Analysis of sintering behavior of silicon nitride based on master sintering curve theory of liquid phase sintering

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We propose a new master sintering curve (MSC) theory for liquid phase sintering in consideration of grain rearrangement and solution-precipitation in order to analyze the sintering behaviors of silicon nitride (Si_3N_4) powder compacts. We found that the MSC for liquid phase sintering is theoretically the same expression as that for solid-state sintering. Very fine high-purity powders of Si_3N_4 , Y_2O_3 , Al_2O_3 , AlN , and TiO_2 were used as the raw materials to make powder compacts. The degree of sintering shrinkages of the powder compacts, which contained different amounts of the sintering aids, were measured directly by the laser displacement measurement method using a dilatometer. Based on the displacements and the specimen dimensions, the shrinkage ratios and rates could be calculated. The sintering shrinkage behavior depended on the sintering aid used and the heating rate. The MSCs were obtained for shrinkage ratios of 0–2 and 2–15% corresponding to grain rearrangement and the solution-precipitation process, respectively. Finally, the apparent activation energies of sintering of Si_3N_4 for grain rearrangement and the solution-precipitation process were found to be 251–294 and 345–430 kJ/mol, respectively, depending on the sintering aid used.

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1. Introduction

Silicon nitride (Si_3N_4) ceramics have excellent mechanical properties, such as high strength and toughness.^{1)–11)} As a result, they are used in glow plugs, cutting tools, bearings, and turbo-charger rotors, among other devices.^{12)–14)} Si_3N_4 itself is difficult to densify, owing to its low self-diffusion coefficient.¹⁵⁾ Therefore, dense Si_3N_4 ceramics are fabricated through liquid phase sintering, which involves the addition of sintering aids, such as Y_2O_3 and Al_2O_3 .^{16),17)} The densification of Si_3N_4 through liquid phase sintering occurs because of the grain rearrangement by the formation of the liquid phase and by the solution-precipitation process, which is controlled by interfacial reactions or by the diffusion of atoms or ions in the liquid phase as well as in the other materials.^{18)–21)} In particular, the phase transformation from α - Si_3N_4 to β - Si_3N_4 and the Ostwald ripening of the β - Si_3N_4 grains occurs during the solution-precipitation process.

During the sintering process, the dimensions of the green body change because of densification. Therefore, controlling the liquid phase sintering behavior is important for preventing unnecessary sample deformation as well as the failure of the product and to obtain near-net shapes. Su and Johnson have proposed a theory for the master sintering curve (MSC).²²⁾ Based on this theory, a unique MSC corresponding to densification and independent of the heating profile can be obtained from the shrinkage curves measured at various heating rates. This theory assumes that solid-state sintering, which is a primary densification process, occurs during sintering and that abnormal grain growth does not. Further, this theory has been applied in the case of various ceramics.^{23)–26)} In addition, the degree of sintering shrinkage can be controlled on the basis of the MSC.²⁷⁾ An MSC theory

analogous to that for solid-state sintering has been proposed for liquid phase sintering. This theory, too, has been applied in the case of many different materials made by liquid phase sintering.^{28)–32)} However, its exact form has not yet been derived. In order to do so, several controlling steps of the liquid phase sintering process have to be considered. For instance, the grain rearrangement process and the solution-precipitation process are controlled by the diffusion rate and the interfacial reaction.³³⁾ In this study, we proposed a new MSC theory for liquid phase sintering and applied it to analyze the sintering shrinkage behaviors of Si_3N_4 ceramics formed by adding different sintering aids.

2. Theory

2.1 MSC for grain rearrangement

In the initial stage of the liquid phase sintering process, grain rearrangement occurs owing to capillary pressure. It is known that the capillary pressure, ΔP , results in the presence of the liquid between the two parallel plates forming the capillary:

$$\Delta P = \frac{2\gamma_{LV} \cos \theta}{d} \quad (1)$$

where d is the space between the two plates. Further, γ_{LV} and θ are the surface energy and contact angle, respectively; these depend on not only the nature of the liquid phase but also the temperature. For this stage, the changes in the geometry of the grains need not be considered. It has been reported that the shrinkage rate attributable to the grain rearrangement caused by the capillary pressure can be calculated as follows:³⁴⁾

$$-\frac{dL}{Ldt} = \frac{\Delta P \delta}{G\eta} = \frac{d\rho}{3\rho dt} \quad (2)$$

where L is the instantaneous length of the sample, t is the time, δ is the width of the liquid phase, G is the grain size, η is the viscosity, and ρ is the relative density. In the case of Andrade-

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type viscous flow, the temperature dependency of the viscosity can be expressed as follows:

$$\eta = \frac{k_B T}{A} \exp\left(\frac{Q}{RT}\right) \quad (3)$$

where k_B is the Boltzmann constant, A is a constant, Q is the activation energy of viscosity, R is the gas constant, and T is the temperature. Assuming that the temperature dependency of γ_{LV} and $\cos\theta$ is the Arrhenius type, the following equation can be obtained by combining the ones given above:

$$\frac{d\rho}{3\rho dt} = \frac{K_{gr}\delta A}{Gk_B T} \exp\left(-\frac{Q_{gr}}{RT}\right) \quad (4)$$

Where K_{gr} is a constant including the effect of the viscosity, the surface energy and the contact angle, and Q_{gr} is the apparent activation energy of grain rearrangement process. By separation of variation and integration,

$$\frac{k_B}{3K_{gr}\delta AG} \int_{\rho_0}^{\rho} \frac{d\rho}{\rho} = \int_0^t \frac{1}{T} \exp\left(-\frac{Q_{gr}}{RT}\right) dt \quad (5)$$

The left-hand side of Eq. (5) is a function of the density as follows:

$$\Phi_{gr}(\rho) \equiv \frac{k_B}{3K_{gr}\delta AG} \int_{\rho_0}^{\rho} \frac{d\rho}{\rho} \quad (6)$$

The right-hand side of Eq. (5) is a function of Q as well as of the time and temperature (it is a standardized firing profile) as follows:

$$\Theta(t, T) \equiv \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (7)$$

This results in the following equation:

$$\Phi_{gr}(\rho) = \Theta(t, T) \quad (8)$$

This relationship indicates that the MSC for liquid phase sintering is theoretically similar to that for solid-state sintering.²²⁾

2.2 MSC for solution-precipitation process

In the solution-precipitation stage, the rate of densification is controlled by two mass transfer processes, namely, diffusion and the interfacial reaction. Furthermore, it is assumed that the geometry of the grains changes, because a solution is formed at the contact area between particles, and precipitation occurs outside the contact area. In this study, a new MSC theory was proposed based on a combined sintering model³⁵⁾ in a manner similar to that for the MSC theory for solid state sintering,²²⁾ while taking into account the model used by Kingery for liquid phase sintering.³³⁾

When spherical particles come in contact because of the capillary pressure of the liquid phase, a negative pressure, P^0 , acts on the pores:

$$P^0 = -\frac{2\gamma_{LV}}{r_p} \quad (9)$$

where r_p is the pore radius. This pressure results in a compressive stress on the particles in the contact area. The increase in the chemical potential or activity because of the pressure can be expressed as follows:³³⁾

$$\mu - \mu_0 = k_B T \ln \frac{a}{a_0} = \Delta \Pi \Omega_a \quad (10)$$

$$\ln \frac{a}{a_0} \approx \ln \frac{C}{C_0} = \frac{k_1 \gamma_{LV} \Omega_a}{r_p k_B T} \quad (11)$$

where μ and μ_0 are the chemical potentials at the contact area and the free surface, respectively; a and a_0 are activities of the contact area and the precipitation region, respectively; $\Delta \Pi$ is the capillary pressure between the contact surface and the free region; C and C_0 are the concentrations of the material under consideration in the contact area and the precipitation region, respectively; k_1 is a constant; γ_{LV} is the energy of the interface between the gas and liquid phases; Ω_a is the atomic volume; and r_p is the radius of the pores. Further, r_p can be expressed using scale factor C_p as follows:

$$r_p = C_p G \quad (12)$$

In the case of diffusion rate control, the diffusion flux out of a circular contact area along the circumference can be described using Fick's first law.

$$j_{asd} = \frac{D(C - C_0)}{\Omega \lambda} \quad (13)$$

where D is the diffusion coefficient. The diffusion distance of the atoms from the solution to the precipitate, λ , can be expressed using G and C_λ as follows:

$$\lambda = C_\lambda G \quad (14)$$

The concentration gradient can be expressed as follows:

$$\frac{C - C_0}{\lambda} = \frac{C_0}{\lambda} \left(\frac{C}{C_0} - 1 \right) \approx \frac{C_0 k_1 \gamma_{LV} \Omega_a}{C_p C_\lambda G^2 k_B T} \quad (15)$$

Therefore, the diffusion flux in the contact area, j_{asd} , is the following:

$$j_{asd} = \frac{C_0 D k_1 \gamma_{LV}}{C_p C_\lambda G^2 k_B T} \quad (16)$$

In the case of interfacial-reaction control, the diffusion flux out of the contact region, j_{asr} , can be determined by assuming that it is proportional to the difference in the activities of the solid between the contact area and the neighborhood and that in the precipitation region as follows:

$$j_{asr} = \frac{k_2}{\Omega_a} (a - a_0) \quad (17)$$

where k_2 is a constant related to the interfacial reaction. Using Eqs. (3) and (9), one can derive j_{asr} :

$$j_{asr} = \frac{k_2}{\Omega_a} \left[\exp\left(\frac{k_1 \gamma_{LV} \Omega_a}{r_p k_B T}\right) - 1 \right] \approx \frac{k_1 k_2 \gamma_{LV}}{C_p G k_B T} \quad (18)$$

Equations (16) and (18) represent the normalized flux of the atoms arriving at the surface of the generalized pore in a manner similar to that used in Ref 35.

The total atomic diffusion flux, J , for any element is

$$J = \int_S j_{asd} dA \quad (19)$$

This integral can be calculated by multiplying the average local flux for diffusion-rate control, j_{asd} , and that for interfacial-reaction control, j_{asr} , by the area available for the diffusion of the atoms, if the diffusion distance and the curvatures are uniform or if it possible to approximate them using their respective average values.

$$J = \frac{1}{2} j_{asd} \delta L_d + j_{asr} A_r \quad (20)$$

where $(1/2)\delta L_d$ and A_r are the areas corresponding to diffusion-rate and interfacial-reaction control, respectively. Further, δ is the

thickness of the liquid phase at the contact area, L_d is the total length of the intersection between the contact area and the pore, and A_r is the area of the concave curvature. Although L_d and A_r are unknown and generally difficult to estimate, they can be expressed using G and G^2 in the case of any microstructure as follows:

$$\frac{1}{2} L_d = C_d G \quad (21)$$

$$A_r = C_r G^2 \quad (22)$$

where C_d and C_r are the scaling factors, which should be valid when the microstructure is self-similar. Further, they are not always constant during sintering.

In order to relate the diffusion of the atoms to the shrinkage of the sintered body, in this study, we used the polyhedral model developed by DeHoff;³⁶⁾ this model is the same as that used for the MSC theory for solid-state sintering. In the model, the polyhedron consists of flat surfaces, and each cell is divided into a number of pyramids. As a result, the densification rate could be derived in a manner similar to that in the case of the MSC theory for solid-state sintering:

$$\frac{dV}{Vdt} = -\frac{d\rho}{\rho dt} = -\frac{3J\Omega_a}{hS^b} = -\frac{3J\Omega_a}{C_h C_a G^3} \quad (23)$$

where h and S^b are the height of the pyramids and the contact area, respectively. In addition, $C_h (=h/G)$ and $C_a (=S^b/G^2)$ are the scaling factors. By substituting Eqs. (16), (18), (20), (21), and (22) into Eq. (23), we get

$$\frac{d\rho}{\rho dt} = \frac{3\gamma_{LV}C_0\Omega_a}{k_B T} \left(\frac{\delta D\Gamma_d}{G^4} + \frac{k_2\Gamma_r}{G^2} \right) \quad (24)$$

where

$$\Gamma_d = \frac{k_1 C_d}{C_p C_\lambda C_h C_a} \quad (25)$$

$$\Gamma_r = \frac{k_1 C_r}{C_p C_h C_a} \quad (26)$$

In the case of isotropic shrinkage, the densification rate can be converted into the linear shrinkage rate as follows:

$$-\frac{dL}{Ldt} = \frac{d\rho}{3\rho dt} \quad (27)$$

If a single mechanism is dominant during the sintering process, Eq. (24) can be simplified to

$$\frac{d\rho}{\rho dt} = \frac{3\gamma_{LV}C_0\Omega_a K_0 \Gamma(\rho)}{k_B T [G(\rho)]^n} \exp\left(-\frac{Q}{RT}\right) \quad (28)$$

In the case of diffusion-rate control, Q is the activation energy for the diffusion of the solid through the liquid phase and should be the same as the viscosity of the liquid phase. Further, $K_0 = \delta D_d$ and $n = 4$. For interfacial-reaction control, Q is the activation energy for the interfacial reaction. Further, $K_0 = k_2$ and $n = 2$. In the case of this equation, G and Γ are assumed to be functions only of the density. By separating the variables and integrating the equation, we get the following:

$$\frac{k_B}{3\gamma_{LV}C_0\Omega_a K_0} \int_{\rho_0}^{\rho} \frac{[G(\rho)]^n}{\rho \Gamma(\rho)} d\rho = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (29)$$

The left-hand side of Eq. (29) is a function of the density, microstructure, and material properties (the exception is the activation energy of sintering) as follows:

$$\Phi_{sp}(\rho) \equiv \frac{k_B}{3\gamma_{LV}C_0\Omega_a K_0} \int_{\rho_0}^{\rho} \frac{[G(\rho)]^n}{\rho \Gamma(\rho)} d\rho \quad (30)$$

The right-hand side of Eq. (29) is a function of Q as well as the time and temperature—this suggests a standardized firing profile:

$$\Theta(t, T) \equiv \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (31)$$

Consequently, the following equation is obtained:

$$\Phi_{sp}(\rho) = \Theta(t, T) \quad (32)$$

This relationship indicates that the MSC for liquid phase sintering is the same as that for solid-state sintering. The MSC can be plotted

3. Experimental procedure

Very fine high-purity powders of Si_3N_4 (Ube Industries, Ltd., E-10), Y_2O_3 (Shinetsu Chemical Co., Ltd., RU), Al_2O_3 (Sumitomo Chemical Co., Ltd., AKP-30), AlN (Tokuyama Corp., F-Grade), and TiO_2 (Sakai Chemical Industry Co. Ltd., R-11P) were used as the raw materials. The compositions of the various batches are listed in **Table 1**. The raw materials were mixed in ethanol by ball milling along with 2 wt % dispersant (Seruna E503, Chukyo-yushi Co., Japan). After the ethanol had been removed, 4 wt % paraffin (melting point 46–48°C, Junsei Chemical Co., Japan) and 2 wt % Bis(2-ethylhexyl) phthalate (Wako Junyaku Co., Japan) were added as the binder and lubricant, respectively. The powder mixtures were molded into specimens with a diameter of 15 mm and length of 7 mm by uniaxial pressing and cold isostatic pressing. The green bodies were dewaxed at 500°C in air. The degree of sintering shrinkage was measured in-situ directly using a dilatometer equipped with a gas pressure furnace (Himulti 5000, Fujidenpa Kogyo Co., Japan), in keeping with previous studies.^{37),38)} This apparatus calculates the degree of sintering shrinkage of the test sample on the basis of the difference in the displacement of the sample with respect to a reference carbon rod. A BN plate was used to prevent the sample and the carbon rod from reacting with each other. The maximum temperature was 1800°C, the soaking time was 2 h, and the firing atmosphere was 0.9 MPa N_2 . In order to determine the MSC, the heating rate was varied from 10 to 30°C/min.

4. Results and discussion

Figure 1(a) shows the sintering shrinkage curves of Si_3N_4 ceramics produced using different sintering aids. The curves were measured at a heating rate of 10°C/min. Although all the samples measured shrinking at almost the same temperature (~1350°C) and exhibited the same final shrinkage ratio (approximately 20%), their shrinkage behaviors varied with the sintering aid used. **Figure 1(b)** shows the shrinkage rates as calculated from the experimental data shown in **Fig. 1(a)**. Three peaks were observed in the case of all the samples. The first peak was observed at approximately 1500°C. In a previous study, we had observed that the α -to- β phase transformation of Si_3N_4 commenced at temper-

Table 1. Batch compositions (weight ratio) of the samples used to evaluate the sintering shrinkage behaviors of Si_3N_4 ceramics

Sample	Si_3N_4	Y_2O_3	Al_2O_3	TiO_2	AlN
0T0A	92	5	3	0	0
5T0A	92	5	3	5	0
0T5A	92	5	3	0	5
5T5A	92	5	3	5	5

atures higher than 1500°C and finished at temperatures equal to or higher than 1800°C; this was true for all the samples.³⁷⁾ Therefore, the three peaks in Fig. 1(b) were considered to be related to grain rearrangement, solution-precipitation, and Ostwald ripening, respectively. On comparing Figs. 1(a) and 1(b), it can be seen that the grain rearrangement occurred when the shrinkage ratio was lower than 2%. This was followed by solution-precipitation, which occurred when the ratio was between 2 and 18%.

Figure 2 shows the shrinkage ratios measured at different heating rates. The temperature at which shrinkage started increased and the shrinkage ratio decreased with an increase in

Fig. 1. (a) Shrinkage ratios and (b) shrinkage rates of Si_3N_4 ceramics produced using different sintering aids.

the heating rate; again, this was the case for all the samples. The MSC was obtained by minimizing the square of the residual error of $\Theta(t, T)$ for the same shrinkage ratio for different heating rates; this was done by varying the activation energy, Q , as was done in a previous study on the solid-state sintering of Al_2O_3 .²⁷⁾ $\Theta(t, T)$ was estimated from the numerical calculation of the integral in Eqs. (7) and (31) using the time-temperature relationship and the activation energy. In order to obtain the MSC, the specific values of the parameters in the Eqs. (6) and (30), such as A , G , γ_{LV} , C_0 , K_0 , are not used as is the case with the previous study.^{22)–26)} Furthermore, the MSC was separately estimated using the shrinkage ratio data of 0–2%, 2–15%, and over 15%, respectively.

Figures 3(a) and 4(a) show the MSC of sample 0T0A. The MSC was obtained for ratios of 0–2% [Fig. 3(a)] and 2–15% [Fig. 4(a)], with the activation energies being 294 and 345 kJ/mol, respectively. This meant that the apparent activation energies of sintering by grain rearrangement and solution-precipitation were 294 and 345 kJ/mol, respectively, for sample 0T0A. As shown in Figs. 3(b)–3(d) and Figs. 4(b)–4(d), the MSCs corresponding to grain rearrangement and the solution-precipitation process were obtained for all the samples. However, the MSCs could not be obtained for ratios greater than 15%.

Fig. 2. Shrinkage ratios of sample 0T0A when fired at various heating rates.

Fig. 3. MSCs of the Si_3N_4 ceramics for shrinkage ratios of 0–2%: (a) 0T0A, (b) 5T0A, (c) 0T5A1, and (d) 5T5A.

Fig. 4. MSCs of the Si_3N_4 ceramics for shrinkage ratios of 2–15%: (a) 0T0A, (b) 5T0A, (c) 0T5A, and (d) 5T5A.

Fig. 5. SEM images of sample 0T0A, which was fired at 1800°C for 120 min at heating rates of 10 and 30°C/min.

Table 2. Apparent activation energies of sintering of the Si_3N_4 ceramics (unit: kJ/mol)

Sample	Range of shrinkage ratios	
	0–2%	2–15%
0T0A	294	345
5T0A	273	371
0T5A	251	430
5T5A	270	350

Figure 5 shows SEM images of sample 0T0A, which was fired at 1800°C for 120 min at heating rates of 10 and 30°C/min. Significantly elongated grains of $\beta\text{-Si}_3\text{N}_4$ were observed. Further, the microstructure depended on the heating rate used. In addition, it has been reported that the growth of elongated grains can lead to the expansion of the sintered body.³⁹⁾ It is for this reason that the MSC could not be measured for shrinkage ratios greater than 15%.

Table 2 lists the apparent activation energies of sintering of the Si_3N_4 ceramics, which were approximately 250–290 and 350–430 kJ/mol for grain rearrangement and the solution-precipitation process, respectively. The apparent activation energy of sintering of Si_3N_4 for grain rearrangement also depended slightly on the sintering aid used. Abe has reported that the activation energy

for the initial stage of sintering of Si_3N_4 is 244.0 kJ/mol.⁴⁰⁾ The apparent activation energies determined in the present study were almost similar to those reported by Abe, even though the sintering aids used in the two studies had different compositions.

The apparent activation energy of sintering for the solution-precipitation process has been reported by a number of researchers.^{41)–47)} The value (approximately 350 kJ/mol) determined during a grain growth study⁴¹⁾ was relatively low. However, the apparent activation energy estimated in the present study was almost similar. The diffusion of nitrogen through the oxynitride liquid phase is believed to result in a higher activation energy, because the number of chemical bonds in nitrogen is greater than that of the bonds in oxygen. The nitrogen content of the liquid phase can be increased by adding AlN. Furthermore, TiN is formed during the sintering of Si_3N_4 , owing to a reaction between TiO_2 and AlN.³⁷⁾ As a result, the apparent activation energy of sample 0T5A was higher than those of the other samples.

5. Conclusions

The MSC theory was extended to liquid phase sintering for grain rearrangement and the solution-precipitation process. The sintering behaviors of Si_3N_4 powder compacts were observed directly using a dilatometer. Further, the MSC theory was applied to determine the validity of the experimentally obtained sintering

shrinkage ratios. The MSCs of the Si_3N_4 ceramics corresponding to grain rearrangement and the solution-precipitation process were measured; these were related to shrinkage ratios of 0–2 and 2–15%, respectively. Finally, the activation energies corresponding to grain rearrangement and the solution-precipitation process were 251–294 and 345–430 kJ/mol, respectively, depending on the sintering aid used.

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