Control of $\beta$-Si$_3$N$_4$ Crystal Morphology and Its Mechanism (Part 2)

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$\beta$-Si$_3$N$_4$ 結晶モフォロジーの制御とそのメカニズム（第2報）

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1. Introduction

Since the high toughness of Si$_3$N$_4$-based ceramics has been attributed to its rod-like grain shape due to the anisotropic grain growth of $\beta$-Si$_3$N$_4$, many works have focused on controlling the grain morphology of $\beta$-Si$_3$N$_4$ by changing the $\alpha$-$\beta$ ratio of starting powders$^{2,3}$ sintering conditions$^{3,4,5}$ and the ratio and amount of additives.$^{4,5}$ Recently, it was reported that the radii of lanthanide (Ln) ions had a significant effect on grain growth behavior of $\beta$-Si$_3$N$_4$ in the Ln-Si-Al-O-N liquid phase during the $\alpha$$\rightarrow$$\beta$ transformation.$^{6,7}$ Radii of lanthanide ions showed a good positive correlation with mean aspect ratios at the end of the phase transformation. Due to the lanthanide contraction, the viscosity of the Ln-Si-Al-O-N liquid phase is expected to increase with the increase of atomic number as experimentally demonstrated.$^{8,9}$ It is well-known that the liquid viscosity relates to diffusion constant by the Stokes-Einstein equation,

$$\eta = \frac{kT}{6\pi r D}$$

where $\eta$, $r$ and $D$ are the liquid viscosity, the radius of diffusing specie, and diffusion constant, respectively. Thus, it is expected that diffusion constant in the liquid phase containing Ln decreases with the increase of atomic number. When diffusion constant/diffusion distance ($D/\Delta x$) is much lower than the interfacial reaction constant ($K$), $D/\Delta x \ll K$, grain growth is controlled by diffusion. In the opposite case, $D/\Delta x \gg K$, grain growth is controlled by interfacial reaction. When they are comparable, $D/\Delta x \approx K$, we call the case as intermediate control. Thus, the viscosity change due to the lanthanide contraction can solely alter the rate controlling step for grain growth. Krämer et al. performed a periodic bond chain (PBC) analysis of $\beta$-Si$_3$N$_4$ crystal, and found that its elongated grain shape was originated from much higher activation energy for nucleation on the (100) facet than on the (001) facet.$^{10}$ This strongly suggests that grain growth to the [210] direction is controlled by the interfacial reaction. They also predicted diffusion-controlled growth kinetics to the [001] direction. If growth kinetics at the (100) facet were altered from interfacial reaction controlled to diffusion controlled by the increase of Ln atomic number, the morphology change from an elongated shape to a spherical shape could happen. This is one hypothesis which could explain the trend experimentally observed. However, it was not consistent with the phase transformation rates experimentally observed. If the phase transformation rate is controlled by diffusion, heavier lanthanide ions should provide slower phase transformation rates. The observed trend was just opposite to the expectation. Thus, a kind of catalytic effect of lanthanide ions on the prism and/or basal planes was proposed for explaining this puzzling experimental result.$^{7}$

In this work, only lanthanide oxides were used as sintering additives to elucidate their effects on the grain growth behavior of Si$_3$N$_4$. Annealing at much higher temperatures than in the previous works$^{6,7,9}$ was done to investigate grain growth behaviors of $\beta$-Si$_3$N$_4$ with different lanthanide additives during Ostwald ripening. The method developed by Hiroi et al.$^{11}$ was used for obtaining $\beta$-Si$_3$N$_4$ crystallites to quantitatively evaluate the morphologies of $\beta$-Si$_3$N$_4$ crystals, since it has been proven to be a viable method for investigating the anisotropic Ostwald ripening in $\beta$-Si$_3$N$_4$.$^{12}$ Recently, we proposed a model for anisotropic Ostwald ripening that utilized a formulation of weighted mean curvature for completely faceted crystals instead of mean curvature for isotropic surfaces.$^{13}$ Grain growth simulations based on this model were performed for analyzing the effect of lanthanide ions on grain growth of $\beta$-Si$_3$N$_4$.

2. Experiment

Alpha-Si$_3$N$_4$ (E-5 Grade, Ube Industries Ltd., Japan), SiO$_2$ (Hokko Chemicals Ltd., Japan) and Ln$_2$O$_3$ (Ln=La, Gd or Yb) (Hokko Chemicals Ltd., Japan) powder mixtures with a molar ratio of Si$_3$N$_4$:SiO$_2$:Ln$_2$O$_3$=20:2:1 were planetary-milled in a Si$_3$N$_4$ pot using methanol as a mixing medium. The powder mixtures were dried, passed through a 60-mesh nylon sieve, charged into BN crucibles, and heat-treated at 1700, 1750, 1800, 1850 or 1900°C for 2 h under a nitrogen pressure of 1 MPa.
The product, an aggregated porous body, was lightly ground by using a mortar and pestle, and passed through a 100-mesh sieve. The screened powders were then subjected to the following treatments: (1) a mixed solution of concentrated hydrofluoric acid (HF) and nitric acid (HNO₃) at 60°C to dissolve the residual glassy phase, (2) a concentrated sulfuric acid (H₂SO₄) at 160°C to eliminate lanthanide compounds possibly formed during the previous treatment.¹¹

X-ray diffraction (XRD) analyses were performed for phase identification. Morphologies of β-Si₃N₄ crystals were observed by scanning electron microscope (SEM). Because β-Si₃N₄ has a hexagonal rod shape, its width and length were measured for each crystal appeared in the micrograph.

3. Results and discussion

XRD identified that Si₃N₄ powders heat-treated at 1750–1900°C consisted only of the β-phase. No other phases were detected, which indicates that grain growth at 1750–1900°C is categorized as Ostwald ripening. Figures 1(a)–(c) show width-length (upper row) and width-aspect ratio (lower row) distributions of β-Si₃N₄ crystals heat-treated at 1750–1900°C for 2 h with La₂O₃, Gd₂O₃ and Yb₂O₃, respectively. At 1750°C, lanthanide additives make little difference in both distributions. However, they make significant differences at higher temperatures. La₂O₃ yields almost one-dimensional growth in the length direction, while Yb₂O₃ gives an appreciable growth in the width direction. As a result, wide distributions are observed in length for La₂O₃ and in width for Yb₂O₃. Gd₂O₃ shows an intermediate
behavior between both additives. Figure 2 shows mean widths, lengths and aspect ratios of $\beta$-Si$_3$N$_4$ crystals heat-treated with La$_2$O$_3$, Gd$_2$O$_3$ and Yb$_2$O$_3$ at 1750-1900°C. La$_2$O$_3$ causes the lowest width growth and the highest length growth rates among the additives, while Yb$_2$O$_3$ shows the lowest length growth rate. As a result, the larger the atomic number of lanthanide is, the smaller the aspect ratio becomes at higher temperatures. Figure 3 shows the morphologies of $\beta$-Si$_3$N$_4$ crystals heat-treated at 1850°C with (a) La$_2$O$_3$, (b) Gd$_2$O$_3$ and (c) Yb$_2$O$_3$, which evidently demonstrates the morphology difference among three additives above mentioned. A fibrous shape of $\beta$-Si$_3$N$_4$ crystals heat-treated with La$_2$O$_3$ makes a remarkable contrast with a rather isotropic shape of those with Yb$_2$O$_3$.

As already mentioned in the introduction, it was reported that radii of lanthanide ions showed a good positive correlation with their mean aspect ratios at the end of the phase transformation in Ln-Si-Al-O-N system. In this work, it has been found that lanthanide ions have a strong effect on grain growth behavior not during the phase transformation but during Ostwald ripening. This might be due to the difference of the additive composition like Al$_2$O$_3$ addition. If the viscosity of the liquid phase is high enough to make diffusion rate slower than interfacial reaction rates, grain growth kinetics shifts from interfacial reaction controlled to diffusion controlled. This could solely explain the observation that La$_2$O$_3$ and Yb$_2$O$_3$ additions give a fibrous grain shape and a rather isotropic grain shape, respectively; interfacial reaction controlled and diffusion controlled kinetics for La$_2$O$_3$ and Yb$_2$O$_3$ additions, respectively. However, Fig. 3 demonstrates that the morphologies of $\beta$-Si$_3$N$_4$ crystals heat-treated with Yb$_2$O$_3$ are faceted as well as those with La$_2$O$_3$. As mentioned in the introduction, a PBC analysis predicts a high activation energy for nucleation at the (100) plane of $\beta$-Si$_3$N$_4$, which results in an atomically flat crystal surface, namely a facet. Thus, the appearance of facet is clear evidence of interfacial reaction controlled kinetics. Also, it contradicts with the observed phase transformation rates: the $\beta$-fractions of powders heat-treated at 1700°C are 49, 16 and 34% for La$_2$O$_3$, Gd$_2$O$_3$ and Yb$_2$O$_3$, respectively. This suggests the trend of the phase transformation rate is in the order of La$_2$O$_3$ > Yb$_2$O$_3$ > Gd$_2$O$_3$ if it is controlled by diffusion. This is not consistent with the order expected from the lanthanide contraction, La$_2$O$_3$ > Gd$_2$O$_3$ > Yb$_2$O$_3$. Thus, a proposed catalytic effect of lanthanide ion on the prism and/or basal planes would be expressed as that lanthanide ions alter the interfacial reaction rates at the (100) and/or (001) planes.

To further investigate the effect of lanthanide additives on grain growth of $\beta$-Si$_3$N$_4$, grain growth simulations based on the anisotropic Ostwald ripening model were performed. Followings are the starting conditions for performing simulations.

Particle size distribution of starting powders: Since powders heat-treated at 1700°C contained a significant amount of $\alpha$-phase, powders heat-treated at 1750°C are those just after the completion of the $\alpha$-to-$\beta$ transformation (the beginning of Ostwald ripening). It was reported that the lengths of $\beta$-Si$_3$N$_4$ crystals are independent of width, and are constant at the end of the phase transformation, and also that crystals with the smaller width preferentially reduced their lengths at the beginning of Ostwald ripening. According to these experimental facts, an initial particle size distribution of $\beta$-Si$_3$N$_4$ crystals are expected to be very close to that of powders heat-treated at 1750°C. Mean grain width and length were set to be 0.7 and 4.0 μm, respectively, and their standard deviations were set to be 0.5 and 1.4 μm, respectively. A particle size distribution was computer-generated assuming the normal distribution.
**Table 1. Summary of Diffusion and Interfacial Reaction Constants for Performing Grain Growth Simulations of ْSi₃N₄**

<table>
<thead>
<tr>
<th>Additives</th>
<th>Activation energy (kJ/mol)</th>
<th>Pre-exponent constant (m/s)</th>
<th>Activation energy (kJ/mol)</th>
<th>Pre-exponent constant (m/s)</th>
<th>Activation energy (kJ/mol)</th>
<th>Pre-exponent constant (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂O₃</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Gd₂O₃</td>
<td>545</td>
<td>2×10⁻²</td>
<td>686</td>
<td>1×10⁰</td>
<td>772</td>
<td>5×10⁰</td>
</tr>
<tr>
<td>Yb₂O₃</td>
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*The relationship between diffusion or interfacial reaction constants (D or K), activation energies (E_a), and pre-exponent constants (D_0 or K_0) are expressed as D = D_0 exp(-E_a/RT) or K = K_0 exp(-E_a/RT).*

**Kinetic parameters**:  
The activation energy of diffusion was taken from the densification of Si₃N₄–Y₂O₃–SiO₂ mixtures under hot pressing, which explicitly took grain boundary widths into account for calculations using known amounts of grain boundary phases. The appearance of prismatic facets dictates interfacial reaction controlled kinetics in the [210] direction. The activation energies of grain growth in the [001] and [210] directions were selected from the data taken by Lai and Tien, which were determined through the observation of individual grains disintegrated from Si₃N₄ polycrystals using molten alkali hydroxides. The activation energies might vary for different lanthanide additives. However, no other data is currently available. Since the purpose of performing simulations is to examine the effect of the relationships between diffusion and interfacial reaction constants, the activation energies for grain growth were assumed to be identical for different lanthanide additives in this work. The pre-exponent constants of interfacial reaction constant K₀ were set to make interfacial reaction constant K higher than diffusion constant D, because the tip shape of ْSi₃N₄ crystal was observed to be rounded, which suggested that the growth in the [001] direction was diffusion controlled. The (100) and (001) interfacial energies were assumed to be identical and to be 0.1 J/m², respectively. This implies that the anisotropy be not due to the difference in the interfacial energies. After numerous tries of calculations varying diffusion and interfacial reaction constants, a set of parameters given by Table 1 provided the closest grain growth behaviors for different lanthanide additives. Figure 4 visualizes the temperature dependencies of diffusion and interfacial reaction constants given in Table 1. The diffusion distance was set δx = 1.0 μm to compare diffusion constants with interfacial reaction constants. Usually, the diffusion distance equals a radius of spherical particle in the highly dispersed system. However, it is not applicable to the current case, and thus, an average of width and length of starting powder, approximately 1 μm, was used in this work. From Fig. 4, the following information could be deduced:

1. **Diffusion constants of the liquid phases containing different lanthanide oxides have the following relationship, D(Ln₂O₃)/3 = D(Gd₂O₃)/2 = D(Yb₂O₃).** This is consistent with the order of ionic field strength of lanthanide ions.

2. **The interfacial reaction constants Kᵢ have the following relationships with diffusion constants, D/δx = Kᵢiores;** for La₂O₃, Gd₂O₃ and Yb₂O₃, respectively.

Figures 5(a)–(c) show simulated width-length (upper row) and width-aspect ratio (lower row) distributions of ْSi₃N₄ crystals heat-treated at 1750–1900°C for 2 h with La₂O₃, Gd₂O₃ and Yb₂O₃, respectively. Although there are some inconsistencies between experimental results and simulations probably due to the existence of finely ground crystals (specially for Yb₂O₃ additive, since its powder aggregate was the hardest) and the effects of gas phase reaction at higher temperatures (1850°C <) where the decomposition of Si₃N₄ and/or the volatility of additives (specially for Yb₂O₃ additive) would be more active, general tendencies in grain growth behavior agree quite well between them. This suggests that the difference experimentally observed in grain growth behaviors among three lanthanide additives would be due to the different relationships between diffusion and interfacial reaction constants above mentioned; D/δx = Kᵢiores; for La₂O₃, Gd₂O₃ and Yb₂O₃, respectively. Since the difference in diffusion constants is small, it could be concluded that the morphology difference of ْSi₃N₄ crystals heat-treated with different lanthanide additives is mainly caused by the difference in the (100) interfacial reaction constants, Kᵢiores. The observed order of the phase transformation rates, La₂O₃ > Yb₂O₃ > Gd₂O₃, would be a mixed effect of diffusion constants (viscosities), La₂O₃ > Gd₂O₃ > Yb₂O₃, and interfacial reaction constants, La₂O₃ < Gd₂O₃ < Yb₂O₃. Nakayasu et al. performed a first-principle molecular orbital calculations of the interface between the prismatic plane of ْSi₃N₄ and Ln-Si-O-N glass by the discrete variational X₀ method using model clusters of ْSi₃N₄. Total overlap populations suggests that the bond strength between a lanthanide ion and the (100) interface of ْSi₃N₄ is negligibly small for La³⁺, and increases with the atomic number of lanthanide, while they are far less stable in the bulk of ْSi₃N₄ crystal. Strongly bonded lanthanide ions (Gd³⁺ and Yb³⁺) at the (100) interface of ْSi₃N₄ might act to reduce the activation energy for nucleation on this facet plane, which could explain the experimental results obtained in this work. To rationalize this effect, the interface between ْSi₃N₄ crystal and glassy phase should be examined carefully.

Because experimental results were obtained for ْSi₃N₄
Crystal powders fabricated in a loose powder compact state that allows much easier particle redistribution upon the appearance of the liquid phase than in a pressed powder compact, the effect of impingement of elongated β-crystals are expected to be small. Because it was demonstrated that the Y-Si-O-N liquid phase formed a uniform film on the surface of Si₃N₄ particles even in a porous state during the early stage of sintering, the Ln-Si-O-N liquid phases are also expected to wet all the surfaces of Si₃N₄ particles, and thus, mass can transfer through this liquid film even if powder compacts are in a loose state. Because grain growth is controlled by the interfacial reaction as demonstrated in this work, the amount of the liquid phase and distance between particles have little effect on it. These are probably the main reasons why experiments and simulations agreed quite well in this work.

4. Conclusion
Grain growth behaviors of β-Si₃N₄ with different lanthanide (Ln) oxide additives during Ostwald ripening were quantitatively analyzed. The aspect ratio of the β-Si₃N₄ crystals doped with different lanthanide oxide increased in the order of La₂O₃ > Gd₂O₃ > Yb₂O₃ at higher annealing temperatures. Excellent agreements of size distributions between experimental results and simulations based on the anisotropic Ostwald ripening model suggests that the observed difference in grain growth behaviors be mainly due to the change in the interfacial reaction rates between the (100) facets of β-Si₃N₄ crystals and the Ln-Si-O-N liquid phase.
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