

Effect of Si/ α -Si₃N₄ Ratio on the Shape of Silicon Nitride Particles Produced by SHS Method

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ABSTRACT

Si and α -Si₃N₄ powder mixtures added with 3 wt% Y₂O₃ were reacted under 5 MPa nitrogen pressure. The reaction products contained α -Si₃N₄ particles with elongated shapes. Length and width of the elongated grains were the maximum when the starting powder mixture of 50 wt% Si - 47 wt% α -Si₃N₄ and 3 wt% Y₂O₃ was used. Aspect ratio of the elongated grains were between 4.4 and 5. When the starting powder mixture contained 70 wt% Si, large particles with irregular shapes appeared. Meanwhile, the reaction did not proceed when the starting powder mixture contained 30 wt% Si and less. The SHS product was easy to crush and the elongated particles obtained from the starting powder mixtures of 40 wt% Si - 57 wt% α -Si₃N₄ - 3 wt% Y₂O₃ and 50 wt% Si - 47 wt% α -Si₃N₄ - 3 wt% Y₂O₃ were good candidates for the seeds.

Key words : SHS, Silicon nitride, Elongated grains

1. Introduction

Silicon nitride has been studied for its excellent properties including high strength, high fracture toughness and others.¹⁾ The excellent properties of silicon nitride result from the unique microstructure consisting of elongated grains of bi-modal size distribution. Those large elongated grains are often called as reinforcing grains while those fine grains as matrix grains. Even though silicon nitride with randomly oriented reinforcing grains exhibited high strength and high fracture toughness among ceramics, the properties need further improvement for a wider application. Furthermore, the strength and the fracture toughness of silicon nitride were often showed a trade-off, i.e. high strength with low fracture toughness or high fracture toughness with low strength.²⁾ Recent development of silicon nitride with aligned reinforcing grains provided a way to overcome the problem, and silicon nitride with high strength and fracture toughness was successfully demonstrated.³⁻⁸⁾

In order to fabricate silicon nitride with aligned reinforcing grains, seed particles with elongated shapes are used. By tape casting³⁻⁶⁾ or extrusion,^{7,8)} those seed particles were aligned in the green body. Those seed particles grew and dominated the microstructure of the sintered silicon nitride resulting in the highly anisotropic microstructure and properties. Size and shape of those seed particles exert a strong influence upon the degree of orientation of those reinforcing grains⁹⁾ and the properties of the silicon nitride ceramics.⁸⁾ β -Si₃N₄ whiskers were used as good seed crystals since they

were single crystals with high aspect ratio and purity.⁹⁾ However, another way to obtain the seed particles should be found for taking advantage of seed particles with various sizes and shapes. There have been some reports on making seed crystals.^{6,10,11)} Most of those methods consisted of the powder mixing and sintering to make porous body that was crushed into powder. The powder went through the acid treatment for separating the particles by dissolving the glassy phase between the particles. It took a large amount of energy to heat the powder mixture to a temperature higher than 2023 K to obtain those seed particles with elongated shape. Also, it is important to crush the sintered porous body into particles easily. Self-propagating high temperature synthesis (SHS) method has been used for various kinds of ceramics and other compounds by taking advantage of the heat generated during the chemical reaction.¹²⁾ Basically, it requires very small amount of energy to initiate the reaction, and the reaction is self-sustaining to completion. SHS usually gives highly porous products and seems an attractive way to preparing those seed particles.¹³⁾ In this study, powder mixtures of Si and α -Si₃N₄ added with 3 wt% Y₂O₃ were used for making elongated β -Si₃N₄ particles by SHS method. Effect of Si/ α -Si₃N₄ ratio on the reaction and the reaction product was examined.

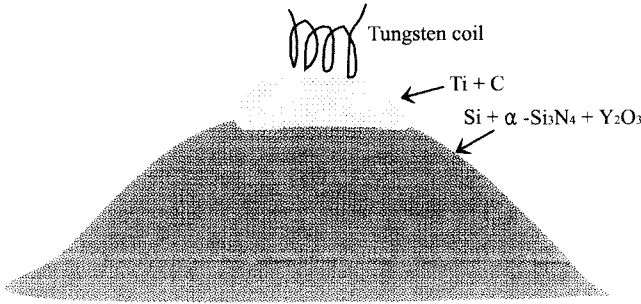
2. Experimental Procedure

Commercially available Si powder (Grade 4FP, Sicomill, Permascand AB, Ljungaverk, Sweden), Si₃N₄ powder (E10, Ube Industries Ltd., Tokyo, Japan) and Y₂O₃ powder (Grade C, H.C.Starck Co., Berlin, Germany) were used. The powders were weighed as shown in Table 1, and were mixed

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Table 1. SHS Results of the Powder Mixtures

Sample #	Si (wt%)	α -Si ₃ N ₄ (wt%)	Y ₂ O ₃ (wt%)	Results
1	20	77	3	Not ignited
2	30	67	3	Not ignited
3	40	57	3	Ignited
4	50	47	3	Ignited
5	60	37	3	Ignited
6	70	27	3	Ignited

**Fig. 1.** A schematic diagram of the sample for SHS reaction.

using a planetary ball mill for 8 h. A plastic jar, silicon nitride balls with 5 mm in diameter and ethanol were used for milling. The slurry was dried using a rotary evaporator and a drying oven at 373 K. The cake was gently crushed and passed through 70 mesh nylon sieve. The mixed powder was poured in a graphite container lined with graphite foil, and was brought into the high gas pressure SHS reactor. Since the powder mixture alone was hard to ignite, small amount of (Ti + C) powder was placed on top of it and below tungsten coil for facilitating the ignition as shown in Fig. 1. After the tungsten coil was properly positioned, the reactor cap was screw tightened and nitrogen gas starts to flow into the reactor chamber. After nitrogen pressure reached 5 MPa, electric power was on and the tungsten coil was heated up until the (Ti + C) powder mixture starts to react to form TiC. The heat generated from the reaction of (Ti + C) mixture ignited the powder mixture of Si, Si₃N₄ and Y₂O₃. The reaction product was analyzed by XRD using Cu k radiation. The morphology was examined using SEM.

3. Results and Discussion

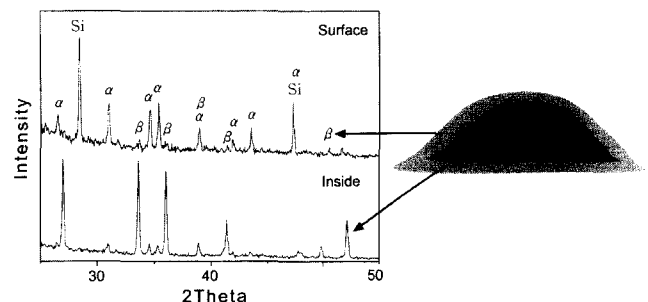
Table 1 shows the results. When the Si content in the starting powder mixture was 30 wt% or lower, the SHS reaction did not occur. Reaction between Si and nitrogen is highly exothermic, i.e. $3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$, $\Delta H_{298}^\circ = -744.752$ KJ.¹⁴⁾ Heat capacity of Si₃N₄ as a function of temperature was obtained as follows by fitting the data from the literature.¹⁴⁾

$$C_p \text{ (J/mol K)} = 65.273 + 0.127 \times T - 3.32 \times 10^{-5} \times T^2 \quad (298 \text{ K} < T < 2000 \text{ K})$$

$$C_p \text{ (J/mol K)} = 175.733 + 0.0062 \times T - 6.684 \times 10^{-7} \times T^2 \quad (T > 2000 \text{ K})$$

The adiabatic temperature based on the thermodynamic data was calculated as 4550 K according to the method provided in the literature.¹⁵⁾ To be more specific, the adiabatic temperature can be obtained by equating standard heat of formation of Si₃N₄ to the heat needed to increase the temperature of Si₃N₄ from 298 K to the adiabatic temperature. According to Holt,¹⁶⁾ making Si₃N₄ by SHS reaction between Si and nitrogen actually required nitrogen pressure higher than 46 MPa in order to suppress decomposition of Si₃N₄. In other words, the reaction did not proceed due to decomposition of Si₃N₄ if nitrogen pressure was lower than 46 MPa. Since decomposition of Si₃N₄ depends on the temperature, one way to make Si₃N₄ by SHS reaction is using diluents, decreasing the heat generated and suppressing its decomposition. Si₃N₄ and Y₂O₃ in the current powder mixture worked as diluents that reduced the amount of heat generated during the reaction. It was reported that SHS reaction occurred if the calculated adiabatic temperature was higher than 1800 K.¹⁵⁾ It suggests that more than 6.25 wt% of Si was needed for SHS reaction in the current powder mixture if the heat of transformation from β -Si₃N₄ is ignored. However, it turned out that more than 30 wt% Si was needed for SHS reaction of the powder mixture. One of the reasons why more than 30 wt% Si was needed for the SHS reaction is that the actual system was not adiabatic and the diluents as well as highly pressurized nitrogen conducted the generated heat away from the reaction front. In other words, the region neighboring the reaction front was not heated enough for the reaction if the starting powder mixture contained less than 30 wt% Si. Even though Holt reported that the yield of Si₃N₄ from the above SHS reaction was increased slightly by adding the diluent,¹⁶⁾ there should be a limit to the content of diluent for SHS reaction and the limit was 30 wt% in the current study.

Fig. 2 shows XRD patterns from the products. While the pattern from surface region of the product had the peaks for Si and α -Si₃N₄ with an appreciable intensity, that from internal region has only weak α -Si₃N₄ peaks besides β -Si₃N₄ peaks. The XRD results were consistent with the appearance of the reaction product. In other words, color of the surface of the product was similar to that of the starting powder mixture, i.e. brown while the internal region was

**Fig. 2.** XRD results of the SHS product of the powder mixture with sample 3; the patterns were obtained from surface region and from internal region.

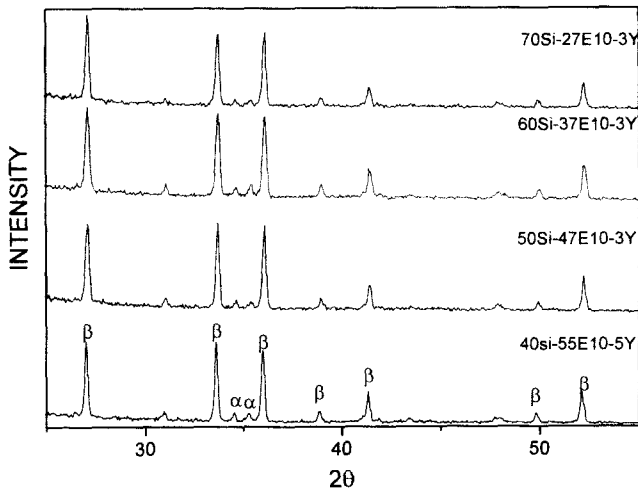


Fig. 3. XRD patterns of the samples after SHS reaction; samples were taken from inside of the product.

light grey. Brown color was from Si and light grey from Si_3N_4 . α - Si_3N_4 / β - Si_3N_4 ratio was obtained from Fig. 3 using Gazzara's equation.¹⁷ It was varied between 16% and 20%, but did not show any consistent dependence on composi-

tions of the starting powder mixtures. Presence of α - Si_3N_4 can be explained in two ways. First, a small portion of α - Si_3N_4 in the starting powder mixture remained unreacted in the product. Second, α - Si_3N_4 as well as β - Si_3N_4 was formed by SHS reaction. Holt reported on the product obtained from SHS reaction of Si in 101 MPa nitrogen pressure that α - Si_3N_4 was present in the internal region as well as in the surface region.¹⁶ If unreacted α - Si_3N_4 powder was the main reason for α - Si_3N_4 peaks appearing in Fig. 2 and Fig. 3, the α - Si_3N_4 peak intensity should be decreased as Si content in the starting powder mixture was increased. Or if α - Si_3N_4 formed by SHS reaction was responsible for those α - Si_3N_4 peaks, α - Si_3N_4 phase content should be increased as more Si was present in the starting powder mixture. In the current study, the fact that α - Si_3N_4 / β - Si_3N_4 ratio did not show any consistent dependence on the starting powder mixtures suggests that both unreacted starting α - Si_3N_4 powder and α - Si_3N_4 formed by SHS reaction were present in the product.

Fig. 4(a)-(d) show morphology of the products according to different compositions of the starting powder mixtures. The products were very porous and easily broken into particles during sample preparation for SEM observation. Fig. 4(a) and (b) show that the elongated particles had a wide size

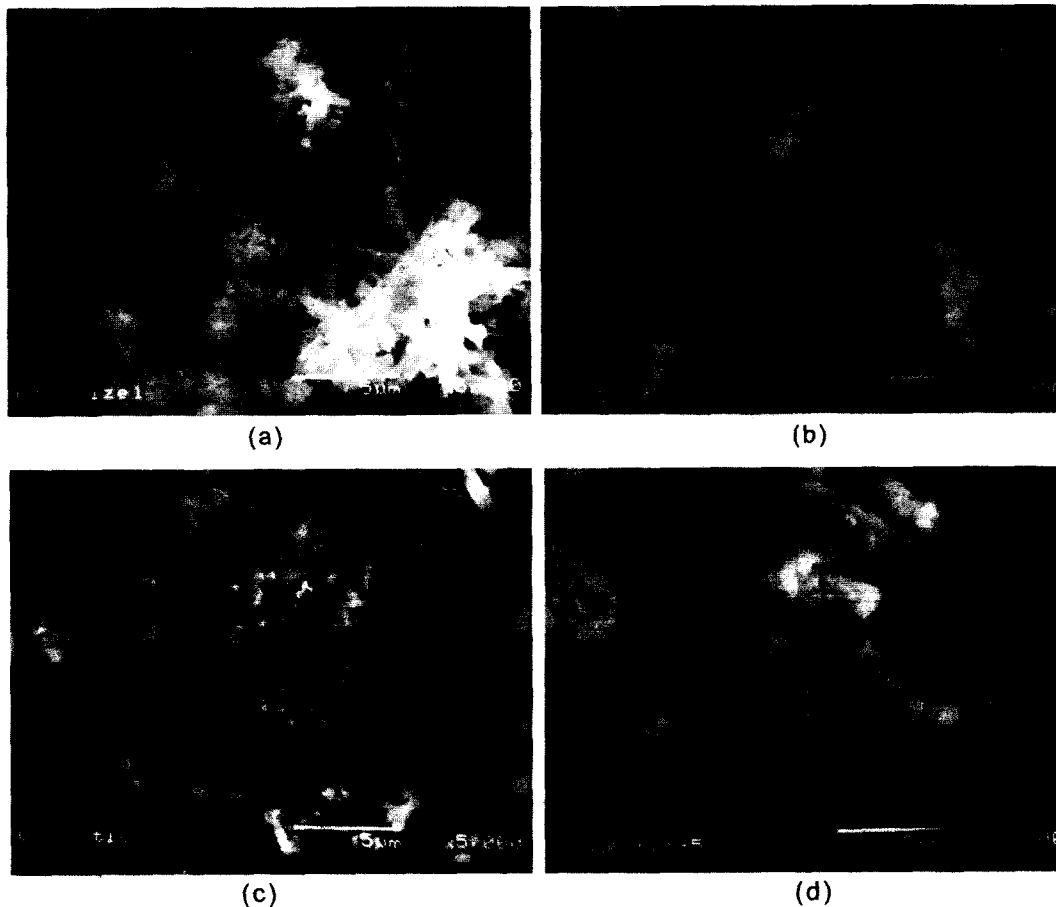


Fig. 4. SEM micrographs of the SHS products of the starting powder mixture with (a) sample 3, (b) sample 4, (c) sample 5, and (d) sample 6.

Table 2. Length, Width and Aspect Ratio of the Whiskers Prepared by SHS Reaction

	Sample 3	Sample 4	Sample 5	Sample 6
Length (μm)	3 ± 1.4	4.21 ± 2	3.37 ± 1.33	2.65 ± 1.13
Width (μm)	0.68 ± 0.35	0.89 ± 0.38	0.84 ± 0.75	0.7 ± 0.47
Aspect ratio	4.77 ± 2	4.86 ± 1.6	4.98 ± 2.21	4.4 ± 1.78

distribution. Fig. 4(c) shows that the product from the powder mixture of 60 wt% Si - 37 wt% $\alpha\text{-Si}_3\text{N}_4$ - 3 wt% Y_2O_3 contained very large particles as well as fine elongated particles. Width of the large particles was as large as 3.5 μm as indicated by the arrow. Some of grains in the product shown in Fig. 4(d) were coarse and in irregular shapes. Average size and aspect ratio of the elongated particles prepared from the powder mixtures are shown in Table 2. The values in Table 2 were obtained from measuring only the elongated particles. The elongated particles obtained from the powder mixture of 50 wt% Si - 47 wt% $\alpha\text{-Si}_3\text{N}_4$ - 3 wt% Y_2O_3 have the maximum length and width. The average aspect ratios of the whiskers were between 4.4 and 5, and did not show a consistent relationship with the composition of the starting powder mixture.

Nitridation of Si has been reported to result in $\alpha\text{-Si}_3\text{N}_4$ or $\beta\text{-Si}_3\text{N}_4$ depending on how it occurs.¹⁸⁾ The former forms by gas phase reaction between silicon monoxide and nitrogen while the latter forms by direct reaction between solid Si and nitrogen. In the current study, $\beta\text{-Si}_3\text{N}_4$ particles formed by direct reaction between Si and nitrogen and they grew into elongated grains when there were proper liquid and enough amount of $\alpha\text{-Si}_3\text{N}_4$ particles. When the starting powder mixtures contained 57 wt% and 47 wt% $\alpha\text{-Si}_3\text{N}_4$, the elongated grains were well developed during SHS reaction. Even though the temperature could not be measured, it must be high enough for the grain growth. As the starting powder mixture contained more Si, more $\beta\text{-Si}_3\text{N}_4$ were formed during the reaction. Growth of the elongated $\beta\text{-Si}_3\text{N}_4$ grain in the length direction was hindered when the grain was impinged upon another $\beta\text{-Si}_3\text{N}_4$ grain as reported by Kramer *et al.*¹⁹⁾ Therefore, low aspect ratios of the elongated grains in Fig. 4(d) can be explained by larger number of $\beta\text{-Si}_3\text{N}_4$ grains formed by reaction between Si and nitrogen. Grains with irregular shapes shown in Fig. 4(d) suggests that there was extensive nitridation reaction between Si and nitrogen in the sample and some grains were sintered during the reaction. Since the particles had low aspect ratio and some of them were too large, the powder mixture with > 70 wt% Si does not seem proper for making the seed particles by SHS method. Even though the particles shown in Fig. 4(a) and (b) had proper shapes, further study is required for separating those particles individually for actual use as seeds.

Conclusion

$\beta\text{-Si}_3\text{N}_4$ particles with elongated shapes were successfully

prepared from the powder mixtures of Si, $\alpha\text{-Si}_3\text{N}_4$ and Y_2O_3 by SHS method when Si content was between 40 wt% and 70 wt%. Average width and length of the elongated particles prepared from the powder mixture of 50 wt% Si, 47 wt% $\alpha\text{-Si}_3\text{N}_4$ and 3 wt% Y_2O_3 was the maximum. Average aspect ratios of the elongated particles were between 4.4 and 5. However, large particles with low aspect ratio appeared in the product prepared from the powder mixture with 60 wt% Si and some of the particles in the product from the powder mixture with 70 wt% Si were larger than 5 μm and had irregular shape. Since the SHS product was very porous and easily broken, it can be used for making the seed particles with elongated shapes when the starting powder mixtures consisted of 40 - 50 wt% Si, 57 - 47 wt% $\alpha\text{-Si}_3\text{N}_4$ and 3 wt% Y_2O_3 .

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