decomposition. Results of the analysis of the elemental composition and the BET surface area imply that the spherical powder formed after the initial weight loss was porous and an intimate mixture of fine free carbon and silica particles.

To characterize the phase of the product formed by the second weight loss reaction, X-ray analysis was performed on the

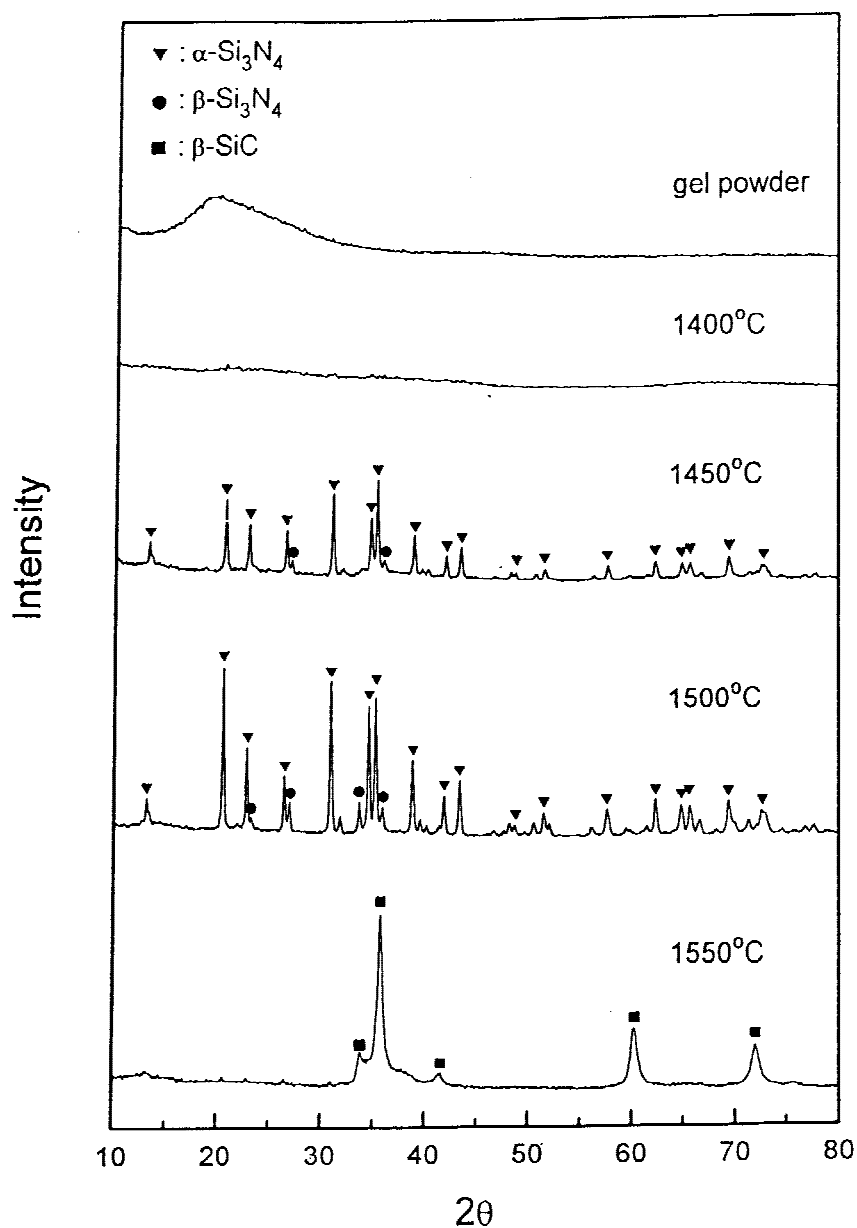


Fig. 4. XRD patterns of the organo-silica powder and powders pyrolyzed at various temperatures for 8 h under nitrogen.

organo-silica powder that was pyrolyzed at a temperature of 1400°–1550°C for 8 h under a nitrogen atmosphere (Fig. 4). No crystalline peaks were visible up to 1400°C, with the exception of α - Si_3N_4 , with a minor amount of β - Si_3N_4 at 1450° and 1500°C, and β -SiC at 1550°C. SiC is known to be thermodynamically more stable than Si_3N_4 above a certain boundary temperature, depending on the carbon activity and the nitrogen pressure, in the Si-O-C-N system.^{24–26} The reported boundary temperature is within the range of 1450°–1550°C.^{27–29} In this study, the boundary temperature is in the range of 1500°–1550°C. It is well-known that Si_3N_4 is produced from a mixture of carbon and silica via carbothermal reduction and nitridation under a nitrogen atmosphere.³⁰ In this work, it can be said that the spherical powder that formed after the initial weight loss, which consisted of a mixture of fine free carbon and silica particulates, was so porous that the powder could accept nitrogen gas into an internal portion of the powder to produce Si_3N_4 via carbothermal reduction and nitridation. In the previous studies on the pyrolytic conversion on nitrogen-free polymers^{18,19} (polycarbosilane and polysilane) to Si_3N_4 , ammonia was used as an external nitrogen source because ammonia has been known to be an active reaction source. In those cases, amorphous Si_3N_4 was formed at low temperatures (1000°C¹⁹ or 1200°C¹⁸) under an ammonia atmosphere, followed by the formation of crystalline Si_3N_4 at higher temperatures (1400°C¹⁹ or 1500°C¹⁸) through an amorphous-to-crystalline transformation under an ammonia or nitrogen atmosphere. From the above-mentioned discussion, pyrolytic conversion behavior of the nitrogen-free polymers to Si_3N_4 under an ammonia atmosphere is different from the behavior of the organo-silica

under a nitrogen atmosphere. Therefore, our work presents some possibilities that nitrogen-free polymers, which have been used as precursors for SiC, can be used as preceramic polymers for crystalline Si_3N_4 through carbothermal reduction and nitridation under a nitrogen (not ammonia) atmosphere.

(3) Characteristics of Si_3N_4 Powder

SEM micrographs of the powders pyrolyzed at 1500° and 1550°C for 8 h under a nitrogen atmosphere are shown in Fig. 5. The pyrolyzed powders retained their spherical shape and the monodispersity of the organo-silica powder (compared with Fig. 1) with a reduced mean particle diameter. Considering that the particle size and size distribution of the spherical organo-silica powder can be controlled in sol-gel processing, these results indicate that spherical Si_3N_4 and SiC powder with a controlled particle size and size distribution can be prepared by using the method presented in this work.

The mean particle diameters of Si_3N_4 and SiC powders (Figs. 5(A) and (B), respectively) were 0.72 and 0.67 μm , respectively. The difference can be attributed to different reactions, as described by the following equations:



The formation of SiC was accompanied by a loss of 2 mol CO per mole SiO_2 in the carbothermal reduction (reaction (1)), whereas the formation of Si_3N_4 is accompanied by a loss of 2 mol CO and the addition of 2/3 mol nitrogen gas per mole SiO_2 in carbothermal reduction and nitridation (reaction (2)). Therefore, the volume constriction was less during Si_3N_4 formation than during SiC formation.

The surfaces of the Si_3N_4 particles observed at higher magnification (Fig. 6) shows that the particles are made up of particulates ~40 nm in size, which is similar to the case of the spherical SiC particles. A bright-field TEM micrograph and an electron diffraction pattern of the particle are shown in Fig. 7. The ringed diffraction pattern implies that the spherical Si_3N_4 particle is composed of fine primary particulates. From the previous section, the spherical powder that formed after the initial weight loss, which was composed of an intimate mixture of fine free-carbon and silica particulates, was porous and can incorporate nitrogen gas as a reaction element. Because the reaction elements (carbon, silica, and nitrogen) are confined within the spherical powder itself during the pyrolysis step, which causes a limited availability of growth space of Si_3N_4 ,

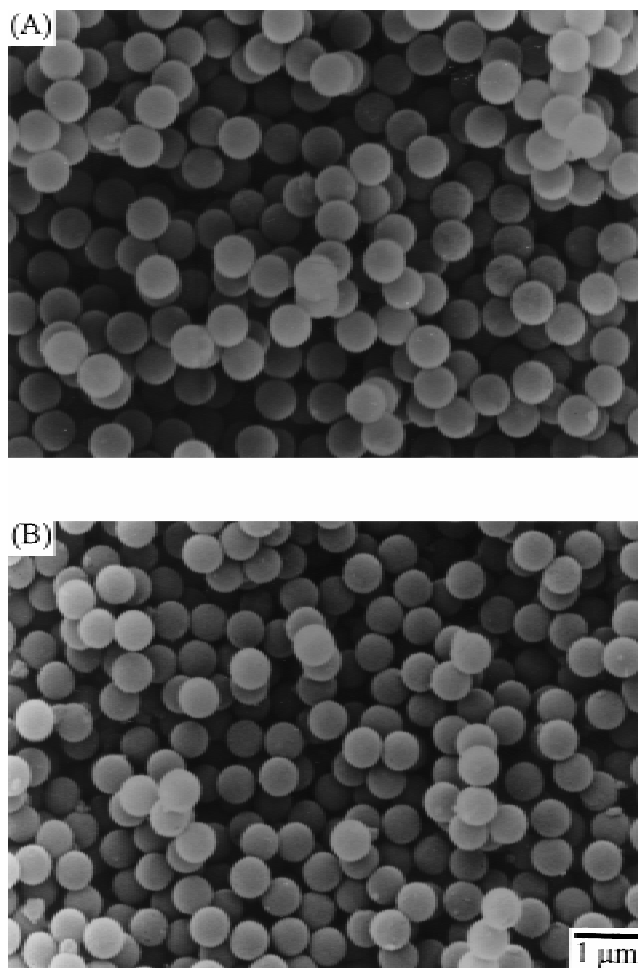


Fig. 5. SEM micrographs of powders pyrolyzed at (A) 1500° and (B) 1550°C for 8 h under nitrogen.

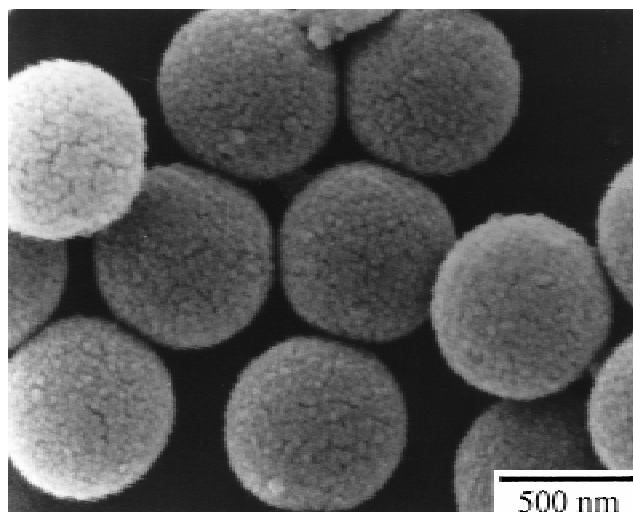


Fig. 6. SEM micrograph of Si_3N_4 powder obtained by pyrolyzing the organo-silica powder at 1500°C for 8 h under nitrogen.

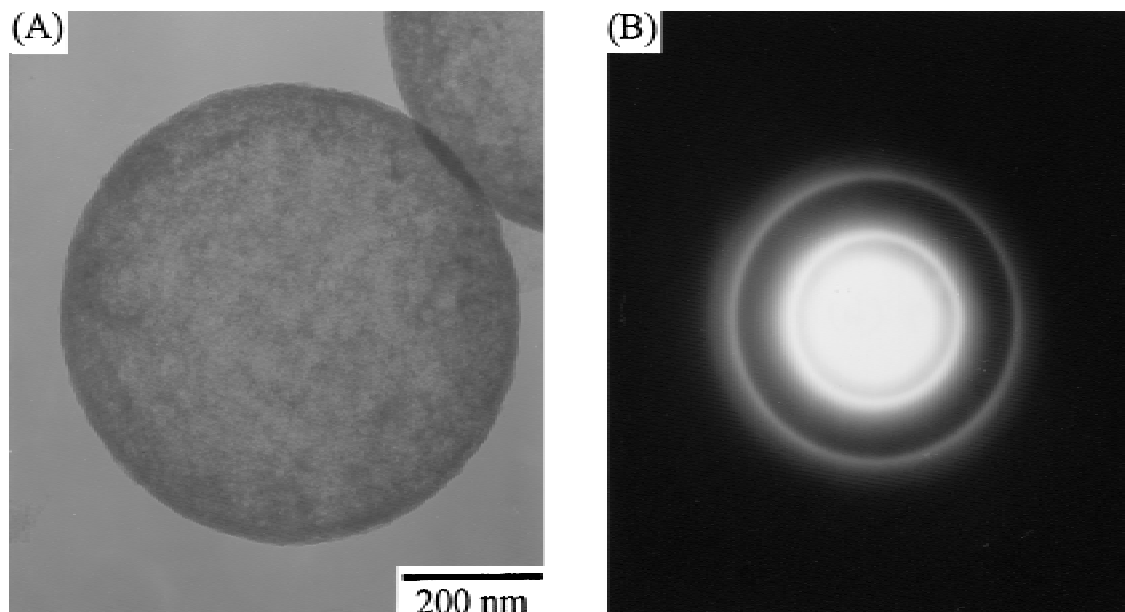


Fig. 7. (A) Bright-field TEM micrograph and (B) electron diffraction pattern of Si_3N_4 powder obtained by pyrolyzing the organo-silica powder at 1500°C for 8 h under nitrogen.

the Si_3N_4 powder that is formed retains its spherical shape and is composed of fine, primary Si_3N_4 particulates.

The elemental composition and BET surface area of the Si_3N_4 powder prepared at 1500°C for 8 h under nitrogen are shown in Table IV. The powder contained ~24.0 wt% carbon and had a high BET surface area of $318.9\text{ m}^2/\text{g}$, which indicates that the powder was an intimate mixture of Si_3N_4 and free carbon. After the powder was oxidized at a temperature of 600°C for 30 min in air, it contained 2.06 wt% oxygen, 1.61 wt% carbon, and 37.8 wt% nitrogen and had a BET surface area of $6.5\text{ m}^2/\text{g}$, which suggests that the high BET surface area of the Si_3N_4 powder before oxidation can be attributed to the fine free-carbon particles. More-precise control of the composition of the organo-silica powder and the conditions of pyrolysis and oxidation seems to result in a monodisperse and spherical Si_3N_4 powder that is composed of fine particulates with low carbon and oxygen content.

IV. Summary

Monodisperse, spherical Si_3N_4 powder that was composed of fine particulates was synthesized by pyrolyzing spherical organo-silica powder in a nitrogen atmosphere. The present organo-silica powder was prepared by hydrolyzing a mixture of 60 mol% phenyltrimethoxysilane (PTMS) and 40 mol% tetraethoxysilane (TEOS) in a methanol solution of water and ammonia; 81.3 at.% of the silicon units in the organo-silica powder came from PTMS and 18.7 at.% of the silicon units in the organo-silica powder came from TEOS.

During the pyrolysis, the organo-silica powder decomposed to a mixture of fine free-carbon and silica particulates, with an

increased surface area at $500^\circ\text{--}670^\circ\text{C}$. The mixture transformed to Si_3N_4 , at temperatures of 1400° and 1500°C (through carbothermal reduction and nitridation), and SiC, at 1550°C (through carbothermal reduction).

The pyrolyzed powders retained the spherical shape and monodispersity of the organo-silica powders ($0.91\text{ }\mu\text{m}$), with a reduced mean particle diameter ($0.72\text{ }\mu\text{m}$ for Si_3N_4 and $0.67\text{ }\mu\text{m}$ for SiC), and consisted of fine particulates that were ~40 nm in size. The elemental composition of Si_3N_4 powders that were pyrolyzed at a temperature of 1500°C for 8 h was 2.06 wt% oxygen, 1.61 wt% carbon, and 37.8 wt% nitrogen after the powder was oxidized in air at a temperature of 600°C for 30 min.

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Table IV. Elemental Composition and BET Surface Area of Si_3N_4 Powder Obtained by Pyrolyzing the Organo-silica Powder at 1500°C for 8 h under a Nitrogen Atmosphere

	Elemental composition (at.%)			BET surface area (m^2/g)
	Carbon	Oxygen	Nitrogen	
As-prepared	24.0 [†]	ND [‡]	ND [‡]	318.9
After oxidation	1.61 [†]	2.06 [§]	27.8 [§]	6.5

[†]Data obtained by using a carbon analyzer. [‡]Not determined. [§]Data obtained by using an oxygen/nitrogen analyzer.

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