

ENGINEERED CERAMICS . . . [I]

Si₃N₄.....Synthesis, Sintering Behavior and Mechanical Property

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High quality Si₃N₄ powder was developed by the method of the thermal decomposition of Si(NH)₂. It was characterized and its sintering behavior was studied.

Densification study indicated that the highly pure, fine Si₃N₄ powder with a narrow particle size distribution was sinter-active, and dense β'-sialon-alloys were produced by reaction sintering of the highly pure, sinterable Si₃N₄, Al₂O₃, AlN, Y₂O₃. High temperature strength was improved by the reduction of excess of oxygen in sialon system.

1. Introduction

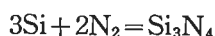
Silicon nitride based ceramics are candidate materials for high temperature applications because of their high strength and thermal shock resistance. However, further improvement in properties of sintered silicon nitride ceramics should be done. Especially, the improvement in high temperature properties, e.g., strength and oxidation resistance is necessary.

As well known, the characteristics of the starting powder affect the properties of final products and the development of the high quality powders plays an important role to fabricate high performance ceramics. Among many methods, the thermal decomposition of Si(NH)₂ is considered to be suitable for use of Si₃N₄ powder because of the powder with high quality and high productivity.

2. Preparation Methods for Silicon Nitride Powders

[1] Nitridation of silicon powder

The most common process for the production is the reaction of the element¹⁾.



The raw silicon nitride formed in the nitridation process is milled and purified by chemical treatments.

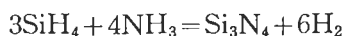
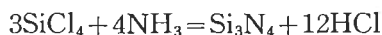
[2] Reduction of silica

Fine grain silica with excessive proportion of carbon reacts according to the equation²⁾:



[3] Vapour phase reactions

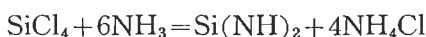
Gaseous silicon compounds such as silicon tetrachloride or silane react with ammonia and amorphous Si₃N₄ powder is produced at about 1000°C³⁾.



The amorphous powder is calcined to crystallize α - Si_3N_4 .

[4] Thermal decomposition of $\text{Si}(\text{NH})_2$

Silicon tetrachloride easily reacts with ammonia to give silicon diimide and ammonium chloride at lower temperature^{4~7)}.



Silicon diimide is calcined to produce Si_3N_4 .

3. Characteristics of Different Types of Silicon Nitride Powders

The general requirement for the powder is shown in Fig. 1.

Silicon nitride powders produced by different production method have different powder characteristics. Table 1 provides the characteristics of four types of silicon nitride powders. Si_3N_4 powder by the thermal decomposition is produced by us.

Regarding the metallic impurity, silicon nitride powders produced by the vapour phase reaction and thermal decomposition of $\text{Si}(\text{NH})_2$ are highly pure. This difference will be due to that of purity of raw material (Si compounds). Remarkable differences occur in particle shape, particle size, particle size distribution. Fig. 2 shows scanning electron micrographes of the four silicon nitride powders.

Silicon nitride powder produced by the thermal decomposition of silicon diimide is more uniform in particle size and shape than those of other powders. Si_3N_4 powder produced by us would almost meet the general requirement.

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- (1) Fine particle
 - (2) Free of oxygen
 - (3) Narrow particle size distribution
 - (4) Equi-axis particle
 - (5) Phase control
 - (6) Composition (purity, stoichiometry)
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Fig. 1 Requirement for the powder.

Table 1 Characteristics of four types of Si_3N_4 powders

Preparation method	Nitridation of Si	Reduction of silica	Vaporphase reaction	Thermal decomposition of $\text{Si}(\text{NH})_2$		
Powder No.	A	B	C	TS-7	TS-8	TS-9
<i>chemical purity</i>						
Fe ppm	300	70	—	50	50	50
Ca ppm	300	100	<10	<10	<10	<10
Al ppm	1,000	2,000	<20	10	60	60
Mo ppm	—	—	<100	—	—	—
O %	2.0	2.0	2.9	1.0	2.0	2.0
<i>phases</i>						
amorphous %	—	—	40	—	—	—
α -phase %	95	98	56	86	93	86
Specific surface area m^2/g	20	5	4	12	15	15
Grain size μm	0.1—1	0.2—1.2	0.2—4	0.1—0.3	0.1—0.3	0.1—0.3

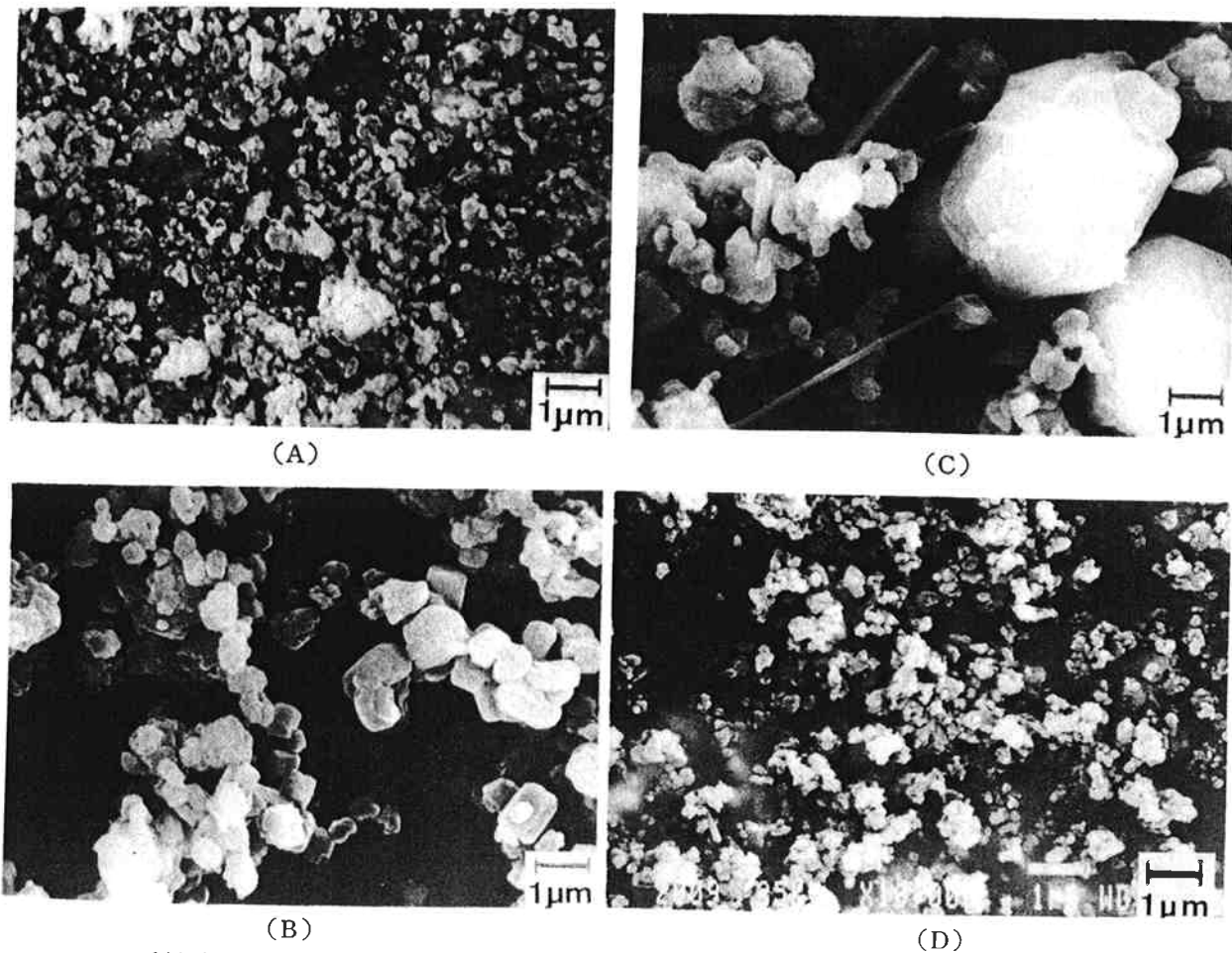
4. Synthesis of Si_3N_4 Powder by Thermal Decomposition of $\text{Si}(\text{NH})_2$

The initial problems for the characteristics of powder by thermal decomposition of $\text{Si}(\text{NH})_2$ were anionic impurities (oxygen, chlorine) and particle shape (needle-like particle). We improved it by following technique.

The synthesis of Si_3N_4 powder by thermal decomposition of $\text{Si}(\text{NH})_2$ is based on the steps shown as follows: Fig. 3. Silicon tetrachloride easily reacts with ammonia to produce $\text{Si}(\text{NH})_2$ and NH_4Cl in inert atmosphere.

In the second step, the mixture of $\text{Si}(\text{NH})_2$ and NH_4Cl are calcined in gaseous ammonia stream to remove the chlorine at about $900^\circ\text{C}^{\text{B}}$. Intermediate silicon compound reacts with HCl dissociated from NH_4Cl to form imidechloride ($\text{Si}_2\text{N}_3\text{H}_2\text{Cl}$) during the sublimation of NH_4Cl . Ammonia is effective to remove chlorine at lower temperature, while the chlorine can't be removed below 1000°C in inert atmosphere.

In the third step, the compacted intermediate product ($\text{Si}_2\text{N}_3\text{H}$, oxygen content 1.0 wt%, chlorine content 0.7 wt%) was calcined to crystallize to $\alpha\text{-Si}_3\text{N}_4$. The compacted intermediate was inserted in hot zone, and kept for five minutes. The calcinated products were analysed by X-ray diffraction, and crystallization temperature under various atmosphere was determined. The crystallization temperature depends on the nitrogen partial pressure as shown in Fig. 4.



(A) Nitridation of Si, (B) Reduction of Silica, (C) Vapour phase reaction, (D) Thermal decomposition of $\text{Si}(\text{NH})_2$.

Fig. 2 Silicon nitride powders formed by 4 preparative methods.

1. Synthesis of $\text{Si}(\text{NH})_2$
 $\text{SiCl}_4 + 6\text{NH}_3 = \text{Si}(\text{NH})_2 + 4\text{NH}_4\text{Cl}$
2. Removal of Chlorine
 $\text{Si}(\text{NH})_2 + 4\text{NH}_4\text{Cl} = 1/2\text{Si}_2\text{N}_3\text{H} + 1/2\text{NH}_3 + 4\text{NH}_4\text{Cl}$
 900°C
 NH_3 stream
3. Crystallization
 $\text{Si}_2\text{N}_3\text{H} = 2/3\text{Si}_3\text{N}_4 + 1/6\text{N}_2 + 1/2\text{H}_2$
 1500°C
4. Dry milling

Fig. 3 Silicon nitride powder production.

In lower nitrogen pressure region than solid line, silicon is formed, accompanied with Si_3N_4 . In higher nitrogen pressure region than solid line, crystallization doesn't occur. The solid line (experimental data) is parallel to broken line (equilibrium pressure). These results suggest that the mechanism of crystallization occurs by dissociation and precipitation via gas phase such as silicon and nitrogen. The compaction of the intermediate compounds was effective to produce spherical particles, due to reduction of space that allowed the formation of needle-like particle. The silicon nitride powder formed in the crystallization process consists of agglomerates of fine particles with a narrow particle size distribution.

In the final step, a fine powder is produced by dry milling.

5. Sintering of Si_3N_4

A primary objective of our silicon nitride research has been the development of a sinterable powder and the improvement of the mechanical properties at high temperature using it. Improved mechanical properties of dense Si_3N_4 are anticipated by reducing the amount of residual glassy phase. However, the sintering rate of Si_3N_4 is decreased by reducing the amount of glassy phase or increasing the viscosity of the glassy phase, therefore, sinterable powder is required to densify to high density with small amount of additive.

[1] Sintering behavior of Si_3N_4 powder

Fig. 5 shows densification curves for two different powders. Compacts were embedded in BN powder and sintered under 0.1 MPa nitrogen. The TS-9 powder densified to nearly theoretical density, while powder A resulted in lower density (the much finer

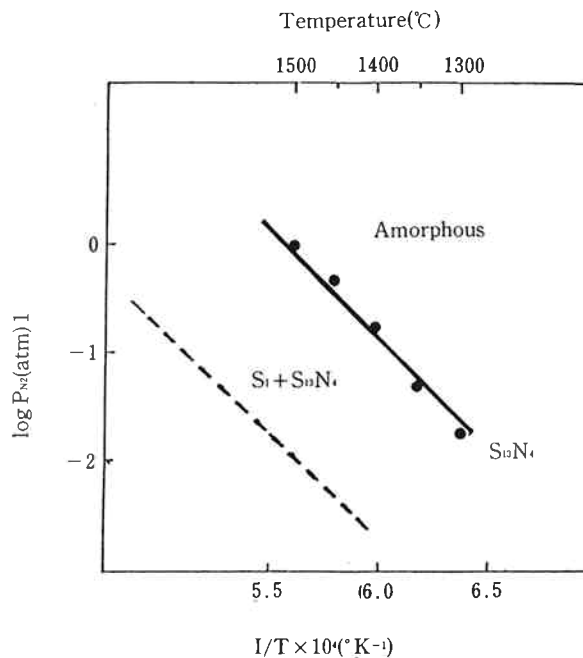


Fig. 4 Dependence of nitrogen partial pressure on crystallization temperature. Solid line represents experimental data and broken line represents equilibrium pressure.

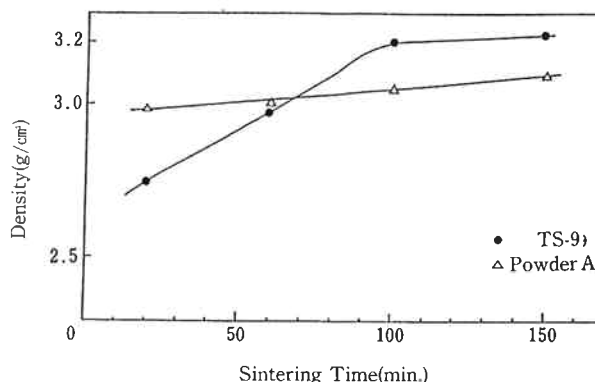


Fig. 5 Densification curves of $\text{Si}_3\text{N}_4/5\text{wt}\% \text{Y}_2\text{O}_3/5\text{wt}\% \text{Al}_2\text{O}_3$ at 1750°C.

and the high oxygen content). Electron micrographs of sintered Si_3N_4 specimens are shown in Fig. 6. Remarkable grain growth could be seen in Fig. 6 (A). Higher rate of grain growth could be related to wider particle size distribution and higher metallic impurities in powder A than in TS-9 powder. The difference in bulk density of sintered material might be based on that of the grain growth during sintering. On this viewpoint, the important characteristics for sinterable powder might be not only fine particles but also narrow particle size distribution and low metallic impurities.

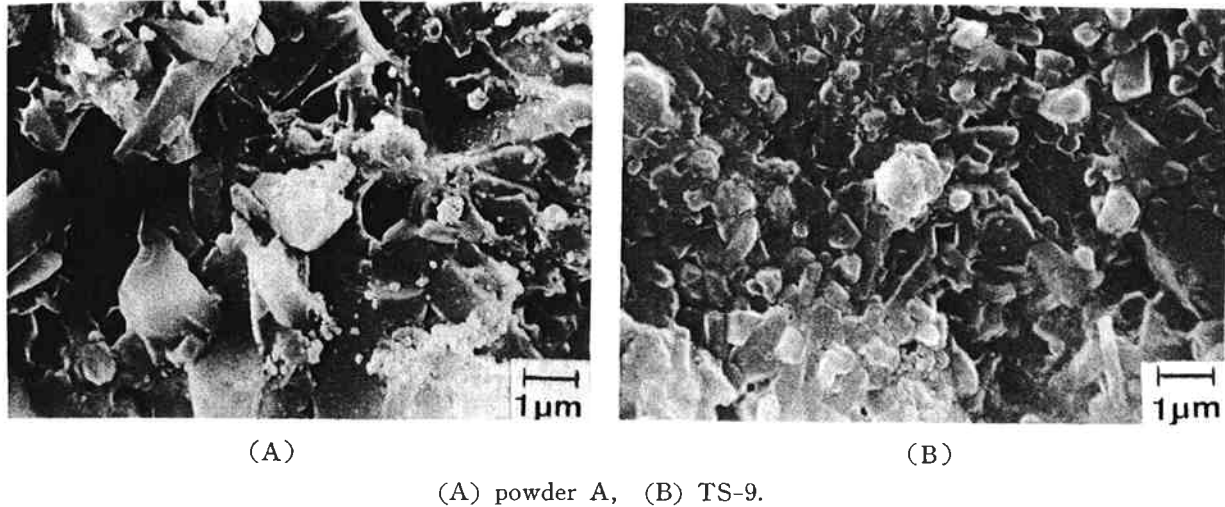


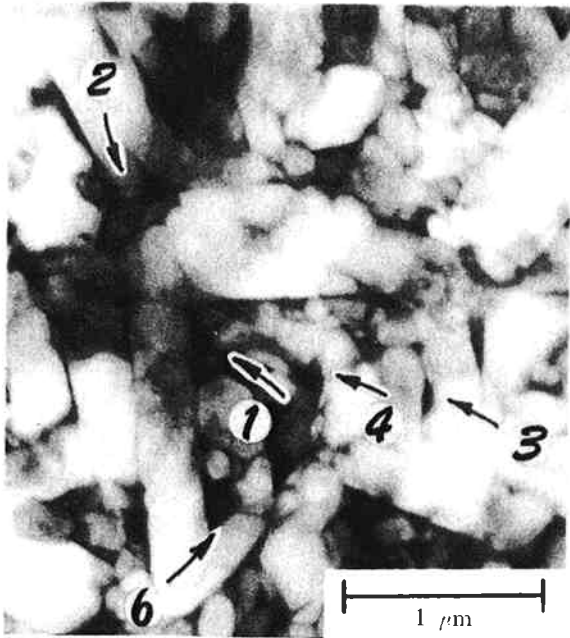
Fig. 6 Microstructure of $\text{Si}_3\text{N}_4/5\text{wt}\% \text{Y}_2\text{O}_3/5\text{wt}\% \text{Al}_2\text{O}_3$ sintered at 1750°C for 150min.

Table 2 Powder composition and properties of sintered materials

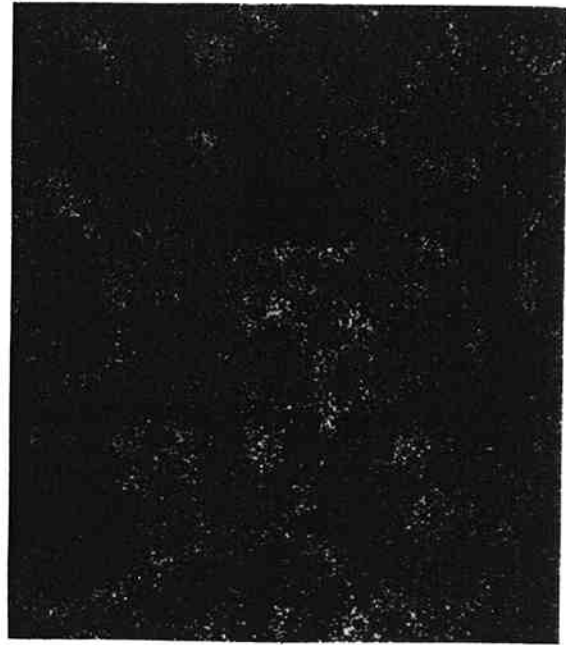
Powder	Sintering aids					Bulk ¹⁾ density (g/cm ³)	Bending strength ²⁾	
	Al_2O_3 (wt%)	AlN (wt%)	Z-value	excess O (eq%)	Y_2O_3 (wt%)		$\sigma_{\text{R.T.}}$ (Mpa)	$\sigma_{1200^\circ\text{C}}$ (Mpa)
TS-7	5	—	0.29	3.35	5	3.24	810	410
	2.5	2.0	0.29	1.51	5	3.25	820	510
	1.2	3.0	0.29	0.56	5	3.19	720	440
	—	4.0	0.29	-0.33	5	3.10	740	560
	—	6.5	0.41	-1.43	5	3.17	760	550
TS-8	5	—	0.29	3.94	5	3.24	790	350
	2.5	2.0	0.29	2.04	5	3.25	820	490
	1.2	3.0	0.29	1.13	5	3.25	740	470
	—	4.0	0.29	0.18	5	3.18	740	680
	—	6.5	0.41	-0.87	5	3.22	750	640
TS-9	5	—	0.29	3.94	5	3.23	820	410
	2.5	2.0	0.29	2.09	5	3.26	980	410
	1.2	3.0	0.29	1.13	5	3.25	810	450
	—	4.0	0.29	0.18	5	3.26	790	580
	—	6.5	0.41	-0.87	5	3.25	800	660

1) Sintering condition, 1850°C 4 hrs, Gas pressure 1 Mpa

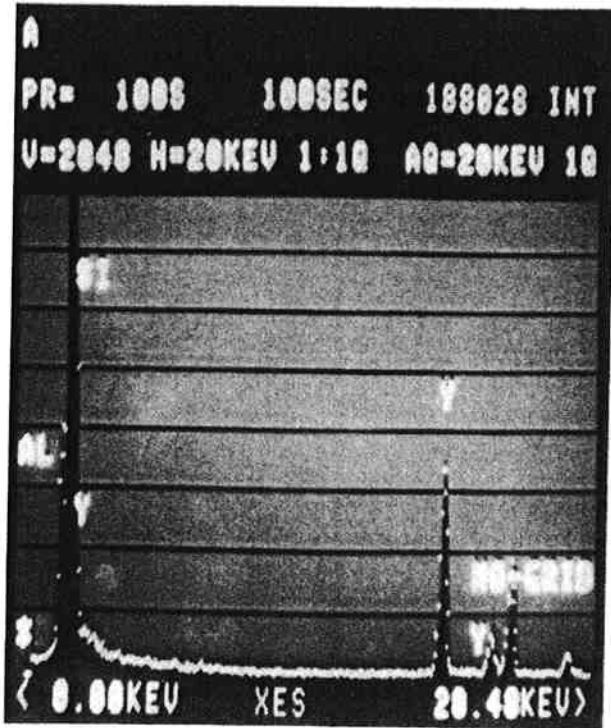
2) Test method, 3 point bend, side $3 \times 4 \times 40$ span 30 mm



STEM image



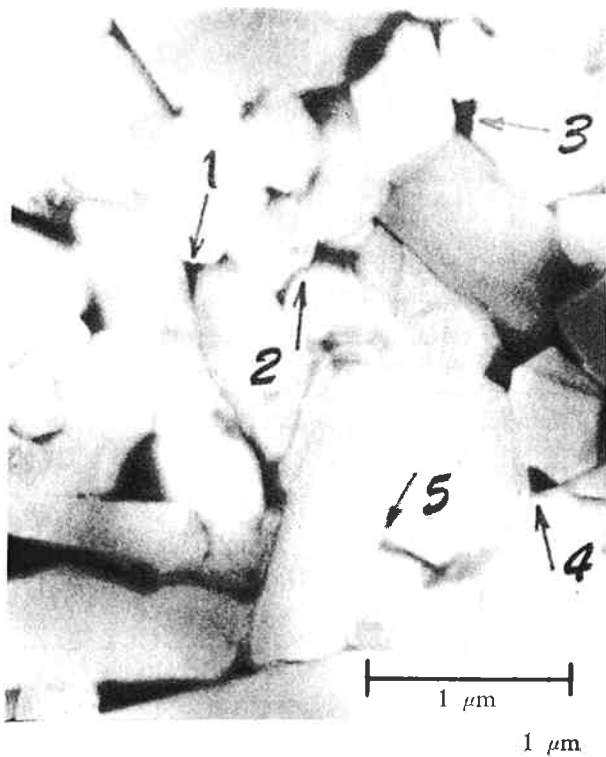
Y mapping



(A)

(A) $\text{Si}_3\text{N}_4/5\text{wt}\% \text{Y}_2\text{O}_3/5\text{wt}\% \text{Al}_2\text{O}_3$.

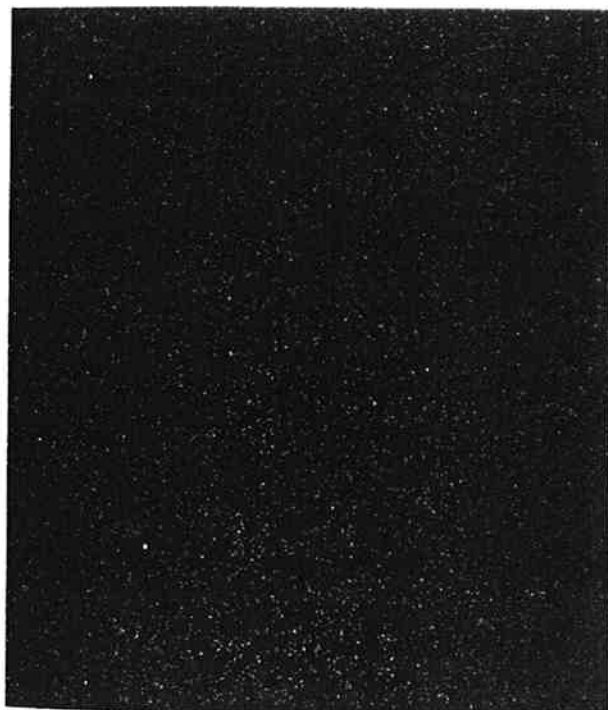
Fig. 7 Scanning transmission electron micrographs.



STEM image



Y mapping



AL mapping

(B)

(B) $\text{Si}_3\text{N}_4/5\text{wt}\% \text{Y}_2\text{O}_3/4\text{wt}\% \text{AlN}$

Fig. 7 Scanning transmission electron micrographs,

[2] Improvement of high temperature strength

Dense silicon nitride materials can be pressureless sintered using sintering aids. Though use of sintering aids promotes the densification, it results in the existence of intergranular glassy phase. This glassy phase will be responsible for the degradation of high temperature strength. Better high temperature strength was achieved by crystallization of the glassy phase in ceramics of SiYAION system⁹⁾.

It is the purpose of the present investigation to achieve the improvement of high temperature strength using highly pure, sinterable powder without annealing treatments. β' -sialon alloys with excess of oxygen as compared to the theoretical solid solution composition were sintered using 5wt% Y_2O_3 as a sintering aid (Table 2). High temperature strength was dependent on composition and improved by the reduction of excess of oxygen. Scanning transmission electron micrographs show existence of glassy phases (dark region) (Fig. 7). The element of Si, Al, Y were concentrated in the glassy phases while other impurities were not detected. Table 3 shows the amount of Si, Al, Y in intergranular phases. The differences in the amount of the glassy phase for both materials were observed. These results would support the importance of highly pure, sinter-active powder.

Table 3 Elementary analysis of intergranular glassy phases

Material	No.	Si (atm%)	Al	Y
A	1	81	9	10
	2	77	13	16
	3	75	11	14
	4	74	12	14
	5	65	15	21
B	1	77	10	13
	2	74	10	16
	3	45	18	38
	4	68	11	22
	5	69	11	20

6. Conclusions

[1] $Si(NH)_2$, which was prepared by the ammonolysis of $SiCl_4$, was calcined to remove chlorine in ammonia stream at about $900^\circ C$, and amorphous intermediate product (Si_2N_3H) was obtained. Crystallization of amorphous intermediate product was strongly dependent on the nitrogen partial pressure, and crystallization mechanism via gas phase was suggested. Si_3N_4 powder by this method was highly pure and composed of equiaxed particles with a narrow particle size distribution.

[2] Si_3N_4 powder by this method was very sinter-active, and highly dense sintered material with fine grained microstructure was obtained.

[3] The series of ceramics of SiYAION system with excess of oxygen as compared to β' -Sialon, $Si_{6-z}Al_zN_8-zO_z$ were prepared. High temperature strength was improved by reduction of excess of oxygen without annealing treatments.

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