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Effect of Heat Treatment on the Microstructure of
Amorphous Si-N-C Fine Powders*

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Synopsis

Crystallization processes of four kinds of amorphous Si-N-C fine powders were studied by X-ray diffraction, IR spectroscopy, transmission electron microscopy, analytical electron microscopy and chemical analysis. The samples examined had varying contents of Si, N and C (Si: 53-58 mass%, N: 24-36 mass%, C: 5-20 mass%), and were prepared by pyrolysis of hexamethyldisilazane ((Me₃Si)₂NH, Me=CH₃). These samples were heat-treated in an argon atmosphere at a temperature between 1713-1803K for periods of up to 21.6ks. All of the fine powders examined were nearly spherical and were 100-500nm in size before heat treatment. The first sign of crystallization of the powders was observed after 21.6ks heat treatment at 1713K. X-ray diffraction showed that the crystallized phase consisted mainly of β-SiC and α-Si₃N₄. The formation of β-SiC occurred during the early stage of heat treatment. The formation of α-Si₃N₄ then followed. After heat treatment for 21.6ks at 1743K, more than 80% of crystallinity was observed in all of the samples examined. The quantity of α-Si₃N₄ and β-SiC in the samples was related to the carbon content in the powders. The crystallized β-SiC was between 20-100nm in size. On the other hand, the size of α-Si₃N₄ was consistently larger than that of β-SiC and depended on the nitrogen content in the powders.

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I. Introduction

Si_3N_4 -SiC composite materials are receiving a great deal of attention as new engineering ceramics because of their high strength and high tenacity at high temperature (1-4). Traditionally, these composite materials were obtained by merely mixing different powders. However, amorphous fine powders consisting of silicon, nitrogen and carbon have recently been prepared by pyrolysis of organosilicon compounds containing nitrogen (5-8). In order to produce even higher quality composite materials a recent study examined the use of the fine powders as starting materials for the sintering process (9). It is well known that the strength and toughness of ceramics depend on their sinterability. However, there have been very few studies on the process of crystallization of amorphous Si-N-C fine powders. This crystallization process is known to influence the sintering behavior of Si_3N_4 -SiC composite materials.

In the present study crystallization process of amorphous Si-N-C fine powders prepared by pyrolysis of hexamethyldisilazane is examined.

II. Experimental

Amorphous Si-N-C fine powders were produced by the vapor phase reaction of hexamethyldisilazane ($(\text{Me}_3\text{Si})_2\text{NH}$, $\text{Me}=\text{CH}_3$) and NH_3 gas in the Al_2O_3 reaction tube at the temperature of 1273K. H_2 was used as a carrier gas. The combined total gas flow rate was $2.8 \times 10^{-6} \text{m}^3 \text{s}^{-1}$ (8). Four kinds of amorphous fine powders having varied contents of silicon, nitrogen and carbon were prepared by changing the amount of NH_3 during the reaction. These powders easily reacted with oxygen or water in air and had exothermic reactions. For this reason the powders were pre-treated by heating them under 101kPa nitrogen atmosphere at 1623K for 14.4ks. Nominal compositions of the samples are listed in Table 1. Amorphous structure was identified for all of the samples by X-ray diffraction. One gram sample placed on the alumina boat was treated for periods of 7.2 and 21.6ks at 1713K and of 1.8, 7.2 and 21.6ks at three different temperatures of 1743, 1773 and 1803K in Ar atmosphere. The mass of the samples was

Table 1. Chemical compositions of Si-N-C powders.

Powder	Analyzed composition/mass%				
	Si	N	C*	O	Free C
C5	Bal.	35.8	4.8	1.2	1.8
C8	Bal.	32.8	8.1	1.8	4.9
C17	Bal.	29.0	17.3	1.0	9.3
C20	Bal.	24.2	19.7	2.3	11.5

*Total carbon

measured before and after heat treatment to calculate the mass loss due to the reaction. The samples were examined for their characteristics with X-ray diffraction (Rigaku RAD-B), an IR spectroscope (Nippon Kogaku IR-G), a transmission electron microscope (JEOL 2000EX), an analytical electron microscope (JEOL 2000FX) and by chemical analysis.

III. Results and discussion

1. Mass loss

The mass loss of the samples was measured after heat treatment at the end of a specified time period at each temperature. The mass loss of all of the samples increased with an increase of temperature and time of heat treatment as well as with the increase in carbon content. Figure 1 shows mass loss of the samples after heat treatment at 1743 and 1773 K for three heat treatment times. The rate of mass loss for all of the samples was larger at the early stage of heat treatment and later became more gradual. After heat treatment for 7.2 ks at 1803 K, the mass losses of S1, S2, S3 and S4 powders were 13.1, 18.6, 24.2 and 26.8%, respectively. The mass loss of S1, S2, S3 and S4 powders at the same temperature but after a period of 21.6 ks was respectively, 17.0, 24.9, 31.1 and 33.6%. Therefore, the increase of mass losses of S1, S2, S3 and S4 powders between these two time periods was 3.9, 6.3, 6.9 and 6.8%, respectively. More of these results will be discussed in a later section.

2. Crystallinity*

Crystallized phases of the samples identified by X-ray diffraction were α -Si₃N₄ (containing small amounts of β -Si₃N₄), and β -SiC (containing small amounts of α -SiC). Small

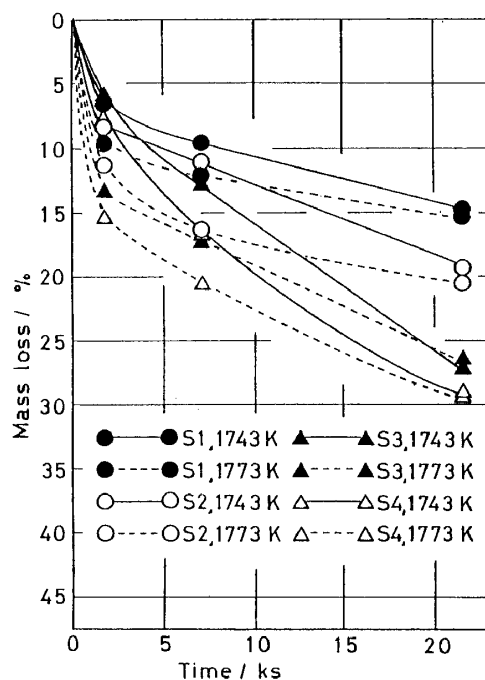


Fig. 1 Mass loss of Si-N-C powders heat-treated at 1743 and 1773 K in Ar.

*Crystallinity(%) = $(\alpha\text{-Si}_3\text{N}_4 + \beta\text{-SiC}) \times 100 / (\text{amorphous phase} + \alpha\text{-Si}_3\text{N}_4 + \beta\text{-SiC})$

peaks of silicon were detected for S2 powder after heat treatment for 21.6ks at 1743, 1773 and 1803K and for S1, S3 and S4 powders after heat treatment for 21.6ks at 1803K. A quantitative analysis of the crystallized phase was conducted using X-ray diffraction methods with NaCl as an internal standard. Peaks of NaCl (200), β -SiC (220) and α -Si₃N₄ (201) were used for this quantitative analysis.

Figure 2 shows phase composition and crystallinity of the samples heat-treated at 1713K (Fig. 2a), 1743K (Fig. 2b), 1773K (Fig. 2c) and 1803K (Fig. 2d). From these figures it can be seen that with

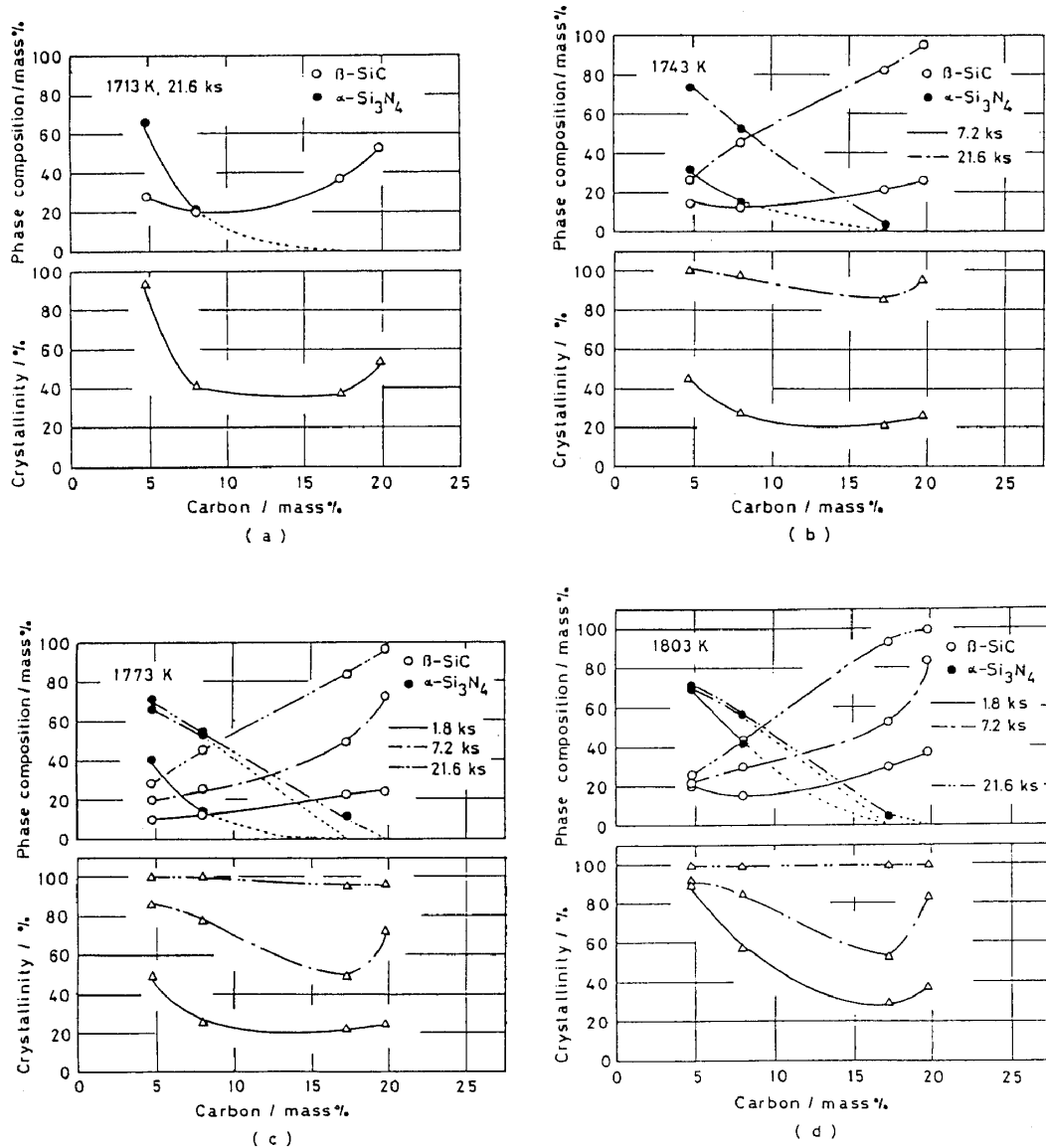


Fig. 2 Phase composition and crystallinity of Si-N-C powders heat-treated in Ar. (a) After heat treatment at 1713K for 21.6ks. (b) After heat treatment at 1743K for 7.2 and 21.6ks. (c) After heat treatment at 1773K for 1.8, 7.2 and 21.6ks. (d) After heat treatment at 1803K for 1.8, 7.2 and 21.6ks.

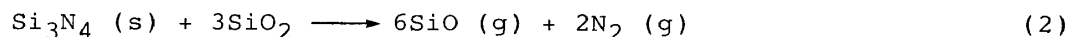
an increase of carbon content α -Si₃N₄ decreases while β -SiC tends to increase. The crystallinity of the samples decreases with increased carbon content and showed a minimum value for S3 powder but showed a higher value for S4 powder. The time required to initiate the crystallization of the samples at the temperature 1713, 1743, 1773 and 1803K were correspondingly 21.6, 7.2, 1.8 and 1.8ks. After heat treatment at 1743K for 21.6ks, all of the samples showed more than 80% crystallinity. The crystallinity of S1 powder was about 90% after heat treatment at 1803K for 1.8ks. At 1803K, crystallinity of sample powders for 7.2ks was 92% for S1, 86% for S2, 52% for S3 and 83% for S4. The crystallinity of S1, S2, S3 and S4 powders after 21.6ks was nearly 100%. Therefore, crystallinity of the samples heat-treated for 7.2ks at 1803K increased in the order of S3<S4<S2<S1 powders. On the other hand, at 1803K the difference of mass loss between heat treatment time of 7.2 and 21.6ks increased in the order of S1<S2<S4<S3 powders (Section 3.1).

These results show that the samples having high crystallinity after heat treatment for 7.2ks lose much less mass during the heat treatment of up to 21.6ks at 1803K. This difference in mass loss of the samples in first 7.2 vs 21.6ks of heat treatment was 4-7%. Therefore it is conjectured that even after crystallization continuous mass loss of the samples takes place during heat treatment.

The formation of α -Si₃N₄ was observed for all of the samples used in the present study (α -Si₃N₄ was detected by electron diffraction in S4 powder after heat treatment). Silicon nitride decomposes at high temperatures above 1773K, according to the following reaction (10, 11).



A small amount of oxygen was contained in the samples used in the present study. Therefore, the following reaction is also considered (11).



Moreover, when the crystallinity of the samples is less than 100%, the evolution of excess substance due to crystallization takes place causing some mass loss.

Okabe et al. (12) have reported that SiC powders synthesized from the vapor phase reaction of (CH₃)₄Si-H₂ system at 1073 to 1473K show only one very broad peak of β -SiC. They recognized very sharp peaks of β -SiC by X-ray diffraction when the sample powders were heat-treated for 3.6ks at 1673K in a hydrogen atmosphere. Endo et al. (13) have found that SiC powders synthesized by the vapor phase

reaction of $(\text{Si}(\text{CH}_3)_2)_2\text{H}_2$ at 973-1673K show some broad peaks of β -SiC. Existence of broad peaks in β -SiC powders implies that the SiC powders are already crystallized soon after they are produced. On the other hand, Si_3N_4 powders prepared by the vapor phase reaction were amorphous (14-20). Prochazka and Greskovich (14) have synthesized amorphous Si_3N_4 powders from the vapor phase reaction of SiH_4 - NH_3 at 773-1173K. They found that weak peaks of α - Si_3N_4 were observed by X-ray diffraction after the samples were heat-treated for 1.2ks at 1753K in N_2 . In the present study, the formation of α - Si_3N_4 was detected by X-ray diffraction in S1 and S2 powders which were heat-treated for 1.8ks at 1773K in Ar. This result is consistent with the data obtained by Prochazka and Greskovich (14). They pointed out that the crystallization of amorphous Si_3N_4 containing free silicon takes place at the temperature between 1523 and 1623K. They also claimed that these amorphous Si_3N_4 form α - Si_3N_4 after crystallization. In the present study, a trace of silicon was recognized in S2 powder after heat treatment for 21.6ks at three different temperatures of 1743, 1773 and 1803K and in S1, S3 and S4 powders after heat treatment for 21.6ks at 1803K. However, the temperature where crystallization began remained unchanged for the powders. From the result, it is suggested that because the amount of free silicon in Si_3N_4 is so minute the initiation temperature of crystallization for the samples was not affected by the existence of free silicon.

Hojo et al. (7) have reported the formation of amorphous SiC- Si_3N_4 composite powders by the vapor phase reaction of $\text{Si}(\text{CH}_3)_4$ - NH_3 - H_2 system at 1473K. They showed that the amorphous powders were crystallized into β -SiC and α - Si_3N_4 (partially including β - Si_3N_4) after heat treatment at 1823K in Ar- N_2 atmosphere. Depending on the NH_3 concentration used, three crystallized phases were obtained from amorphous powders produced in low temperature mixing (less than 1173K). They were SiC phase, SiC- Si_3N_4 composite and α - Si_3N_4 phase. Hojo et al. also found that the size of Si_3N_4 powders in α - Si_3N_4 phase was $1\mu\text{m}$ which corresponds to growth of 25 times in size from the size of the original powders. On the other hand, the size of SiC powder and SiC- Si_3N_4 composite was 0.1 - $0.2\mu\text{m}$ showing a suppression of grain growth for these samples. In the present study the growth of α - Si_3N_4 with the length of heat treatment time was identified for S1 and S2 powders containing large amounts of nitrogen. This result is in good agreement with the data obtained by Hojo et al. (7). However, for S3 and S4 powders containing a large amount of carbon, only a trace of α - Si_3N_4 was observed and the growth of α - Si_3N_4 was

hardly observable for these samples. In this way, the composition of the samples is believed to play an important role in the growth of α - Si_3N_4 .

Hirai et al. (21) have studied the high-temperature reactions between α - and β - Si_3N_4 with carbon by heat treating samples in N_2 atmosphere under the pressure of 101kPa and the temperature range of 1593 to 2033K. They showed that SiC formed at temperatures above 1763K by the reaction given by



Thus, it is important to examine the reaction between Si_3N_4 and C in the present study. However, in the present study, the amount of free carbon decreased at the early stage of the heat treatment and the necessary binding carbon was consumed in the formation of SiC. Therefore, it becomes impossible to form SiC by the reaction given by Equation (3) under the present heat treatment conditions.

3. Infrared spectroscopy

Figure 3 shows the spectra of S1 (Fig.3a), S2 (Fig. 3b), S3 (Fig. 3c) and S4 (Fig. 3d) powders. Samples were prepared by the KBr powder technique. Broad infrared spectra were observed at 960cm^{-1} for all of the samples heat-treated for 1.8ks at 1743K. From the samples of pure α - Si_3N_4 (Toshiba Ceramics Co.) and pure β -SiC (Ibigawa Electric Industries Co.), the absorption band based on the Si-N bond was recognized at 950 and 500cm^{-1} , and the absorption band based on the Si-C bond was observed at 850cm^{-1} . Therefore, it can be concluded that all of the amorphous powders heat-treated for 1.8ks at 1743K have a band structure close to the Si-N bond. As shown in Fig. 3(a), the absorption peak of S1 powder heat-treated for 7.2ks at 1743K is shifted slightly toward the shorter wave number and the splitting of this band is also observed. The absorption peaks of S1 powder are observed at 950cm^{-1} based on the Si-N bond with the splitting of this absorption band after heat treatment at 1743 and 1773K for 21.6ks. However, the absorption peak near 860cm^{-1} based on Si-N bond is larger than any of the absorption peaks of pure Si_3N_4 or of Si_3N_4 by Prochazka and Greskovich (14), or Futaki et al. (19). This result is attributable to the addition of absorption peak near 850cm^{-1} based on Si-C bond of β -SiC.

The absorption peak of S2 powder (Fig. 3b) heat-treated at 1743K for 7.2ks is shifted from 960cm^{-1} to slightly toward shorter wave number but no splitting of the absorption band is observed. This result was obtained because the crystallinity of S2 powder is lower than that of S1 powder. After heat treatment at 1743 and 1773K for

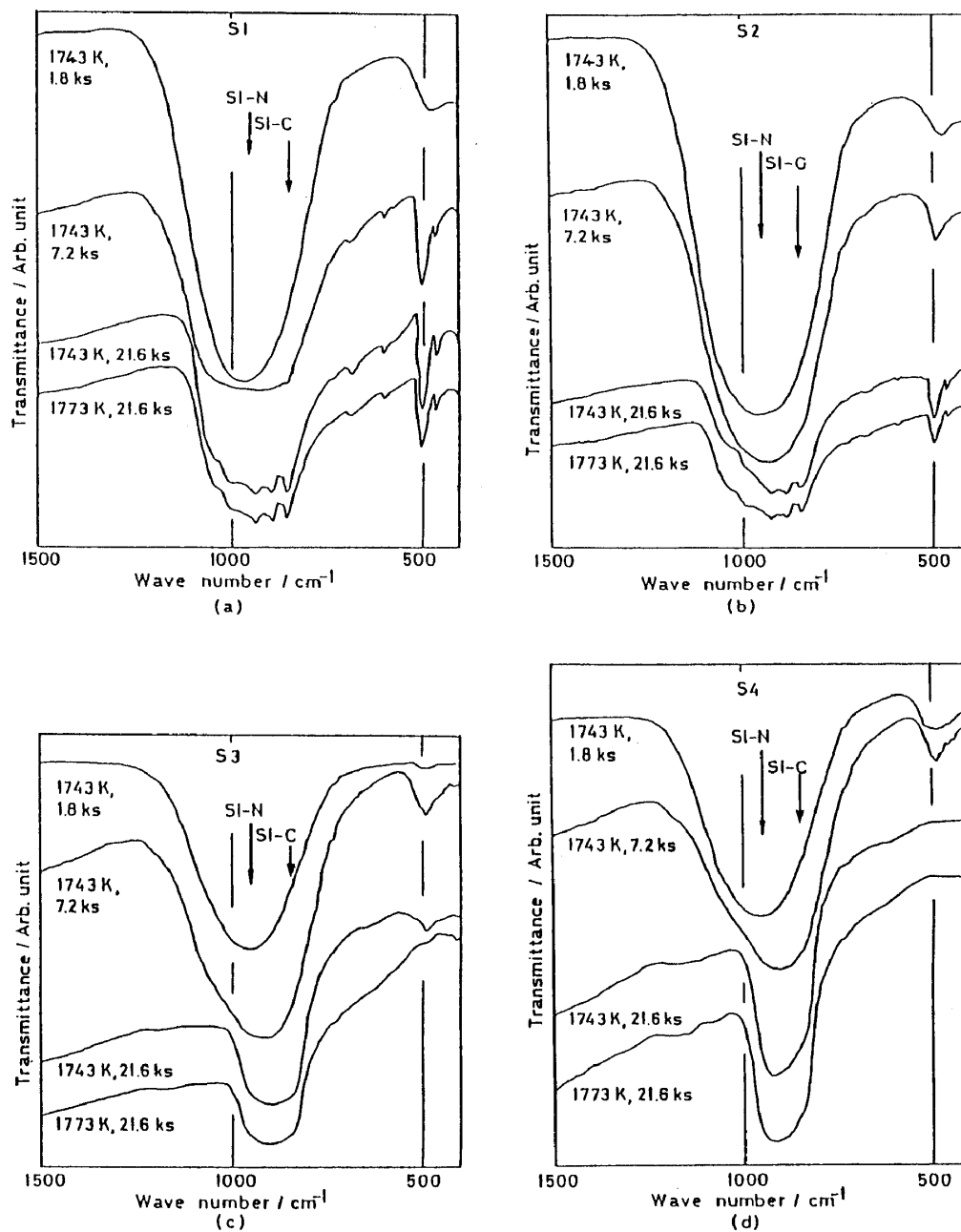


Fig. 3 Optical transmittance spectra of Si-N-C powders heat-treated in Ar. (a) S1 powder. (b) S2 powder. (c) S3 powder. (d) S4 powder.

21.6ks, the absorption band due to Si-N bond of α - Si_3N_4 and to Si-C bond of α -SiC was observed for S2 powder.

As shown in Fig. 3(c), the absorption peaks of S3 powder heat-treated at 1743K for 7.2ks and 21.6ks, and at 1773K for 21.6ks are observed at 914, 900 and 900 cm^{-1} , respectively. These absorption peaks are nearly equal to the absorption peaks based on Si-C bond of

pure β -SiC and of β -SiC by Endo et al. (13). Therefore, it is suggested that β -SiC is a predominant crystallized phase for S3 powder. However, these absorption peaks are somewhat broader than the absorption peaks of pure β -SiC and of β -SiC by Endo et al. (13). The broadening can be considered to be a result of the addition of the absorption peak based on Si-N bond of α -Si₃N₄.

As shown in Fig. 3(d), the absorption peaks of S4 powder heat-treated at 1743K for 7.2ks and 21.6ks, and at 1773K for 21.6ks are recognized at 907, 900 and 900cm⁻¹, respectively. These absorption peaks are nearly equal to the absorption peaks of S3 powder under the same conditions of heat treatment. However, the absorption peaks of S4 powder are sharper than those of S3 powder. The result points out that the proportion of β -SiC in S4 powder is larger than that of β -SiC in S3 powder.

4. Transmission electron microscopy

All of the samples used in this study were found to be amorphous by X-ray diffraction before heat treatment. These samples were spherical and were 100-500nm in size. Figure 4 shows morphologies and electron diffraction patterns of S1 powder before and after heat treatment. S1 powder was again found to be amorphous by TEM observation before heat treatment. The morphology of the sample heat-treated for 1.8ks at 1743K in Ar changed from original spherical shape to a rod shape. An arrow points to a flower-like particle which was found to be β -SiC by electron diffraction as shown in Fig. 4(b).

After heat treatment of 1743K for 21.6ks, crystallized β -SiC from the S1 powder was rod-shaped and angular and 20-80nm in size as shown in Fig. 4(c). Morphology of β -SiC for the S1 powder was also observed after heat treatment at 1773 and 1803K for 21.6ks. The morphologies of these samples were rod-shaped and angular and the

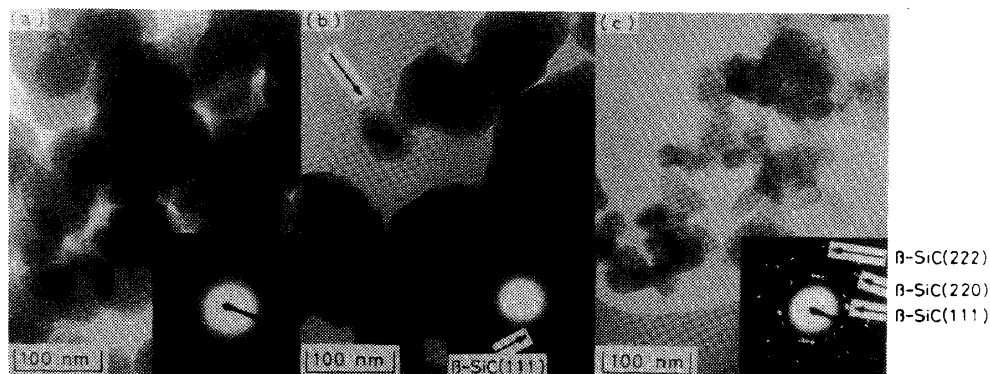


Fig. 4 Transmission electron micrographs and electron diffraction patterns of S1 powder. (a) Before heat treatment. (b) After heat treatment at 1743K for 1.8ks in Ar. (c) After heat treatment at 1743K for 21.6ks in Ar.

size of the samples were 20-100nm. After heat treatment at 1743K for 7.2ks, α - Si_3N_4 was formed. Figure 5 shows the morphology of α - Si_3N_4 . The α - Si_3N_4 was needle-like with hexagonal ends and had the size of 0.5 μm in width and about 5 μm in length. As shown in Fig. 5(b), a small amount of hexagonal Si_3N_4 was also formed. In S1 powder heat-treated for 21.6ks at 1713K, needle-like α - Si_3N_4 had a width of 0.3 μm and a length of 3 μm . After heat treatment at 1803K for

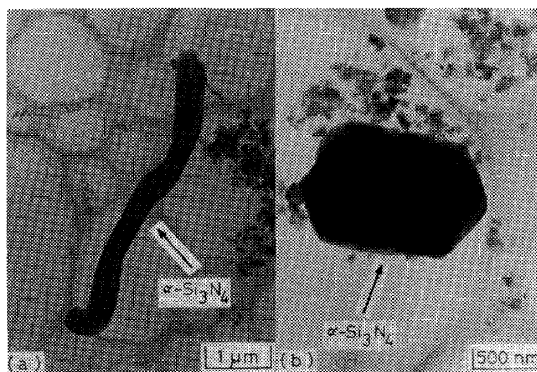


Fig. 5 Transmission electron micrographs of S1 powder heat-treated at 1743K for 7.2ks in Ar. (a) Typical needle-like α - Si_3N_4 . (b) Hexagonal α - Si_3N_4 .

21.6ks, the needle-like α - Si_3N_4 was formed from the S1 powder and its size was 0.5 μm in width and about 5 μm in length. From these results, it can be seen that α - Si_3N_4 grows along with the progress of crystallization of amorphous Si-N-C fine powders but it ceases to grow when crystallization is completed. The hexagonal α - Si_3N_4 was also observed by Kasai et al. (16) and Kubo et al. (20) after heat treatment of amorphous Si_3N_4 at more than 1703K. Crystallized α - Si_3N_4 and β -SiC were observed from S2 powder after heat treatment as shown in Fig. 2. The morphologies of this S2 powder were similar to those of S1 powder. For S3 and S4 powders, mainly β -SiC was obtained after heat treatment at 1743 K for 7.6ks but a trace of α - Si_3N_4 was also observed by electron diffraction. Observation by transmission electron microscope revealed that the β -SiC formed in this study was due to the solid state reaction of Si and carbon contained in the sample, and the α - Si_3N_4 was believed to be formed by the vapor phase reaction of Si and nitrogen.

Figure 6 shows morphologies of S3 powder before and after heat treatment. The sample was dense and spherical before heat treatment. After heat treatment at 1743K for 1.8ks, the outermost surface of the sample changed from dense to porous because of the thermal decomposition of amorphous Si-N-C fine powders. After 7.2ks even the internal parts of the sample became porous and crystallized β -SiC was detected by electron diffraction at the projected area on the surface as shown in Fig. 6(c).

Figure 7 shows a bright-field image and a (111) dark-field image of β -SiC for S3 powder heat-treated for 21.6ks at 1773K. Crystallized β -SiC was main product for S3 powder. This β -SiC was 20-100nm in size and was rod-shaped and angular. Based on the dark-

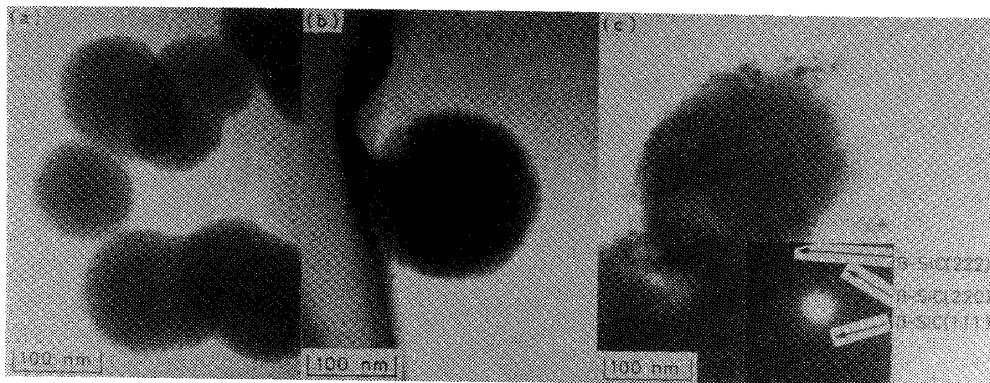


Fig. 6 Transmission electron micrographs and electron diffraction patterns of S3 powder. (a) Before heat treatment. (b) After heat treatment at 1743K for 1.8ks in Ar. (c) After heat treatment at 1743K for 7.2ks in Ar.

field image in (111) Bragg orientation for β -SiC (Fig. 7(b)), the crystallite of the β -SiC was 20-80nm in size. After heat treatment of 1773K for 21.6ks, a particle size of 20-100nm and crystallite size of 20-80nm was observed for β -SiC contained in S1, S2 and S4 powders.

As mentioned earlier, for the sample used in the present study, β -SiC formed in the early stage of heat treatment and was followed by the formation of α -Si₃N₄. Small amounts of crystallized SiC were observed soon after SiC fine powders were synthesized by the vapor phase reaction (10, 11). On the other hand, no crystallized Si₃N₄ was recognized when Si₃N₄ fine powder was synthesized by the vapor phase reaction, and crystallized Si₃N₄ was detected after heat treatment at high temperatures of more than 1753K (12). Therefore, the result that the crystallization of β -SiC was followed by the formation of crystallized α -Si₃N₄ in the present study seems to be plausible.

5. Analytical electron microscopy

Analytical electron microscopy of the non-treated samples clearly revealed that each fine powder of the samples used in this study consisted of silicon, nitrogen, carbon and a small amount of oxygen. Figure 8 shows relative intensities of carbon, nitrogen and oxygen by an analytical electron microscope for typical fine powders

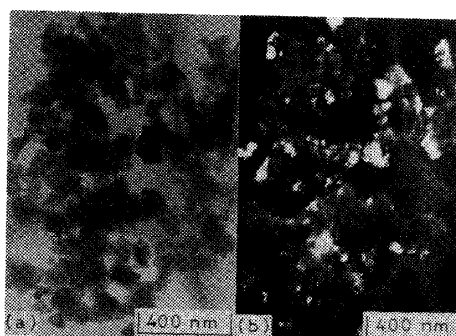


Fig. 7 Transmission electron micrographs of S3 powder heat-treated at 1773K for 21.6ks in Ar. (a) Bright-field. (b) dark-field in (111) Bragg orientation of β -SiC.

of S3 powder before and after heat treatment. After heat treatment at 1743K for 1.8ks, the intensity of carbon decreased (Fig. 8b) and then nitrogen peak decreased when the sample was further heat-treated for 7.2ks at 1743K (Fig. 8c). After 21.6ks at 1743K, the peak of nitrogen has considerably diminished. The intensity of oxygen for S3 powder heat-treated for 1.8 and 7.2ks at 1743K increased slightly compared with the other conditions of heat treatment. This result is not due to oxidation of the sample but caused by significant decrement of carbon and nitrogen during the early stage of heat treatment. The significant decrement of nitrogen shown in Fig. 8(d) relates to the evolution of excess nitrogen accompanied by crystallization of amorphous Si-N-C fine powders. The decrement of oxygen can be explain by the reaction of α -Si₃N₄ and oxygen given by Equation 2 (Section 3.2).

6. Chemical analysis after heat treatment

Nominal compositions of the heat-treated samples are listed in Table 2. The free carbon of all the samples decreased rapidly in the early stage of heat treatment as clearly shown in Tables 1 and 2. The decrement of the free carbon was explained by the increment

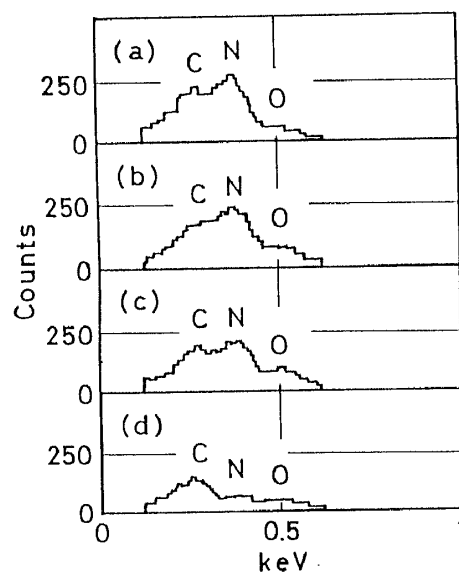


Fig. 8 Relative intensities of carbon, nitrogen and oxygen by an analytical electron microscope for S3 powder. (a) Before heat treatment. (b) After heat treatment at 1743K for 1.8ks in Ar. (c) After heat treatment at 1743K for 7.2ks in Ar. (d) After heat treatment at 1743K for 21.6ks in Ar. (e) After heat treatment at 1743K for 7.2ks in Ar. (f) After heat treatment at 1743K for 21.6ks in Ar.

Table 2. Chemical compositions of Si-N-C powders heat-treated in Ar.

Powder	T/K	t/ks	Analyzed composition/mass%		
			N	C*	Free C
S1	1743	1.8	36.1	4.6	0.22
	1743	7.2	36.7	4.7	0.06
	1743	21.6	37.4	3.8	0.02
	1803	21.6	37.8	3.4	0.02
S2	1743	1.8	30.4	8.4	0.64
	1743	7.2	29.3	8.2	0.15
	1743	21.6	31.0	7.5	0.10
	1803	21.6	31.2	7.5	0.10
S3	1743	1.8	26.3	17.9	4.40
	1743	7.2	22.8	19.1	3.10
	1743	21.6	11.1	22.1	0.20
	1803	21.6	9.7	22.6	0.16
S4	1743	1.8	20.8	21.6	5.20
	1743	7.2	18.6	22.2	3.90
	1743	21.6	7.3	23.5	0.45
	1803	21.6	6.5	24.3	0.43

*Total carbon

of the mass loss of the samples as shown in Fig. 1. Therefore, the mass loss is mainly associated with the evolution of CO and CO₂, which are formed by reaction of free carbon and oxygen contained in the samples. The increased mass loss accompanying the increment of the carbon content is attributable to the increased content of free carbon of the samples. Total carbon content of S1 and S2 powders decreased slightly with an increase of heat treatment time. On the other hand, the total carbon content of S3 and S4 powders increased with increasing time of heat treatment. Increased total carbon content of S3 and S4 powders is due to the decrement of nitrogen.

Nitrogen was little affected by temperature and time of heat treatment for both S1 and S2 powders, while it decreased with increasing temperature and time of heat treatment for S3 and S4 powders. The decrement of nitrogen in S3 and S4 powders is well illustrated by the increased mass loss with time of heat treatment in excess of 7.2ks as shown in Fig. 1.

IV. Summary

The crystallization process of four kinds of amorphous Si-N-C fine powders having different compositions prepared by pyrolysis of hexamethyldisilazane, has been studied by heat treating them at 1713-1803K for as long as 21.6ks. The following results were obtained:

1) All of the samples examined were almost spherical and were 100-500nm in size before their heat treatment. Crystallized phases were α -Si₃N₄ (containing partially β -Si₃N₄) and β -SiC (containing partially α -SiC). With an increase of carbon content in the samples, the amount of α -Si₃N₄ decreased and that of β -SiC increased.

2) In the crystallization processes of all the samples, β -SiC was first formed by the solid state reaction of Si and carbon contained in the samples. The morphology of β -SiC was rod-shaped and angular. The size of β -SiC was 20-100nm and was almost independent of time and temperature of heat treatment. On the other hand, α -Si₃N₄ was formed by the vapor phase reaction. The morphology of α -Si₃N₄ was needle-like and hexagonal. The size of α -Si₃N₄ was larger than that of β -SiC. The growth of α -Si₃N₄ was observed for S1 and S2 powders. However, for S3 and S4 powders only a trace of α -Si₃N₄ was found, and the growth of the α -Si₃N₄ decreased considerably. Therefore, the composition of the samples is believed to play an important role in the growth of α -Si₃N₄.

3) Mass loss of the sample increased with increasing temperature

and time of heat treatment, as well as with increase of carbon content. Mass loss was caused by the decrement of free carbon for S1 and S2 powders. On the other hand, for S3 and S4 powder, mass loss was caused by the decrement of free carbon at the early stage of heat treatment and decrement of nitrogen at a later time of heat treatment.

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References

- (1) F. F. Lange, *J. Am. Ceram. Soc.* 56(1973), 445.
- (2) P. D. Shalek, J. J. Petrovic, G. F. Hurley and F. D. Gac, *Am. Ceram. Soc. Bull.* 65(1986), 351.
- (3) R. Lundberg, L. Kahlman, R. Pompe and R. Carlsson, *Am. Ceram. Soc. Bull.* 66(1987), 330.
- (4) S. T. Buljan, J. G. Baldoni and M. L. Huckabee, *Am. Ceram. Soc. Bull.* 66 (1987), 347.
- (5) D. Seyferth and G. H. Wiseman, *J. Am. Ceram. Soc.* 67(1984), C-132.
- (6) G. W. Rice, *J. Am. Ceram. Soc.* 69(1986), C-183.
- (7) J. Hojo, H. Maeda and A. Kato, *Yogyo-Kyokai-Shi* 95(1987), 45.
- (8) T. Suzuki, T. Kawakami, T. Koyama, K. Izaki, R. Nakano, T. Shitara, K. Hakkei, T. Hirai and K. Niihara, *Yogyo-Kyokai-Shi* 95(1987), 81.
- (9) K. Niihara, A. Nakahira, K. Suganuma, T. Hirano, S. Kihara, K. Izaki and T. Kawakami, *Spring Meeting of the Japan Inst. Met.* (1988), 263.
- (10) H. D. Batha and E. D. Whitney, *J. Am. Ceram. Soc.* 56(1973), 365.
- (11) F. F. Lange, *J. Am. Ceram. Soc.* 65(1982), C-120.
- (12) Y. Okabe, J. Hojo and A. Kato, *J. Less-Common Met.* 68(1979), 29.
- (13) M. Endo, T. Sano, K. Mori, N. Urasato and M. Shiraishi, *Yogyo-Kyokai-Shi* 95(1987), 104.
- (14) S. Prochazka and C. Greskovich, *Amer. Ceram. Soc. Bull.* 57(1978), 579.

- (15) A. Kato, Y. Ono, S. Kawazoe and I. Mochida, *Yogyo-Kyokai-Shi* 80 (1972), 114.
- (16) K. Kasai, Y. Kubota and T. Tsukidate, *Yogyo-Kyokai-Shi* 88(1980), 358.
- (17) T. Yamada, T. Kawahito and T. Iwai, *J. Mat. Sci. Let.* 2(1983), 275.
- (18) T. Tani, T. Yoshida and K. Akashi, *Yogyo-Kyokai-Shi* 94(1986), 1.
- (19) S. Futaki, K. Shiraishi, T. Shimizu and T. Yoshida, *Yogyo-Kyokai-Shi* 94(1986), 7.
- (20) N. Kubo, S. Futaki, K. Shiraishi and T. Shimizu, *Yogyo-Kyokai-Shi* 95(1987), 59.
- (21) T. Hirai, K. Niihara and A. Ohkubo, *J. Japan Inst. Metals (Nippon Kinzoku Gakkaishi)* 41(1977), 367.