

## Homogeneous Mixing of $\text{Si}_3\text{N}_4$ with Sintering Additives by Coprecipitation Method

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### 질화규소와 소결첨가제의 공침법에 의한 균일혼합

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#### ABSTRACT

Chemically and geometrically homogeneous mixing of  $\text{Si}_3\text{N}_4$  powders with sintering additives( $\text{YAG}$ ,  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ ) was attempted via coprecipitation method. X-ray dot maps for the additive elements(Al and Y) showed that the additives are evenly distributed in the powder mixture prepared by coprecipitation method(CP). TEM observation of the coprecipitation-treated  $\text{Si}_3\text{N}_4$  powders revealed that they are covered with extremely fine crystallites of additive. The shift in isoelectric point(IEP) of  $\text{Si}_3\text{N}_4$  powders from pH 6.7 to pH 7.9 after coprecipitation mixing gave another evidence for coating of  $\text{Si}_3\text{N}_4$  powders with YAG additives. SIMS analysis for composition on the surface and in the matrix of mixed powders showed that the YAG additives are highly enriched on the surface of coprecipitation-treated  $\text{Si}_3\text{N}_4$  powders. Especially when a small amount of additive was used, the effect of homogeneous additive distribution on densification was perceptible: After pressureless-sintering of powder compacts containing 5 mol% YAG at  $1800^\circ\text{C}$  for 0.5h, a sintered density of 96.5% theoretical was obtained from the specimens prepared by coprecipitation in comparison with 93.8% from the mechanically-mixed one.

#### 요 약

공침법을 이용한 질화규소와 소결첨가제( $\text{YAG}$ ,  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ )의 균일혼합 가능성을 조사하였다. 혼합분말 내의 소결첨가제를 구성하고 있는 Al과 Y 원소에 대한 X-선 mapping 결과, 공침혼합된 분말 내의 첨가제 분포가 매우 균일함을 알 수 있었으며, 이들 첨가제들이 질화규소 분말표면에 미세한 입자형태로 존재함을 투과전자현미경으로 관찰하였다. 또한, 공침혼합 전의 질화규소 분말의 등전점(isoelectric point)이 pH 6.7임에 반해 혼합 후에는 pH 7.9로서, 첨가된 YAG의 등전점 측으로 이동함을 확인하여, 소결첨가제의 혼합이 피복에 가까운 형태로 이루어짐을 알 수 있었다. 혼합분말의 표면과 내부의 조성을 SIMS로 분석한 결과, 기계적 혼합분말에 비해 공침혼합분말의 경우, 표면에서의 소결첨가제 조성이 내부에서보다 월등히 높은 것으로 나타나, 이상의 결과들과 함께 공침법을 통한 균일혼합의 가능성을 확인하였다. 공침법에 의한 균일혼합은 특히 소량의 소결첨가제가 혼합된 경우 소결성에 영향을 미쳐,  $1800^\circ\text{C}$ 에서 0.5시간 동안 상압소결시켰을 때, 기계적 혼합의 경우에는 이론밀도의 93.8%의 소결밀도를 나타낸 반면, 공침혼합에서는 96.5%의 소결밀도를 얻을 수 있었다

#### 1. Introduction

It is impossible to obtain a complete densification of  $\text{Si}_3\text{N}_4$  by pressureless sintering without sintering ad-

ditives due to its strong covalent bonding character and low volume diffusion coefficient even at high temperature. The melt which forms from the reaction of additives with inherent oxide layer on  $\text{Si}_3\text{N}_4$  powders

enhances the densification through a liquid-phase sintering mechanism. However, most of this liquid phase remains as glassy grain-boundary phase which affects high temperature properties in a detrimental way. Therefore, a small amount of sintering additive is needed to reduce the amount of residual glassy phase. But when a small amount of additives are used, it is difficult to mix them homogeneously with  $\text{Si}_3\text{N}_4$  powders. Inhomogeneous distribution of additives may cause a formation of microstructural inhomogeneities in consequence of undesirable sintering behaviors like local densification and decrease in mechanical properties<sup>12</sup>.

Other previous works on the surface characters and the electrophoretic behavior of  $\text{Si}_3\text{N}_4$  powders<sup>5-8</sup> have pointed out that  $\text{Si}_3\text{N}_4$  powders have highly negative zeta-potential in high pH range and thereby form a stable suspension. This suggested the possibility of a precipitation method for additive doping onto the  $\text{Si}_3\text{N}_4$  powders. Recently, several investigations have been performed for the homogeneous mixing of  $\text{Si}_3\text{N}_4$  powders with additives through precipitation from salt-solution<sup>9</sup> and hydrolysis of metal alkoxides<sup>10-12</sup>.

Shaw et. al.<sup>9</sup> added  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  to  $\text{Si}_3\text{N}_4$  through precipitation of aluminium and yttrium salt-solution. An improvement in the sinterability due to a homogeneous distribution of additives was obtained for the precipitation-mixed powder in comparison with the mechanically-mixed one. Kishi et al.<sup>10</sup> used a method of Al-alkoxide hydrolysis for the addition of  $\text{Al}_2\text{O}_3$  to  $\text{Si}_3\text{N}_4$  and obtained higher strength than for mechanically prepared powder mixtures. Similar results have been reported by Greil et al.<sup>11</sup>, where MgO and  $\text{Al}_2\text{O}_3$  were concurrently added also with use of alkoxides.

In this work, an improved geometrical and chemical homogeneity of sintering additive ( $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ ) in  $\text{Si}_3\text{N}_4$  powders was studied by coprecipitation of metal hydroxides from nitrate salt-solution. The distribution of additive elements (Al and Y) and the mixing homogeneity were investigated with WDS (Wavelength Disper-

sive Spectrometry) and SIMS (Secondary Ion Mass Spectrometry). As an alternative way for the same purpose, zeta-potentials of  $\text{Si}_3\text{N}_4$  powders were measured at different pH values and the change in isoelectric point (IEP) before and after mixing was determined. The sintered properties such as sintered density, weight loss, and linear shrinkage were measured. Microstructures of sintered powder compacts were observed.

## 2. Experimental Procedure

Two different kinds of  $\text{Si}_3\text{N}_4$  powder mixtures were prepared by coprecipitation of metal hydroxides from nitrate salt-solutions (CP) and by conventional mechanical mixing (MM), respectively. As an additive,  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  (YAG) compound was chosen. The additive contents were 5, 10 and 15 mol%. The characteristics of the  $\text{Si}_3\text{N}_4$  used are given in Table 1.

For preparation of powder mixtures through coprecipitation, a solution of  $\text{Y}(\text{NO}_3)_3/\text{Al}(\text{NO}_3)_3$  with 3:5 molar ratio was sprayed into a suspension of  $\text{Si}_3\text{N}_4$  in  $\text{NH}_4\text{OH}$ , being stirred by mechanical agitation. The liquid including the residual reactant and the product ( $\text{NH}_4^+$ ,  $\text{OH}^-$  and  $\text{NO}_3^-$ ) was eliminated from the precipitation-treated powder suspension through a repeated filtering and washing with neutralized water and ethanol. After drying at 120°C for 24 hr in air, powder mixtures were calcined at 700°C (CPN7) and 900°C (CPN9) for 1 hr in flowing  $\text{N}_2$  gas. Hard agglomerates formed during drying and calcining could be completely destroyed by attrition in isopropanol for 1.5 hr, using 2.6 mm diameter alumina balls. Mechanically mixed  $\text{Si}_3\text{N}_4$  powders with  $\text{Y}_2\text{O}_3$ <sup>2</sup> and  $\text{Al}_2\text{O}_3$ <sup>3</sup> were prepared in attrition mill for 4 hr, also using alumina balls and isopropanol (MM).

To determine the homogeneity of additive distributions, analyses with WDS and SIMS were carried out. As an indirect method for the same purpose, zeta-potential was measured<sup>4</sup> for the as-received  $\text{Si}_3\text{N}_4$ , the YAG powders produced by coprecipitation and the prepared powder mixtures at various pH, respectively.

Table 1. Characteristics of  $\text{Si}_3\text{N}_4$  Powders Used

Element [wt%]							$\alpha$ -fraction	BET surface area
Si	N	O	C	Fe	Al	Ca	(%)	( $\text{m}^2/\text{g}$ )
59.30	38.43	2.01	0.17	0.02	0.05	0.01	$\approx 95$	19.7

**Table 2.** Results of Chemical Analysis for Composition of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  in the YAG Produced by Coprecipitation and the Prepared  $\text{Si}_3\text{N}_4$  Powder Mixtures

Sample	Calculated		Measured		Difference	
	$\text{Al}_2\text{O}_3$	$\text{Y}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Y}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Y}_2\text{O}_3$
YAG	42.9	57.1	42.5	56.8	-0.4	-0.3
5CPN9	2.3	3.0	4.4	3.4	2.1	0.4
5MM			4.1	3.1	1.8	0.1
10CPN9	4.5	6.0	6.0	5.9	1.5	-0.1
15CPN9	6.8	9.0	8.2	8.5	1.4	-0.5

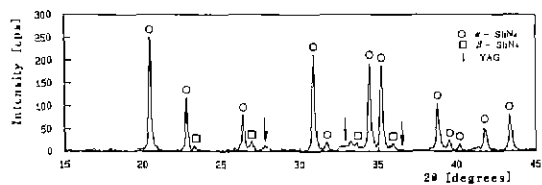
Prepared powder mixtures were cold-isostatically pressed into a cylindrical shape with a dimension of 14 mm diameter  $\times$  12 mm height under a pressure of 200 MPa. Green densities were 55~57% of theoretical which was calculated from the rule of mixtures.

Sintering was performed in a graphite furnace at various temperatures (1500~1800°C) under 0.15 MPa  $\text{N}_2$ -atmosphere in  $\text{Si}_3\text{N}_4$  powder bed. The furnace was heated up to 1000°C with a heating rate of 50°C/min and then to the sintering temperature at 10°C/min. The hold time at sintering temperature was 0.5 hr. After sintering, weight loss, linear shrinkage and sintered density were determined. The phases were identified by XRD<sup>6</sup> with a step speed of 1.2°/min. Powder morphology and microstructure of sintered bodies were observed by TEM<sup>6</sup> and SEM<sup>7</sup> after plasma-etching<sup>8</sup>.

### 3. Results and Discussion

#### 3.1. Chemical Composition and XRD Analysis

The compositions of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  in the YAG powders produced by coprecipitation and the  $\text{Si}_3\text{N}_4$  powder mixtures with various amounts of YAG were analyzed. The results are summarized in Table 2. The measured composition of YAG powders shows that the coprecipitation reaction was successfully performed with a cor-



**Fig. 1.** XRD pattern of coprecipitation-treated  $\text{Si}_3\text{N}_4$  powders containing 10 mol% YAG after calcining at 900°C.

rect stoichiometry. But, irrespective of preparation methods, all the  $\text{Si}_3\text{N}_4$  powder mixtures have an excess  $\text{Al}_2\text{O}_3$  content than expected, whereas any remarkable differences in  $\text{Y}_2\text{O}_3$  content are not detected. This excess  $\text{Al}_2\text{O}_3$  seems to be resulted from the wear of milling media.

Fig. 1 shows the XRD patterns for the  $\text{Si}_3\text{N}_4$ -10 mol% YAG powder mixtures prepared by coprecipitation and calcining at 900°C for 1 hr in flowing  $\text{N}_2$  atmosphere. In spite of the incomplete crystallization, the peaks corresponding to YAG can be easily seen in the given diffraction pattern.

#### 3.2. X-Ray Dot Maps for Additive Elements

Distribution of additive elements (Al and Y) in the prepared powder mixtures containing 10 mol% YAG was investigated with WDS. X-ray dot maps for Al and Y on the surface of green compacts are given with SEM images in Fig. 2. The Al X-ray maps reveal that  $\text{Al}_2\text{O}_3$  is evenly distributed in the coprecipitation-mixed sample (CPN9, Fig. 2(a)), whereas the locally-concentrated bright spots in Fig. 2(b) show that a local enrichment of  $\text{Al}_2\text{O}_3$  can occur in the mechanically-mixed one (MM). Although the difference in Y-distribution between CPN9 and MM is not so noticeable as in the

<sup>1</sup>LC12-S, H. C. Starck, Berlin, FRG

<sup>2</sup>H. C. Starck, Berlin, FRG

<sup>3</sup>A-16G, Alcoa, Pittsburgh, USA.

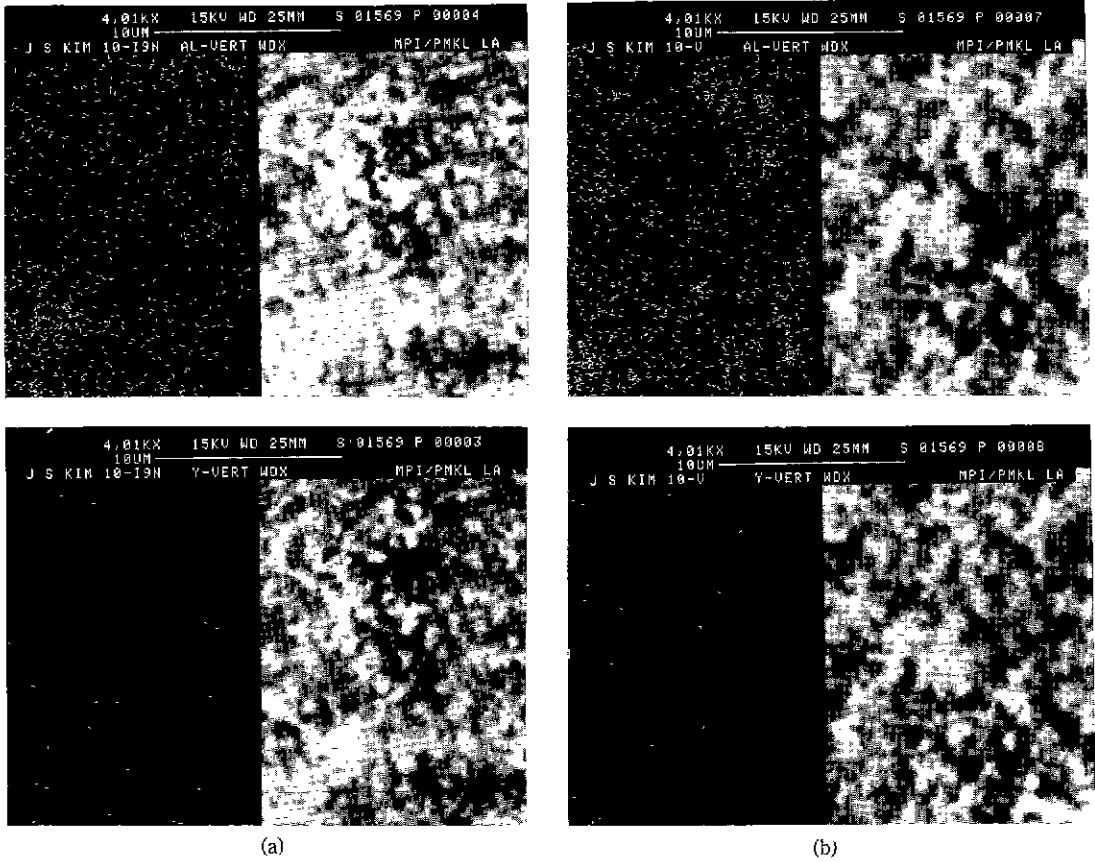
<sup>4</sup>Zetasizer IIc, Malvern, Worcestershire, UK.

<sup>5</sup>PW1820, Phillips, Eindhoven, the Netherlands.

<sup>6</sup>Jeol 2000FX, Japan.

<sup>7</sup>Stereoscan S-200, Cambriggs Instruments, UK.

<sup>8</sup>PT 7150, Bio-Rad Semiconductor Measurement Systems, MA, USA.



**Fig. 2.** SEM images of  $\text{Si}_3\text{N}_4$  powder compacts containing 10 mol% YAG with X-ray dot maps for Al(upper) and Y(lower): Prepared by (a) coprecipitation and (b) mechanical mixing.



**Fig. 3.** TEM image of coprecipitation-treated  $\text{Si}_3\text{N}_4$  powders with 5 mol% YAG.

case of Al, relatively many particles with no detection spots for Y can be observed in MM.

### 3.3. TEM Observation of Coprecipitation-Treated $\text{Si}_3\text{N}_4$ Powders

The morphology of coprecipitation-treated  $\text{Si}_3\text{N}_4$  powders with 5 mol% YAG was observed with TEM and the result is given in Fig. 3. It is clear that  $\text{Si}_3\text{N}_4$  powders with a particle size of 0.2~0.5  $\mu\text{m}$  are covered with extremely fine additive crystallites. However, the agglomerates composed of additive crystallites only and the surface of  $\text{Si}_3\text{N}_4$  free from additives are also observable. This means that a completely ideal coating of  $\text{Si}_3\text{N}_4$  with additive was not still achieved.

### 3.4. Zeta-Potential Measurement

It is well known that a modification of powder

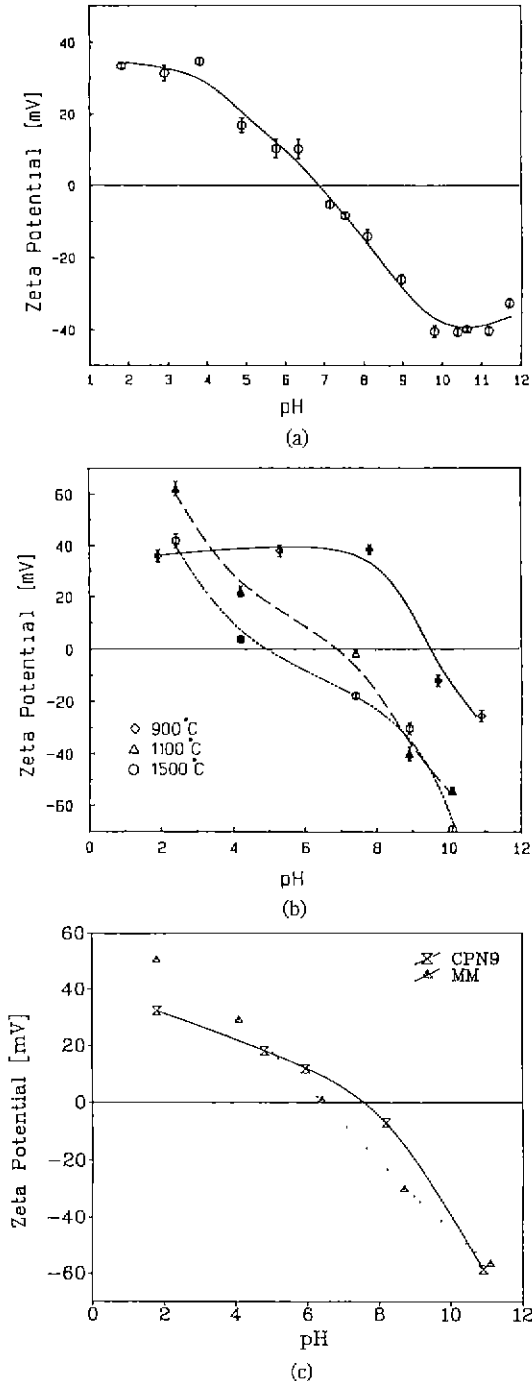


Fig. 4. Change in zeta potentials as a function of pH for (a) as-received  $\text{Si}_3\text{N}_4$ , (b) YAG produced by coprecipitation and subsequent calcination at various temperatures, and (c) prepared powder mixtures (CPN9 and MM) containing 10 mol% YAG.

surface character leads to the change of zeta-potentials<sup>11-15</sup>. Based on this fact, some pretreatments of  $\text{Si}_3\text{N}_4$  powders like surface oxidation<sup>16</sup> or acid leaching<sup>17</sup> have been already attempted to obtain high negative zeta-potentials in a high pH-range through an increase in silanol site density on the  $\text{Si}_3\text{N}_4$  surface. Such treatments of  $\text{Si}_3\text{N}_4$  accompanied a shift in the isoelectrical point (IEP) from pH 6~7 to pH  $\approx$  2, which means a change in surface character of  $\text{Si}_3\text{N}_4$  to that of  $\text{SiO}_2$ . These results indicate that the determination of change in the IEP can be used for an evaluation of coating state: if the surface of  $\text{Si}_3\text{N}_4$  powders was completely coated with additives, the IEP of  $\text{Si}_3\text{N}_4$  powder mixtures will be shifted to that of additive powders.

Curves in Fig. 4(a) and (b) show the change in zeta-potentials for the as-received  $\text{Si}_3\text{N}_4$  and the YAG powders produced by coprecipitation as a function of pH, respectively. The YAG powders were calcined at 900°, 1100°, and 1500°C for 1h in air. The as-received  $\text{Si}_3\text{N}_4$  powders have high negative zeta-potentials at above pH 10 and an IEP at pH 6.7, which agrees well with the results of other previous works<sup>16</sup>. The charge reversal of YAG powders calcined at 900°C occurs at pH  $\approx$  9.2. Here it should be noted that the IEP of YAG is shifted to lower pH with increasing calcination temperature. Such an effect of calcination temperature on the change of IEP has been reported also in other investigations on the surface charge of alumina<sup>18-19</sup>. According to the explanations given by them, the number of surface hydroxyl groups of oxides will be decreased with calcination temperature to an extent that a reversible rehydroxylation cannot take place.

Fig. 4(c) illustrates the zeta-potential curves for CPN9 and MM powders. The IEPs determined from each curve are pH 7.9 for CPN9 and pH 6.4 for MM, respectively. An almost same IEP of MM as the starting  $\text{Si}_3\text{N}_4$  powders (pH 6.7) indicates that it is impossible to mix additives in a form of coating by conventional mechanical mixing. On the contrary, the change of IEP from pH 6.7 to 7.9 for the CPN9 suggests that relatively large parts of CPN9 powder surfaces are covered with YAG additive (pH = 9.2).

### 3.5. SIMS-Analysis

Compositions on the surface and in the matrix of prepared powder mixtures were analyzed by secondary

**Table 3.** Results of SIMS Analysis for Composition on the Surface and in the Matrix of Coprecipitation-Treated and Mechanically-Mixed Si<sub>3</sub>N<sub>4</sub> Powder Mixtures

Preparation	Additive Content	Surface			Matrix			K-factor
		Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub>	
MM	5 mol%	4.1	2.6	93.3	3.0	1.0	96.0	2
CPN9	5 mol%	24.0	18.2	57.8	2.9	2.4	94.7	13
	10 mol%	33.7	39.0	27.3	8.3	9.5	82.2	12
	15 mol%	23.8	36.9	39.3	8.0	12.6	79.4	6

**Table 4.** Sintering Results for Si<sub>3</sub>N<sub>4</sub> Powder Compacts Containing Various Amounts of YAG Additive

Sintering Temperature	Additive content	Specimen	Δm/m <sub>0</sub> (%)	Δl/l <sub>0</sub> (%)	D <sub>s</sub> (g/cm <sup>3</sup> )	RD (% TD)
1700°C	10 mol%	CPN7	1.99	18.1	3.172	96.4
		CPN9	0.81	17.3	3.186	96.8
		MM	0.69	15.6	3.190	96.9
	15 mol%	CPN7	2.99	18.4	3.246	97.1
		CPN9	1.36	18.1	3.265	97.7
		MM	0.49	15.5	3.284	98.2
1800°C	5 mol%	CPN7	1.94	15.9	3.011	92.9
		CPN9	1.85	17.0	3.125	96.5
		MM	1.02	14.4	3.038	93.8
	10 mol%	CPN7	2.50	18.1	3.230	98.1
		CPN9	1.34	17.7	3.224	98.0
		MM	1.27	14.4	3.243	98.5
	15 mol%	CPN7	3.13	18.5	3.283	98.2
		CPN9	2.60	18.1	3.272	97.9
		MM	0.83	16.2	3.288	98.4

ion mass spectrometry(SIMS) to evaluate the state of additive distribution more quantitatively. If Si<sub>3</sub>N<sub>4</sub> powders were completely covered with the coprecipitated additive particles, the composition of powder surface is different from that of the matrix. That is, for the case of ideal coating, only the ions of additives(Al and Y) have to be detected on the surface in the initial stage of measurement. On the contrary, in case of mechanically-mixed powders, any difference in composition between on surface and in matrix cannot be detected because both Si<sub>3</sub>N<sub>4</sub> and additive particles with a nearly same size will be randomly positioned and thereby the Si-ion of Si<sub>3</sub>N<sub>4</sub> has to be detected together with Al and Y even at the beginning of measurement.

On the basis of idea mentioned above, a so-called 'K factor'(or Coating Parameter) was calculated from

the measured intensity of Si(I<sub>Si</sub>) and additive ions (I<sub>additive</sub>) after the following equation:

$$K = \frac{\left( \frac{I_{\text{additive}}}{I_{\text{Si}}} \right)_{t=0}}{\left( \frac{I_{\text{additive}}}{I_{\text{Si}}} \right)_{t=x}}$$

where t is time after the starting of measurement. After t=x the sputtered depth exceeds the coating layer and consequently the intensities will not change also with further sputtering. Powders with K value of ≥4 can be regarded as coated<sup>20)</sup>.

Table 3 shows the results of SIMS analysis for the powder mixtures containing 5, 10 and 15 mol% YAG. As expected, high enrichment of additives on the pow-

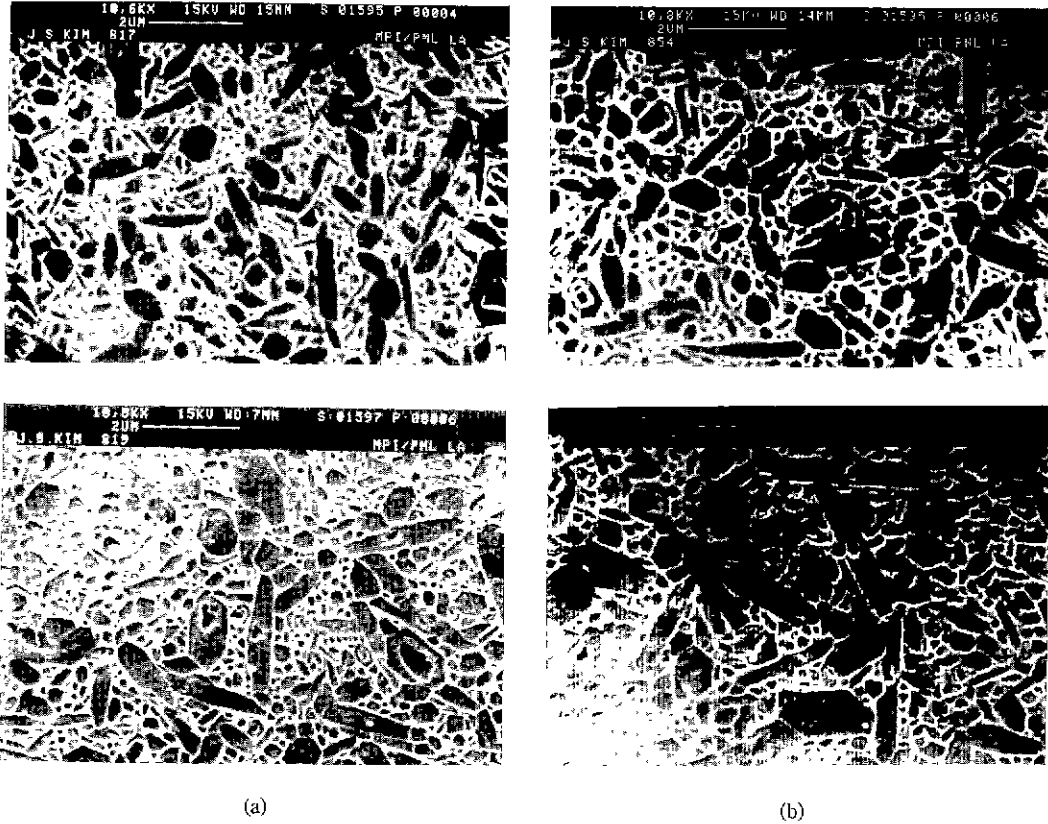


Fig. 5. SEM images of plasma-etched  $\text{Si}_3\text{N}_4$  specimens containing (a) 10 and (b) 15 mol% YAG after sintering at  $1800^\circ\text{C}$  for 0.5 hr, respectively(Upper ones: CPN9, lower: MM).

der surface is found for the coprecipitation mixing(CP series) and consequently all the CP samples show high coating parameters of 6~13 depending on the additive amount. However, the unexpected detection of Si-ion also on the surface of CP powders implies that there are surfaces free from additives. The mechanically-mixed powders(MM) have no difference in composition between the surface and the matrix.

### 3.6. Sintering

Results from the sintering experiments are summarized in Table 4. Without exception MM specimens show lower weight loss and linear shrinkage than CP powders. The difference in linear shrinkage between MM and CP samples is based on the different green density: The green density of MM(57%) is higher by 2% theoretical than CP(55%). The highest weight loss was obtained generally in CPN7 powder compacts. This

seems to be resulted from the faster rehydroxylation of oxide additives during the storage due to a lower calcination temperature than other powders. The effect of homogeneous mixing on the sintered density was evident especially in case of the addition of 5 mol% YAG. The coprecipitation-treated powder compacts (CPN9) show a sintered density of 96.5% theoretical compared to 93.8% for the mechanically-mixed ones. For specimens containing 10 and 15 mol% YAG, a noteworthy difference in sintered density due to the preparation method was not found. However, SEM images of them after plasma-etching(Fig. 5) indicate that relatively homogenous microstructures can be formed in CP specimens.

### 4. Discussion

Effectiveness of coprecipitation method for homoge-

ncous mixing of  $\text{Si}_3\text{N}_4$  with sintering additives was proven from several experimental results. WDS-analysis, TEM observation, zeta-potential measurement and SIMS-analysis showed that  $\text{Si}_3\text{N}_4$  powders can be coated with YAG additive by coprecipitation method, even though a completely ideal coating could not be obtained.

Such an incompleteness of coating might be caused either by insufficiently optimized precipitation processing or by the specific surface character of  $\text{Si}_3\text{N}_4$ . The precipitation of hydroxide particles in  $\text{Si}_3\text{N}_4$  suspension can occur either homogeneously by supersaturation of nitrate salt-solutions or heterogeneously on  $\text{Si}_3\text{N}_4$  particle surfaces. It is obvious for a completely ideal coating of  $\text{Si}_3\text{N}_4$  with precipitates that a homogeneous precipitation must be avoided. However, in this experiment, the first contact place of sprayed nitrate salt-solutions is not necessarily the  $\text{Si}_3\text{N}_4$  surfaces but the upper area of suspension. If the precipitation occurs preferentially on the upper area of the suspension, the formation and growth of precipitates can take place more easily by homogeneous reaction rather than heterogeneous precipitation on  $\text{Si}_3\text{N}_4$  particles. The more the amount of additive, i.e., the more concentrated the salt-solutions are, the more favorable a homogeneous precipitation can be. The decrease of K-factor with increasing additive content supports this assumption. As another reason for an incomplete coating, the damage of additive coating layer by the post-attrition for destroying the hard agglomerates can be given. Besides these possibilities, the surface groups such as  $\text{SiNH}_2$  or  $\text{Si}_2\text{NH}$  on  $\text{Si}_3\text{N}_4$  can provide the unfavorable sites for precipitation of metal hydroxides<sup>17,21</sup>.

As mentioned in 3.6, the improved mixing homogeneity in CP specimens could not affect the sintered density of specimens containing 10 and 15 mol% YAG. In these cases an increased amount of liquid phase can enhance the sintering process so fast as the homogeneity effects are concealed. But the homogeneous mixing of additives might result in an even distribution of liquid phase and thereby hinder local reprecipitation and growth of  $\beta\text{-Si}_3\text{N}_4$ . The fine and homogeneous microstructure could be obtained.

## 5. Conclusion

Chemically and geometrically homogeneous mixing of  $\text{Si}_3\text{N}_4$  powders with sintering additives(YAG) could be realized through coprecipitation of hydroxides from nitrate solution and subsequent calcination. X-ray maps for additive elements showed that Al and Y are evenly distributed in coprecipitation-treated powder mixture. TEM observation of coprecipitation-treated powders confirmed that  $\text{Si}_3\text{N}_4$  particles are covered with fine crystallites of additives. The coating of  $\text{Si}_3\text{N}_4$  particles with YAG caused a shifting of isoelectric point (IEP) from pH 6.7 to pH 7.9. SIMS analysis for composition on surface and in the matrix of prepared powders showed that the surface of coprecipitation-treated powders has considerably high content of additives.

The mixing homogeneity in coprecipitation-treated powder mixture affected the densification of  $\text{Si}_3\text{N}_4$ , especially when a small amount of additive(5 mol%) was used. A higher sintered density of 96.5% theoretical was obtained in coprecipitation-treated specimen compared to mechanically-mixed one(93.8%). Although a difference in sintered density due to the preparation routes could not be determined for the powder mixtures containing 10 and 15 mol% YAG, the microstructural developments seem to be favorable in coprecipitation mixing. The evenly distributed additives in coprecipitation-treated specimens hindered a local reprecipitation and growth of  $\beta$ -phase and consequently resulted in fine and homogeneous microstructure.

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