

Effect of the Interaction between Matrix and Nitrate Additives on the Sintering of Silicon Nitride

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The interaction between commercial Si_3N_4 powder and two types of additives (nitrate and oxide additives) during the sintering of Si_3N_4 was investigated. The nitrates solution or oxide particles were added as a sintering additives. The surface of mixed powder was observed with FT-IR, TG, and HREM. DTA was used to characterize the reactivity of the powders. The formation of crystalline phases and phase transformation were analyzed by XRD. The adsorption of the additives on the surface of silicon nitride was confirmed in the nitrate salts. It was shown that the adsorption occurred by interaction between the amorphous SiO_2 layer on the Si_3N_4 surface and metal cations (Al^{3+} and Y^{3+}) and anions (NO_3^- or OH^-), resulting in a higher degree of homogeneous distribution of additives.

Key words : Silicon Nitride, Nitrate additives, Oxide additives, Phase transformation, Adsorption, HREM

I. Introduction

Silicon nitride-based ceramics have already been put into practical use in tools, bearing balls, and parts of automobile engines such as a turbocharger rotor.¹⁻³⁾ It was generally accepted that Si_3N_4 will be a structural ceramic to be widely used in the future. Like other covalent bonding materials, Si_3N_4 is difficult to sinter without the use of additives,⁴⁾ consequently, various sintering additives have been investigated for densification and lowering the sintering temperature of Si_3N_4 -based materials.⁵⁻⁷⁾ However, if the additive is a powder, intimate mixing may still be difficult and the additives remain at grain boundaries inhomogeneously after sintering because of the finite size of the additive powder particles.⁸⁾ These inhomogeneities inhibit sintering and degrade reliability, and decrease mechanical properties at high temperature because of the softening of glassy phases formed at grain boundaries. Several researchers have reported the homogeneous distribution of sintering additives by adsorption of the sintering additives on the surface of Si_3N_4 .⁹⁻¹³⁾ Liden et al.⁹⁾ have pointed out the effect of electrostatic adsorption of small Y_2O_3 particles (10 nm) on Si_3N_4 particles. In their study, however, the pH during adsorption was limited to 7. This is because the electrostatic adsorption requires that the two species of particles are stable and carry opposite charge. Shih et al.¹⁰⁾ reported that the colloidal coating can occur regardless of whether the two species of particles carry the same sign of charge or not, as long as the size of the coating species, e.g., Al_2O_3 (20 nm), is much smaller than that of the species being coat-

ed, e.g., Si_3N_4 (0.7 μm). Joshi et al.¹³⁾ investigated the adsorption of various metal-organic surfactants as sintering aids in the pH range between 9 and 10. They pointed out the choice of a suitable surfactant depends upon the iep (isoelectric points) of the powder and the hydroxide of the metal existing in the surfactant. Even though the experimental conditions were limited, the results from these studies have shown that the distribution of sintering additives was improved.

In previous studies, Kim et al.¹⁴⁻¹⁶⁾ and Yano et al.¹⁷⁾ have studied that the effects of sintering additives in forms of nitrate solutions or oxide particles on the strength and density of Si_3N_4 and $\text{Si}_3\text{N}_4/\text{SiC}$ composites. The sintering temperature of the monolithic Si_3N_4 with nitrate additives was lowered about 100°C compared to the addition of oxide additives. Furthermore, $\text{Si}_3\text{N}_4/20\text{wt}\%$ SiC composite could be densified to 95% of theoretical density in N_2 atmosphere without applying any pressure.

In this study, the effect of the interaction between commercial Si_3N_4 powder and two types of additive on the sintering of $\alpha\text{-Si}_3\text{N}_4$ was investigated. In order to know the different behaviors from ball-milling to sintering, the type of used additives were two nitrate salts, such as aluminum nitrate and yttrium nitrate, and two oxide powders, such as aluminum oxide and yttrium oxide, which were the same combination with those used in the previous studies.¹⁴⁻¹⁷⁾ The use of nitrate salts as sintering additives is expected the advantage i.e., the uniform distribution of sintering additives, during conventional ball-milling processing. The purpose of this study is to rationalize the improved sintering behaviors

for the powders obtained from different mixing processes.

II. Experimental Procedure

1. Raw Materials

α - Si_3N_4 powder (SN E-10, Ube, Japan) with the average particle size of 0.25 μm was used. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>98.0%, Kanto Chemical, Japan) and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Kanto Chemical, Japan) were chosen as sintering additives. In order to compare the effect of the type of additive between nitrate and oxide additives, Al_2O_3 (average particle size : 0.18 μm , AKP-50, Sumitomo Chemical, Japan) and Y_2O_3 (average particle size : 2-3 μm , 99.9%, High Purity Chemical, Japan) were also used as sintering additives in this experiment.

2. Preparation of Specimens

The composition of specimen was fixed as 92 mass% α - Si_3N_4 , 2 mass% Al_2O_3 , and 6 mass% Y_2O_3 . Amounts of aluminum and yttrium nitrates were calculated on the basis of oxide forms. The Si_3N_4 powder was mixed with the nitrate sintering additives, which will be referred to N-SN, and the oxide sintering additives, which is named as O-SN, respectively. The mixture were ball-milled in plastic bottle with methanol and alumina media for 24 h, prior to drying at 60°C on a hot plate. The dried powders were heat-treated in an N_2 atmosphere for 2 h with 0.1 MPa at each calcining temperature. In the case of nitrate additives, after the nitrate salts were dissolved into methanol, the solutions were added in the bottle before ball-milling. The dried powders with nitrate sintering additives were calcined at 600°C for 2 h in the atmospheric pressure of N_2 to decompose the nitrates.

3. Characterization

(A) *X-ray Diffractometry (XRD)* : X-ray powder diffraction method (XRD, PW-1700, Philips) was used to detect the phase transformation, crystallization and secondary phases of the specimens. The XRD measurement was performed with a Cu tube under an accelerating voltage of 40 kV and current of 20 mA. The scanning angle covered 2θ values from 10° to 80°. The scanning step size was 0.05 deg.

(B) *Thermal Gravimetry-Differential Thermal Analysis (TG-DTA)* : TG-DTA studies were simultaneously performed using thermogravimetric analyzer (TG8110, Rigaku, Japan). Samples were loaded in a Pt pan and heated at 6°C/min up to 1500°C in air or N_2 with a flow rate of 18 cm^3/min . To investigate the reaction that corresponded to the significant peaks, the thermal analysis runs were stopped at 1400°C and the furnace-cooled specimens were analyzed by XRD. TG data that were relevant to the weight change were collected as a function of temperature with constant heating rate.

(C) *Fourier Transformation Infrared Spectroscopy (FT-IR)* : The powders, before and after ball-milling, and after

calcination were analyzed using FT-IR (FT-IR8100M, Shimadzu, Japan) to obtain the data on the surface chemistry between silicon nitride powder and sintering additives. FT-IR spectra in the wavenumber range of 400-4000 cm^{-1} were collected from the powders using the KBr pellet technique.

(D) *Transmission Electron Microscopy (TEM)* : A high-resolution electron microscope (HREM, H-9000, Hitachi, Japan) was used to confirm the presence of oxygen-rich layers on the as-received silicon nitride powder and to observe the surface layers on silicon nitride powders, before and after heat-treatment in N_2 atmosphere. TEM samples were prepared by dispersing the powders in methanol and then dipping the Cu mesh coated with lacy carbon film into the suspension.

III. Results

Crystalline phases of the heat-treated samples were analyzed using XRD, and the fractions of α to β - Si_3N_4 were estimated from their respective X-ray intensities shown in Fig. 1. The peaks of α - Si_3N_4 , α - Al_2O_3 , and Y_2O_3

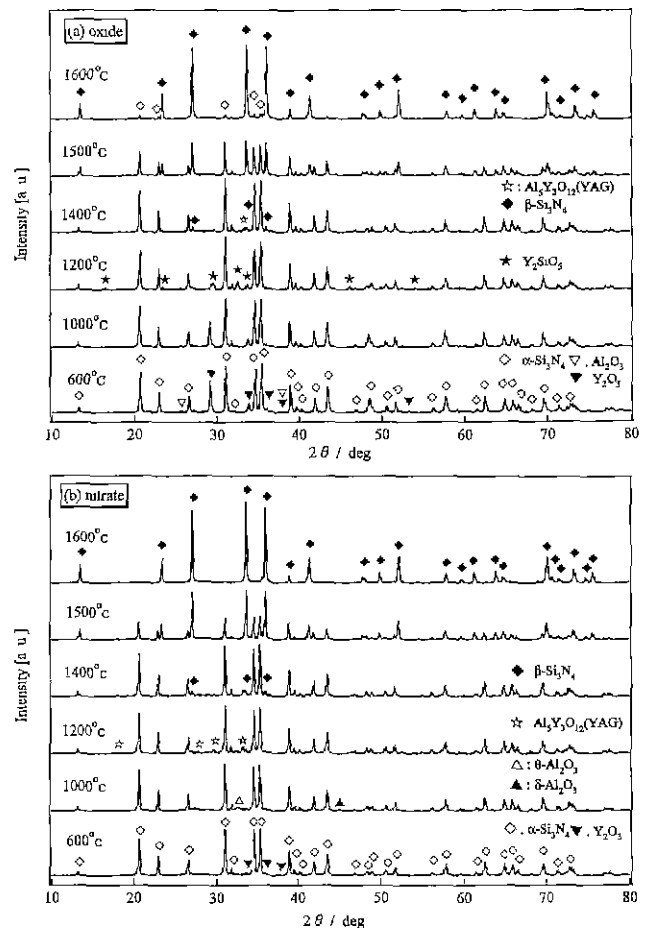


Fig. 1. XRD patterns of the silicon nitride powder added with (a) oxide additives and (b) nitrate additives as a function of heat-treatment temperature in N_2 atmosphere.

were observed in the O-SN powder heat-treated at 600°C, unlike α - Si_3N_4 and Y_2O_3 in the N-SN powder. The detected peaks of α - Si_3N_4 , α - Al_2O_3 and Y_2O_3 were originating from the chemical compositions of raw materials (Fig. 1 (a)). Sintering additives were not changed in the O-SN powder until 1000°C. However, the meager peaks of Y_2SiO_5 were observed at 1000°C, even though the phase was not marked in the figure. The peaks of Y_2SiO_5 were significantly increased at 1200°C. And the peak of $\text{Al}_5\text{Y}_3\text{O}_{12}$ (YAG) as a secondary phase occurred at 1400°C in the O-SN powder.

On the other hand, the detected meager peaks of Y_2O_3 was not included in the raw material but a product through decomposition of yttrium nitrate during heat-treatment at 600°C as shown in Fig. 1(b). Particularly, the main peak of Y_2O_3 could not appear at 29° differently with the case of oxide additives as raw materials. The intermediate phases of Al_2O_3 from aluminum nitrate, θ - Al_2O_3 and δ - Al_2O_3 , were detected at 1000°C in the N-SN powder.¹⁸⁾ And $\text{Al}_5\text{Y}_3\text{O}_{12}$ (YAG) phase was formed at 1200°C, which is lower temperature than the case in the O-SN powder. The α/β phase transformation occurred at high temperature. The equation calculating the fraction of α - Si_3N_4 is as follows¹⁹⁾:

$$\text{The fractions of } \alpha\text{-Si}_3\text{N}_4 \\ = \frac{(I_{\alpha(102)} + I_{\alpha(210)})}{(I_{\alpha(102)} + I_{\alpha(210)} + I_{\beta(101)} + I_{\beta(210)})} \times 100$$

Alpha Si_3N_4 fractions of 92%, 46%, and 4% were recorded in the O-SN powder after heat-treatment at 1400°C, 1500°C, and 1600°C, but, this fraction decreased to 91%, 31%, and 0% in the N-SN powder, respectively. The α/β phase transformation was completed at lower temperature in the N-SN powder compared to that in the O-SN powder. In general, the final densification of silicon nitride during sintering is related with the α/β phase transformation.²⁰⁾ Thus, the higher density was attained at the lower temperature in the N-SN powder compared to the O-SN powder.

DTA curves for Si_3N_4 added with nitrate or oxide additives were obtained at the heating rate of 6°C/min up to 1500°C in air and in N_2 . DTA curves shown in Fig. 2 show that the exothermic peaks for the powder with nitrate additives occurred at 1280°C and 1420°C and exothermic peak for the powder with oxide additives were detected at 1380°C and 1440°C in air atmosphere. In N_2 atmosphere, the peaks were detected at 1210°C and 1420°C in the case of the nitrate additives and 1300°C and 1460°C in the case of the oxide additives, respectively. The first peaks in DTA curves occurred at lower temperature in the N-SN powder compared to in the O-SN powder, irrespective of atmosphere. The difference of temperature was about 90~100°C. This result accords well with the previous study¹⁴⁾ on the initial densification of Si_3N_4 . The density of the bulk added with nitrate additives increased more rapidly than that of bulk added with oxide additives in the range from 1200°C to 1400°C.

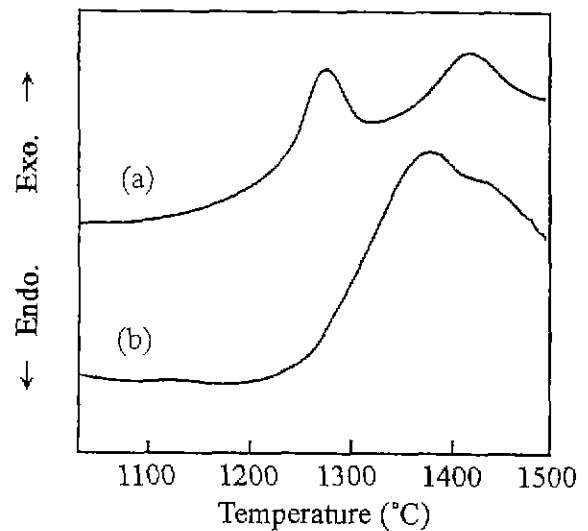


Fig. 2. DTA curves of silicon nitride added with (a) nitrate additives and (b) oxide additives as sintering additives in an air atmosphere.

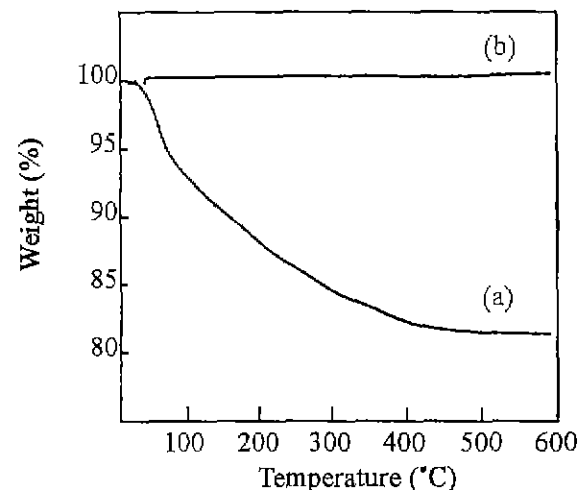


Fig. 3. TG curves of silicon nitride added with (a) nitrate additives and (b) additives as sintering additives in air atmosphere.

These powders, after DTA measurement up to 1400°C in air atmosphere, were defined with XRD. The major phase was α - Si_3N_4 , but the formation of cristobalite (SiO_2) was confirmed.

The TG curves shown in Fig. 3 indicate a large weight loss up to 500°C in the case of the N-SN powder which differs from the O-SN powder. This weight loss corresponds to the decomposition of adsorbates adsorbed on the amorphous SiO_2 layer during ball-milling.

Fig. 4 show the measured IR spectra in the range of 1500 to 400 cm^{-1} . The detected peaks are typical absorption peaks of α - Si_3N_4 ²¹⁾ in 1100~400 cm^{-1} . In the N-SN, a strong absorption peak at 1385 cm^{-1} , and a broad absorption peak at 3200-3600 cm^{-1} appeared after ball-milling and dry process. For the N-SN powder heat-treated at

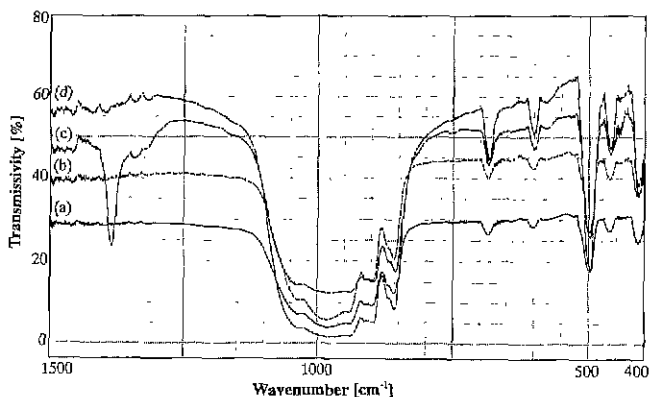


Fig. 4. FT-IR spectra of the silicon nitride powder added with oxide additives (a) before and (b) after heat-treatments at 600°C in N₂ atmosphere, and added with nitrate additives (c) before and (d) after heat-treated at 600°C in N₂ atmosphere.

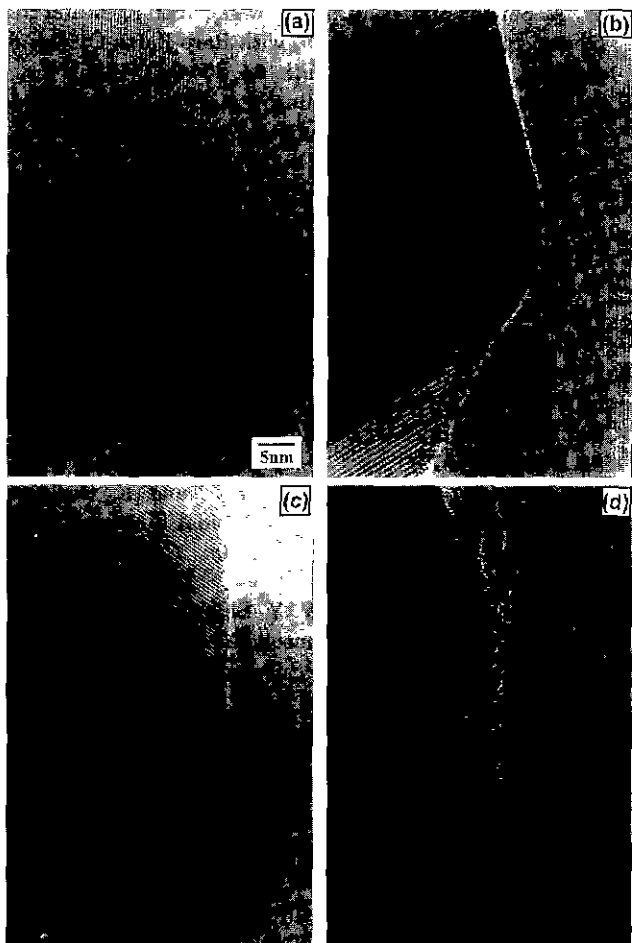


Fig. 5. HREM micrographs showing the morphology of the surface of silicon nitride powder prepared with various conditions: (a) the as-received silicon nitride powder without additives, (b) the N-SN powder after ball-milling process, (c) the O-SN powder and (d) the N-SN powder after heat-treated at 600°C in N₂ atmosphere.

600°C, the two peaks were disappeared. That is, the change of state of the N-SN powder surface was con-

firmed with IR spectra depending on the heat-treatment. The strong and the broad peak are attributed to NO₃⁻ and OH⁻, respectively. These showed that NO₃⁻ and OH⁻ were remained in the N-SN powder, on the surface of the silicon nitride particles, after ball-milling and dry process. But, when the N-SN powder was heat-treated at higher temperature than about 600°C, the remained NO₃⁻ and OH⁻ ions were evaporated. On the other hand, these peaks were not observed in both before and after heat-treatment in the O-SN powder.

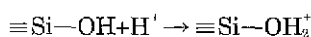
The surface morphologies of the as-received, milled powder containing additive, and the heat-treated powders were observed in a high-resolution transmission electron microscope (HREM), as shown in Fig. 5. The as-received powder showed a thin amorphous SiO₂ layer on the surface of silicon nitride. The dried N-SN and O-SN powders, prior to heat-treatment, hardly showed any adsorption of additives on the surface, irrespective of additives. The coated layer could be removed during the sample preparation process for TEM.

For the powder heat-treated at 600°C, the morphology of the O-SN powder surface was almost same as the non-heat-treated powder, whereas the surface of the N-SN powder showed layer of clusters produced from nitrate additives. Thickness of the coated layer, about 8 nm, was relatively uniform.

IV. Discussion

The N-SN powder showed exothermic peaks at lower temperature in DTA compared to the O-SN powder. It shows that the former have better surface reactivity than the latter. Such results are agreed well with the XRD result indicating that the phase transformation of Si₃N₄ with nitrate additives was completed at lower temperature than that of Si₃N₄ with oxide additives. Thus, the results of DTA and XRD indicate that the sinterability of the Si₃N₄ powder mixed with nitrate additives was improved, because α/β phase transformation was also related with sintering behavior of Si₃N₄. The difference in sinterability of silicon nitride between the N-SN powder and the O-SN powder was indirectly explained using the data of FT-IR spectra, TG curve, and HREM observation. The peak at 1385 cm⁻¹ in IR spectra indicates the presence of NO₃⁻ in the N-SN powder after ball-milling and dry process. The large weight loss in the TG curve implied the desorption and decomposition of adsorbates. The coated clusters in a HREM picture showed the change of adsorbates through the heat-treatment.

A proposed adsorption mechanism of nitrate additives in ball-milling is as follows. The surface charge of amorphous SiO₂ on the Si₃N₄ particles, which have positive charges at low pH,^{9,12)} is as next in an acidic solution.



At first, ionic adsorption on the SiO₂ surface is occurred

as a result of ion exchange²⁰⁾ in which adsorbed hydrogen ions are displaced by metal cations (M^{3+} ; Al^{3+} and Y^{3+}), i.e., ($\equiv Si-O-M^{2+}$) and/or ($\equiv Si-O)_2-M^+$). Then chemical adsorption between the adsorbed metal cations and anions (NO_3^- or OH^-) occurs by the electrostatic attractive force. As a result, the surface of the amorphous SiO_2 layer is coated with a mixture of $M^{3+}-NO_3^-$ - OH^- system. The chemical formula of the compound have not been defined yet.

The coated mixture formed intermediate phases and secondary phases, then the mixture became a liquid phase at high temperature. The liquid phase directly influences the densification and α/β phase transformation of Si_3N_4 in sintering process, and it is made through the reaction between additives and amorphous SiO_2 on Si_3N_4 surface. Generally, a more uniform distribution of additive should provide increased kinetics due to shorter diffusion distance in a well-distributed liquid phase, and requiring less sintering aid, so that homogeneous distribution of additive is important in liquid phase sintering. The coating of sintering additives can further increase homogeneous distribution of aids and powder dispersion. This homogeneous distribution, in this study, was achieved with dissolution and adsorption of the nitrate salts on the amorphous SiO_2 layer during the ball-milling process.

Consequently, the improved density, α/β phase transformation, and sinterability in the case with nitrate additives are contributed to the homogeneous distribution of sintering additives, which is due to interaction between the amorphous SiO_2 on the Si_3N_4 and metal cations (Al^{3+} and Y^{3+}) and anions (NO_3^- or OH^-) during the ball-milling process.

IV. Conclusion

The interaction between commercial Si_3N_4 powder and two types of additives (nitrate and oxide additives) during the sintering of Si_3N_4 was investigated. The α/β phase transformation of silicon nitride was completed and the exothermic peak in DTA was detected at lower temperature in the case of nitrate salts compared to the oxide particles case. A large weight loss in TG curves and the presence of NO_3^- and OH^- in FT-IR spectra were taken place in the case of the N-SN powder which differs from the O-SN powder. Furthermore, the adsorption of additives was directly confirmed with HREM, which could observe the layer of clusters only on the surface of the N-SN powder after heat-treatment at 600°C. It is concluded that the adsorption of the additives on the surface of Si_3N_4 powder occurred during ball-milling and drying process in the case of nitrate additives, resulting in a higher degree of homogeneous distribution of sintering additives.

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