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Densification behaviors and high-temperature characteristics of Si_3N_4 sintered bodies using Al_2O_3–Yb_2O_3 additives

Hirokazu Yamamoto[a,*], Katunori Akiyama[b], Yuichiro Murakami[b]

[a] *Nagasaki R&D Center, Mitsubishi Heavy Industries, Ltd., 5-717-1, Fukahori-cho Nagasaki-shi 851-0392, Japan*
[b] *Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd., 1-8-1, Sachiura, Kanazawa-ku, Yokohama-shi 236-8515, Japan*

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Abstract

The densification behaviors (include α–β transformation) and high-temperature characteristics (especially oxidation resistance and high-temperature strength properties) of Si_3N_4 sintered bodies using Al_2O_3–Yb_2O_3 based sintering additive are investigated.

Densification and α–β transformation behaviors were investigated by varying the compositions of Al_2O_3–Yb_2O_3 additives. In terms of the influence of the Y_2O_3/Al_2O_3 ratio on densification behavior, a greater Yb_2O_3/Al_2O_3 ratio tends to inhibit densification. The α–β transformation tended to be delayed in sintered bodies with a small additive amount of 3.4 mass%. Compared with the transformation behaviors of the sintered bodies using Al_2O_3–Y_2O_3 additives, those using Al_2O_3–Yb_2O_3 additives exhibited a narrower temperature zone for α–β transformation, which attributed to the finer structure for the sintered body using Al_2O_3–Yb_2O_3 additives. This is affected by the difference in solubility of Si_3N_4 in the two kinds of glass phase.

High room temperature strength of 900–1000 MPa was obtained for sintered bodies with a 10.0 mass% addition of additives, and this is considered to be due to the finer micro-structure. Precipitation of a $Yb_4Si_2N_2O_7$ phase at the grain boundary glass phase, as induced by crystallization processing, enables the improvement of 1300 °C strength to about 650–720 MPa. Crystallization processing resulted in a 30% reduction in the amount of weight change during oxidation (from 3.42 to 2.46 mg/cm^2), demonstrating the effectiveness in improving oxidation resistance.

Keywords: Si_3N_4; Grain boundaries; Microstructure-final; Strength; Sintering

1. Introduction

Substantial effort has been devoted to the research and development of Si_3N_4 ceramics aimed at improved efficiency for application to various high-temperature equipment.[1] In order to improve the high-temperature characteristics of Si_3N_4, it is important to control the glass phase formed at grain boundaries with additives (added for densification) and SiO_2 (contained in Si_3N_4 raw powders). Additives such as Y_2O_3–Al_2O_3,[2] Yb_2O_3,[3] and Lu_2O_3[4] have been used for developing Si_3N_4 sintered bodies. The Yb_2O_3–SiO_2–Si_3N_4 phase diagram has been clarified for Yb_2O_3 based additives,[5] and it has been reported that the Si_3N_4 sintered body having superior high-temperature strength has been obtained.[3] The application of Al_2O_3–Yb_2O_3 additives is considered to be effective in obtaining Si_3N_4 with both improved sinterability and excellent high-temperature strength.

The phase equilibrium for Al_2O_3–Yb_2O_3–SiO_2 has already been elucidated.[6] The solidus temperature, at which the liquid phase begins to form during heating, for new additives based on Al_2O_3–Yb_2O_3–SiO_2 system is about 100–150 °C higher than that for conventional Al_2O_3–Y_2O_3–SiO_2 system.[7] It is, therefore, expected that the sintering behavior with Al_2O_3–Yb_2O_3 additives is different from that with Al_2O_3–Y_2O_3 additives, and it is necessary to ascertain correctly this behavior in order to optimize the sintering conditions. And, it is also necessary to determine whether Si_3N_4 with superior high-temperature strength for high-temperature application can be obtained under

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* Corresponding author.
E-mail address: fwip2008@mb.infoweb.ne.jp (H. Yamamoto).

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sintering conditions in a nitrogen atmosphere under 1 MPa by using these additives.

Accordingly, in this paper, densification and α–β transformation behaviors were investigated by varying the compositions of Al_2O_3–Yb_2O_3 additives, and the high-temperature characteristics (especially oxidation resistance and high-temperature strength) of Si_3N_4 sintered bodies were evaluated.

2. Experimental

The raw material powders used for testing were Ube Industries SN-E10 (purity of 99.9% and average grain size of 0.3 μm) for Si_3N_4, Sumitomo Chemical AKP-30 (purity of over 99.9% and average grain size of 0.4 μm) for Al_2O_3, and Shin-Etsu Chemical SU (purity of 99.9% and average grain size of 0.1 μm) for Yb_2O_3.

The compositions of the sintering additives are indicated by the solid dots on the phase diagram[6] in Fig. 1, in which the raw material Yb_2O_3/Al_2O_3 ratios are also shown. After measuring the prescribed amount of raw material powders, wet mixing was performed in butanol, and the mixed powders were obtained after drying in a rotary evaporator. The mixed powders thus prepared were subjected to CIP forming at 392 MPa to produce pellets measuring 30 mm in diameter by approximately 5 mm in thickness. For investigation of densification and α–β transformation behavior, sintering was carried out in a 0.6 MPa nitrogen gas atmosphere in the temperature range of 1500–2000 °C. The rate of temperature rise was 1 °C/min, and the sintering bodies were cooled in furnace after the temperature had risen to the target temperature. And, for evaluation of high-temperature characteristics, sintering was performed in a 0.6 MPa nitrogen gas atmosphere for 0–16 h in the temperature range of 1700–1900 °C. The compositions of the prepared sintered bodies are also shown in Fig. 1.

The sintered bodies obtained were subjected to evaluation of density and pore distribution. Density was measured as bulk density, and the relative density was determined from the theoretical density calculated by allocating the weight ratio of the additive composition. The pore distribution was observed using an optical microscope, after polishing the specimens embedded in plastic. The amount of β-phase was quantified from the ratio of diffractive intensities of α-Si_3N_4 (2 0 1) and β-Si_3N_4 (1 0 1) peaks observed by the X-ray diffraction (XRD). Microstructural observation was carried out using the scanning electron microscope (SEM).

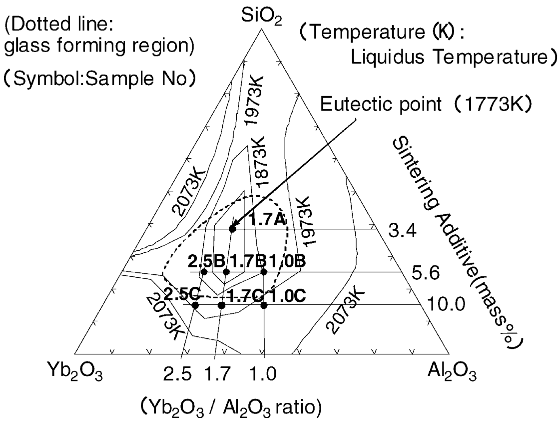
Strength characteristics were evaluated for samples with relative density corresponding to approximately 98% and above. For this purpose, four-point bending strength was measured at room temperature and at 1300 °C. All strength evaluation conditions were based on the JIS-R1601 standard. A large electric furnace was used in the evaluation of oxidation resistance properties. The above-noted JIS-R1601 test pieces were placed in an SiC jig, and kept at 1300–1400 °C for 100–300 h, with oxidation properties evaluated by visual observation and measurement of weight changes during oxidation.

For comparison, Si_3N_4 sintered bodies were also prepared using a representative Al_2O_3–Y_2O_3 additive consisting of 4.0 mass% Y_2O_3 and 1.6 mass% Al_2O_3 (Y_2O_3/Al_2O_3 ratio of 2.5), sintered at 1800 °C for 4 h.

3. Results and discussion

3.1. Densification behavior

Fig. 2 presents the densification behaviors of Si_3N_4 ceramics with different amounts of additives, using additives with Yb_2O_3/Al_2O_3 ratio of 1.0, 1.7, and 2.5, respectively. In specimens having additive amount of 5.6 mass%, densification tends to be inhibited with increasing the Yb_2O_3/Al_2O_3 ratio. In particular, when the Yb_2O_3/Al_2O_3 ratio is 2.5, a sintering temperature of 1900 °C or higher is required in order to obtain a dense sintered body having relative density of above 98%. In the case of an additive amount of 10 mass%, the increase



Sample No.	Composition of Sinterd body (mass%)				Sintering additive (mass%)
	Al_2O_3	Yb_2O_3	SiO_2	Si_3N_4	
1.7A	1.24	2.11	2.05	94.6	3.35
1.0B	2.80	2.80	2.00	92.4	5.60
1.7B	2.07	3.53			
2.5B	1.60	4.00			
1.0C	2.80	2.80	1.90	88.1	10.0
1.7C	2.07	3.53			
2.5C	1.60	4.00			

Fig. 1. Composition of Si_3N_4 sintered body and the position of grain boundary phase on phase diagram of the Yb_2O_3–Al_2O_3–SiO_2 system.

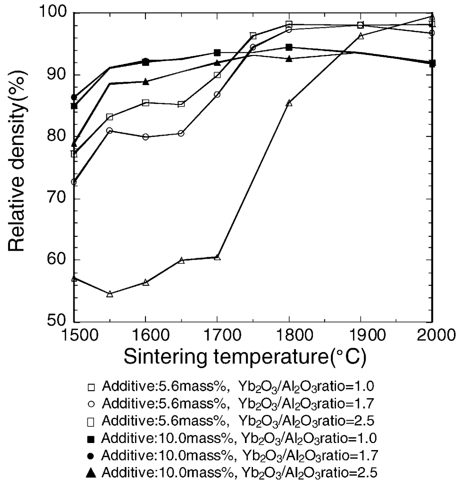


Fig. 2. Sintering temperature dependence of the relative density of Si_3N_4 ceramics (amount of additive: 5.6 and 10.0 mass%).

of additives tends to promote densification, compared with the results of an additive amount of 5.6 mass%. However, the influence of Yb_2O_3/Al_2O_3 ratio tended to become smaller. In order to achieve the dense sintering at the same temperature of 1700–1900 °C using Al_2O_3–Yb_2O_3 based additives, a Yb_2O_3/Al_2O_3 ratio below 1.7 is needed for a low additive amount of 5.6 mass%, or else an additive amount of at least 10.0 mass% is required. The rate of increasing density may be affected by the solubility of β-Si_3N_4 in the liquid phase, although the Si_3N_4 solubility to the liquid phase formed by the Al_2O_3–Yb_2O_3 additives and SiO_2 is unclear.

Fig. 3 shows the densification behaviors of Si_3N_4 having additives with a Yb_2O_3/Al_2O_3 ratio of 1.7 and with different, additive amounts of 3.35, 5.6, and 10.0 mass%, respectively. As is clear from the figure, densification progresses rapidly from 1700 to 1900 °C at a low additive amount of 3.35 mass%, and the corresponding temperature zone for an additive amount of 5.6 mass% is about 100 °C lower, or 1600–1800 °C. For a high additive amount of 10.0 mass%, densification seems to have progressed substantially at 1500 °C. However, the trend with respect to density is reversed at temperatures above 1900 °C; Specimens containing a smaller additive amount clearly exhibit greater density. Densification behavior at temperatures below 1900 °C is considered to be basically dependent on the amount of additives, i.e. probably on the amount of liquid phase formed in the sintered body.

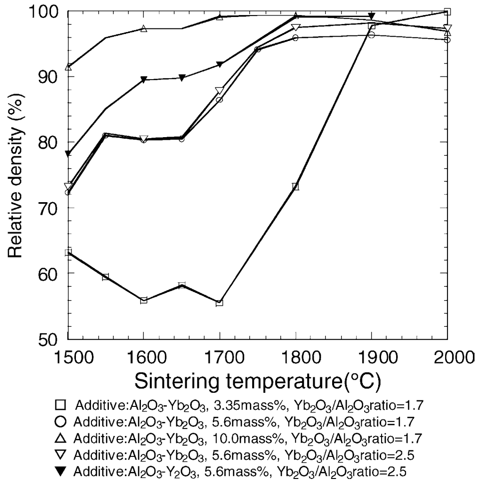


Fig. 3. Sintering temperature dependence of the relative density of Si_3N_4 ceramics (Yb_2O_3/Al_2O_3 ratio: 1.7 and comparison of the additive).

Fig. 3 also presents the comparative results of densification behavior of sintered bodies with different additives, Al_2O_3–Yb_2O_3 and conventional Al_2O_3–Y_2O_3, where the amount of additive is 5.6 mass%, and the Y_2O_3/Al_2O_3 and Yb_2O_3/Al_2O_3 ratios are 2.5. These results indicate that the relative density obtained by using Al_2O_3–Yb_2O_3 additives is about 10% lower than that obtained by Al_2O_3–Y_2O_3 additives in the range of sintering temperatures below about 1750 °C. When the temperature is further increased, density for Al_2O_3–Yb_2O_3 reaches nearly the same relative density as that for Al_2O_3–Y_2O_3 additives, but the relative density tends to be somewhat lower for sintered bodies using Al_2O_3–Yb_2O_3 additives.

Densification tends to be delayed for the Al_2O_3–Yb_2O_3 additive, for which solidus temperatures are higher and the liquid phase is considered to be formed at higher temperatures compared with Al_2O_3–Y_2O_3 additives. In addition, as describe later, the viscosity of Al_2O_3–Yb_2O_3 based glass phase, which has a higher solidus temperature, is greater at the same temperature than that of the Al_2O_3–Y_2O_3 additives.

3.2. *α–β Transformation behavior*

The transformation, which occurs during sintering of Si_3N_4, affects the microstructural morphology of the final sintered body. Consequently, this is an important factor for determining the sintering conditions for structural control. Accordingly, the influence of the Al_2O_3–Yb_2O_3 additive composition on α–β transformation behavior was investigated.

Fig. 4 presents the amount of β-phase as a function of sintering temperature, using additive with Yb_2O_3/Al_2O_3 ratios of 1.0, 1.7, and 2.5, respectively. In the sintering behavior of specimens with an additive amount of 5.6 mass% and with a Yb_2O_3/Al_2O_3 ratio of 1.7, transformation tends to occur at lower temperatures as shown in Fig. 4. Regardless of the Yb_2O_3/Al_2O_3 ratio, however, β-phase amount of nearly 100% is attained at 1650 °C. In the case where the additive amount is 10.0 mass%, the change in the α–β transformation rate is almost similarly independent on the Yb_2O_3/Al_2O_3 ratio, and nearly 100% of β-phase is attained at temperature above 1650 °C.

The compositional dependence of the liquidus line for Al_2O_3–Yb_2O_3–SiO_2 is indicated in Fig. 1, in which the eutectic composition exists on a line with for the Yb_2O_3/Al_2O_3 ratio 1.7.[6] Because a greater amount of liquid phase is considered to be formed at a composition near the eutectic

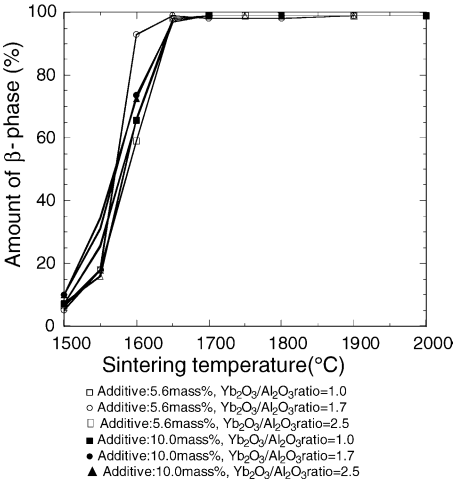


Fig. 4. Sintering temperature dependence of the amount of β-phase of Si_3N_4 ceramics (amount of additive: 5.6 and 10.0 mass%).

composition, the rapid progress of α–β transformation may occur at a low temperature in specimens using additives with a Yb_2O_3/Al_2O_3 ratio of 1.7. In specimens with a large amount of additives, e.g. 10.0 mass%, where a large amount of liquid phase would be formed, the Yb_2O_3/Al_2O_3 ratio dependence of α–β transformation behavior would no longer be exhibited.

Fig. 5 indicates the amount of β-phase as a function of sintering temperature, using additives with a Yb_2O_3/Al_2O_3 ratio 1.7 and with additive amounts of 3.35, 5.6, and 10.0 mass%, respectively. The α–β transformation tends to be delayed in sintering bodies with a low additive amount of 3.35 mass%.

Fig. 5 also presents the comparative results for α–β transformation behavior in specimens with Al_2O_3–Yb_2O_3 and Al_2O_3–Y_2O_3 additives as a function of sintering temperature, where the sintering additives, with an additive amount of 5.6 mass%, and with Y_2O_3/Al_2O_3 and Yb_2O_3/Al_2O_3 ratios of 2.5 are used for sintering. Compared with the Al_2O_3–Y_2O_3 additives, Al_2O_3–Yb_2O_3 additives result in the occurrence of β-phase amount of nearly 100% at 1650 °C: this temperature is approximately 50 °C lower than that for Al_2O_3–Y_2O_3 additives. It is evident, then, that the Al_2O_3–Yb_2O_3 additives affect the transformation behavior such that the α–β transformation takes place in a narrower temperature zone compared with that for Al_2O_3–Y_2O_3 additives. This may be attributed to the difference in the solubility of Si_3N_4 in the liquid phase existing at the Si_3N_4 grain boundary. The reason for this is thought to be that the solubility of Si_3N_4 grains is 7.5 mass% at 1550 °C with respect to the Al_2O_3–Yb_2O_3–SiO_2 based glass phase,[7] and 6–7 mass% at 1500 °C with respect to the Al_2O_3–Y_2O_3–SiO_2 based glass phase,[8] i.e., indicating greater solubility for Al_2O_3–Yb_2O_3. It is considered that the α–β transformation proceeds more quickly when the Al_2O_3–Yb_2O_3 additives, having greater solubility, are used.

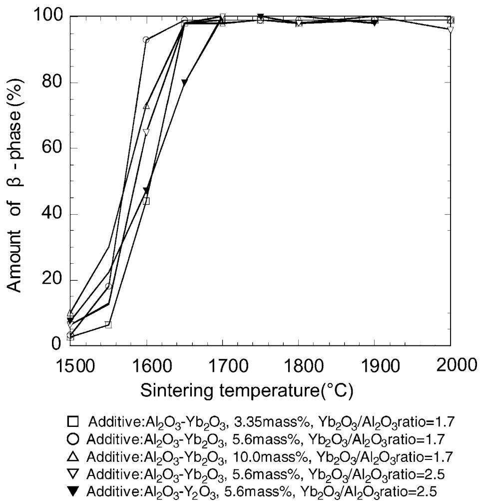


Fig. 5. Sintering temperature dependence of the amount of β-phase of Si_3N_4 ceramics (Yb_2O_3/Al_2O_3 ratio: 1.7 and comparison of the additive).

Fig. 6 shows SEM micrographs of sintered bodies using Al_2O_3–Yb_2O_3 and Al_2O_3–Y_2O_3 additives with identical additive compositions and with identical additive amounts. These are observed immediately after the α–β transformation and after sintering at 1900 °C. The Si_3N_4 sintered body using Al_2O_3–Yb_2O_3 additives (for which transition occurs in a narrow temperature zone) exhibits a finer structure than that of the sintered body using Al_2O_3–Y_2O_3 additives. The influence of Al_2O_3–Re_2O_3 (Re: rare earth element) additives on microstructure of Si_3N_4 sintered body has been reported;[9,10] these results are in agreement with those of Björklund et al.[10]

3.3. Evaluation of strength characteristics

Fig. 7 represents the relative density and the 4-point bending strength of sintered bodies at room temperature and at 1300 °C using additive amounts of 3.35, 5.6 and 10.0 mass%, respectively. Comparison with the results for Al_2O_3–Y_2O_3 is also provided in Fig. 7. Almost all of the samples attained the relative density of 98% or higher, regardless of the amount of additives added or the Yb_2O_3/Al_2O_3 ratio. Accordingly, it was demonstrated that the sintering at 1800–1900 °C for 4 h is sufficient. It was also clarified that the high room temperature strength of 900–1000 MPa can be obtained when the sintered bodies are produced using a large amount of Al_2O_3–Yb_2O_3 additive (i.e., 10.0 mass%). This is thought to result from a finer structure due to the occurrence of α–β transformation in a narrow temperature range. However, although the room temperature strength is sufficient, this is not reflected in the 1300 °C strength, which produced a low result of 300–400 MPa; the results seem to be independent of the amount of additives and the Yb_2O_3/Al_2O_3 ratio.

Based on the evaluation results for the strength characteristics of the sintered bodies produced with 5.6 mass% addition of additives as shown in Fig. 7, a trend was recognized that the 1300 °C strength increased with increasing Yb_2O_3/Al_2O_3 ratio up to 2.5. Also, in comparison with the same Yb_2O_3/Al_2O_3 ratio, room temperature strength tended to increase with larger additions of additives. Thus, Fig. 8 presents the influence of Yb_2O_3/Al_2O_3 ratio and

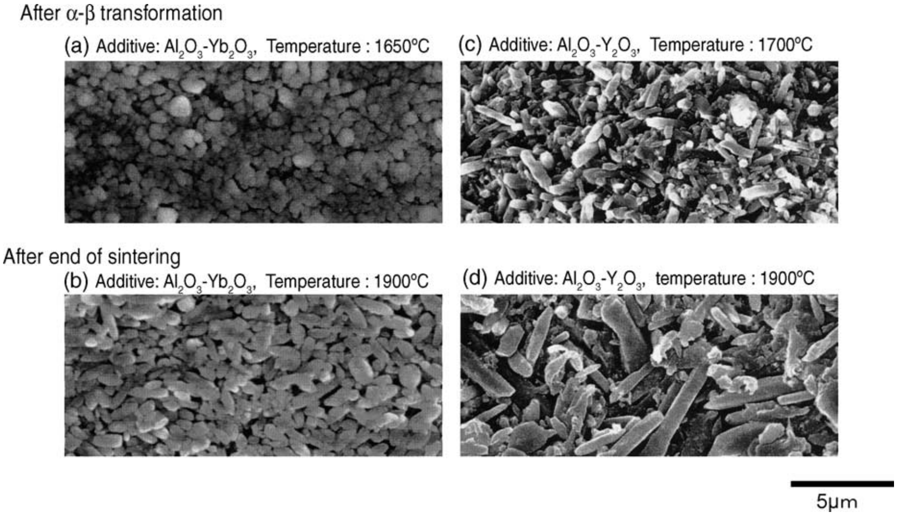


Fig. 6. Microstructure of Si_3N_4 ceramics of just after α–β transformation and after end of sintering (a) and (b) Al_2O_3–Yb_2O_3 sintering additive; (c) and (d) Al_2O_3–Y_2O_3 sintering additive.

additive amount on the high-temperature strength. Here, the Yb_2O_3/Al_2O_3 ratios of the additives are 1.7–20. The amounts of additives are 5.6, 10.0 and 20.0 mass%, and the sintering conditions are 4 h at 1800 °C. Although the room temperature strength tended to decline with increase in the Yb_2O_3/Al_2O_3 ratio for both 5.6 and 10 mass% additive amounts, the 1300 °C strength was conversely found to rise. Structural observation suggests that the reason for decrease in room temperature strength is the increase in porosity resulting from reduced sinterability. However, a clear rising trend was observed in 1300 °C strength. This is considered to be due to a composition outside the glass forming region (shown in Fig. 1) for large Yb_2O_3/Al_2O_3 ratios, which attains the precipitation of a crystal phase in the grain boundary glass phase, as well as greater viscosity of the grain boundary glass phase accompanying the liquidus temperature (viscosity may also be increased due to the precipitated state of the crystal phase). In the sintered body with additive amount of 20.0 mass%, the room temperature strength increases with increase in Yb_2O_3/Al_2O_3 ratio, suggesting that sinterability increases with increase in Yb_2O_3/Al_2O_3 ratio. These results show that sufficiently greater density enables higher 1300 °C strength while maintaining room temperature strength of about 800–900 MPa. With a Yb_2O_3/Al_2O_3 ratio of 20, 1300 °C strength was found to improve to approximately 450 MPa.

In order to clarify the influence of the amount of sintering additive, further evaluation was carried out in a sintered body with a Yb_2O_3/Al_2O_3 ratio of 20.0 and 22.9 mass% of Yb_2O_3, sintered for 4 h at 1800 °C. The room temperature

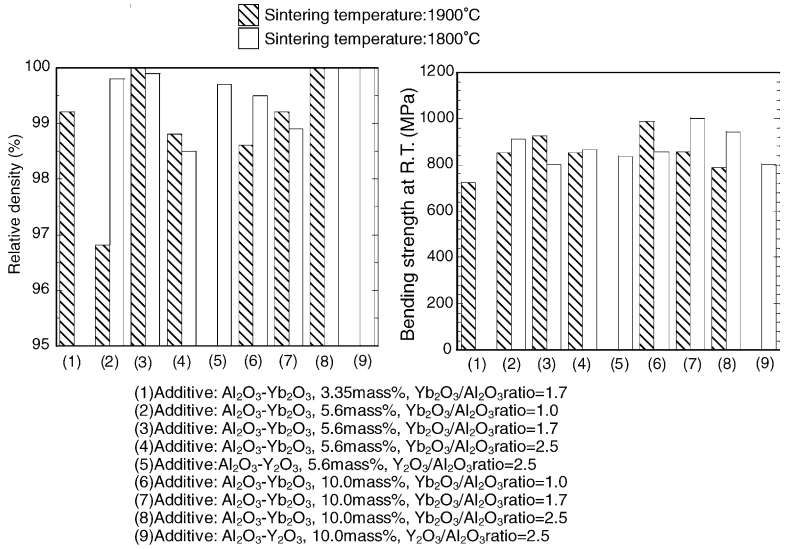


Fig. 7. Sintering additive composition dependence of the relative density and the bending strength at R.T. and 1300 °C of Si_3N_4 ceramics (amount of additive: 3.35, 5.6 and 10.0 mass%).

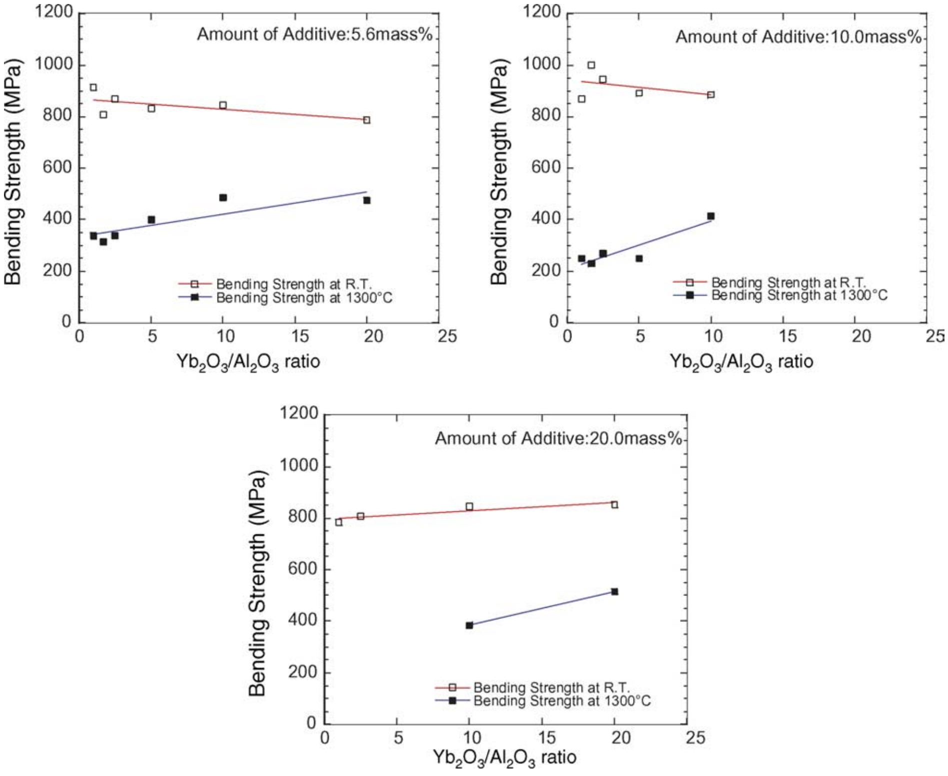


Fig. 8. Bending strength at R.T. and 1300 °C of Si_3N_4 ceramics(amount of dditive:5.6, 10.0 and 20.0 mass%) as a function of Yb_2O_3/Al_2O_3 ratio of additives.

and 1300 °C strengths at this composition were found to improve to 711 and 609 MPa, respectively. The result of 1400 °C strength measurement of this specimen was 480 MPa. A high strength similar to the 1300 °C bending strength of a sintered body using conventional Al_2O_3–Y_2O_3 additives was obtained in the sintered body at 1400 °C with Al_2O_3–Yb_2O_3 additives.

In order to identify the factors responsible for the difference in the high-temperature strength characteristics of Si_3N_4 using Al_2O_3–Yb_2O_3 and Al_2O_3–Y_2O_3 additives, evaluation was attempted with respect to the high-temperature viscosity properties of Al_2O_3–Yb_2O_3–SiO_2 glass. The evaluation method used an ELD type viscosity meter, with a crucible and rotor made of SiC which does not easily react with glass. The glass was first completely melted at 1700 °C in an air atmosphere. After the generation of air bubbles ceased, viscosity coefficient measurement (shearing speed of 0.105–10.5 s^{-1}) was initiated. Measurement was difficult, perhaps due to high viscosity, and the only glass composition for which measurement was successfully conducted was that having a Yb_2O_3/Al_2O_3 ratio of 1.7, with 39.0 mass% Al_2O_3, 38.0 mass% Yb_2O_3, and 23.0 mass% SiO_2. These results are indicated in Fig. 9, showing viscosity coefficient at 1600 °C of 83P (shearing speed of 4.1 s^{-1})–90P (shearing speed of 1.05 s^{-1}). This is high in comparison with the viscosity coefficient measured for Al_2O_3–Y_2O_3–SiO2 based glass. Accordingly the high-temperature strength is considered to have improved by using Al_2O_3–Yb_2O_3 additives.[11]

3.4. Improvement of high-temperature characteristics through grain boundary phase crystallization processing

Sintered bodies using Al_2O_3–Yb_2O_3 based sintering additives were also subjected to crystallization processing, and the possibilities were considered and evaluated for the improvement of high-temperature characteristics such as high-temperature strength and oxidation resistance.

It was clarified that, regardless of the glass composition, the crystallization initiation temperature is 1160–1180 °C and the glass transition temperatures is 880–960 °C.[6] Thus, the

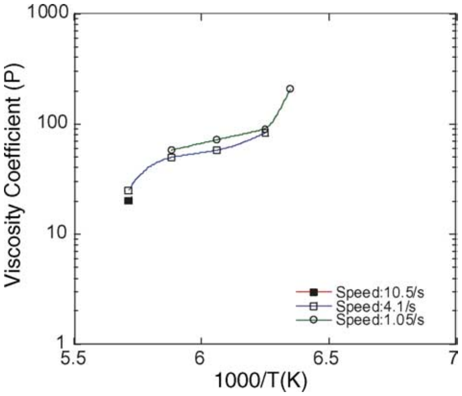


Fig. 9. Temperature dependence of the viscosity coefficient of Al–Yb–Si–O glasses (glasses composition: 39.0 mass% Al_2O_3 + 38.0 mass% Yb_2O_3 + 23.0 mass% SiO_2).

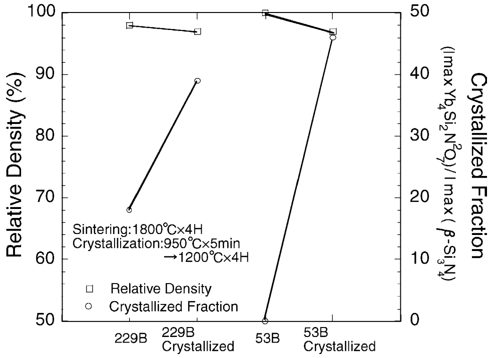


Fig. 10. Crystallized processing dependence of the relative density and the crystallized fraction of Si_3N_4 ceramics.

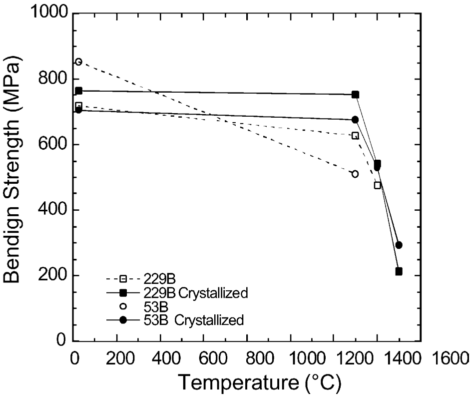


Fig. 11. Temperature dependence of the bending strength of Si_3N_4 ceramics with and without crystallized process.

processing conditions selected for the heat-treatment for crystallization consisted of 5 min holding at a crystal nuclei formation temperature of 950 °C, and 4 h holding at a crystal nuclei growth temperature of 1200 °C.

The Si_3N_4 sintering additive formulations evaluated were characterized by superior high-temperature strength, consisting of a composition with a Yb_2O_3/Al_2O_3 ratio of 20 and an additive amount of 24.07 mass%(229B composition), and a composition with a Yb_2O_3/Al_2O_3 ratio of 20 and an additive amount of 5.6 mass%(53B composition). Fig. 10 indicates an effect of crystallization processing on the relative density and the crystallization fraction in these sintered bodies. Here, the amount of the precipitated crystal phase was defined as the ratio between the maximum intensity of XRD peak for $Yb_4Si_2N_2O_7$ and that for β-Si_3N_4 in XRD. No problem was seen in terms of the sinterability of either the 229B or 53B compositions; they had finely sintered results. In 229B composition, the $Yb_4Si_2N_2O_7$ phase was formed as a crystal phase in the sintered body without crystallization processing, and the amount of $Yb_4Si_2N_2O_7$ phase approximately doubled during crystallization processing after sintering. On the other hand, in the 53B composition, the $Yb_4Si_2N_2O_7$ phase precipitated due to crystallization processing.

The strength characteristics of these samples are presented in Fig. 11. For the 229B composition, crystallization processing of the sintered body served to improve both room temperature and 1300 °C strength, with the latter in particular rising from 620 to 720 MPa as a result. For the 53B composition, room temperature strength declined slightly due to

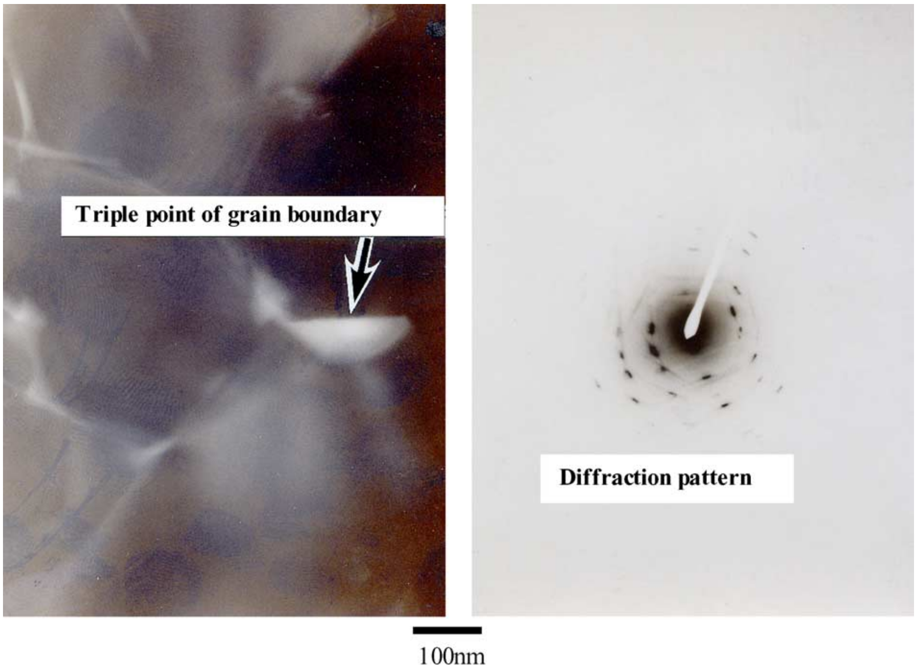


Fig. 12. Electron micrographs and electron diffraction pattern of Si_3N_4 ceramics after crystallized process.

Table 1
Weight change of Si_3N_4 ceramics after oxidation at 1300 °C

	Additive content (mass%)	Crystallized processing	Formed phases (crystallized fraction)	Weight change during oxidation (mg/cm^2)
Al_2O_3–Yb_2O_3 53B	5.6	No	–	3.42
		Yes	$Yb_4Si_2N_2O_7$ (46.2)	2.46
Al_2O_3–Yb_2O_3 229B	24.07	Yes	$Yb_4Si_2N_2O_7$ (39.2)	3.96
Al_2O_3–Y_2O_3	5.6	No	–	5.68

crystallization processing, but 1300 °C strength rose from 500 to 650 MPa. These results demonstrate that the high-temperature strength is improved by the precipitation of a $Yb_4Si_2N_2O_7$ phase in the grain boundary glass phase due to crystallization processing.

In order to investigate the extent of crystallization in the grain boundary glass phase, ultra-micro domain analysis was performed using a transmission electron microscope. Fig. 12 shows TEM photos of the 53B composition sintered bodies. Dot count results for the ultra-micro domain analysis images did not reveal halos (that would accompany non-crystallinity) at the grain boundary triple points. However, although crystallization occurred at the grain boundary triple points, no clear determination was made with respect to even finer domains, such as at the interfaces. In general, it is predicted that crystallization would be difficult from a physics perspective in such extremely fine domains.

3.5. Evaluation of oxidation resistance

The 229B (Yb_2O_3/Al_2O_3 ratio of 20, additive amount of 24.07 mass%) and 53B (Yb_2O_3/Al_2O_3 ratio of 20, additive amount of 5.6 mass%) Si_3N_4 sintered bodies, which possessed excellent high-temperature strength, were subjected to oxidation behavior measurement by holding the crystallization-processed samples for 300 h at 1300 °C in air. The evaluation results are shown in Table 1, which also lists the amount of additives and crystallization processing. It was found that, even for identical amounts of additives, the substitution of Yb_2O_3–Al_2O_3 for Y_2O_3–Al_2O_3 resulted in a reduction of approximately 60% in the amount of weight change during oxidation (from 5.68 to 3.42 mg/cm^2), and that crystallization processing resulted in a further reduction of 30% (from 3.42 to 2.46 mg/cm^2).

4. Conclusions

The densification and α–β transformation behaviors and high-temperature characteristics of Si_3N_4 sintered bodies using Al_2O_3–Yb_2O_3 based sintering additive are summarized as follows.

(1) In terms of the influence of the Y_2O_3/Al_2O_3 ratio on densification behavior, a greater Yb_2O_3/Al_2O_3 ratio tends to inhibit densification. In terms of the influence of additive amount on densification behavior, densification proceeds at a lower temperature in sintered bodies with a greater additive amount, but sintered bodies containing a smaller additive amount tend to attain larger density at sintering temperatures above 1900 °C.

(2) In terms of the influence of the Yb_2O_3/Al_2O_3 ratio on the α–β transformation behavior, transformation was observed to proceed at lower temperatures when the Yb_2O_3/Al_2O_3 ratio was 1.7, but the α–β transformation rate reached nearly 100% at 1650 °C for all of the ratios examined.

(3) In terms of the influence of additive amount on the α–β transformation behavior, a tendency for transformation was delayed in sintered bodies with a small additive amount of 3.35 mass%.

(4) Compared with the transformation behaviors of the sintered bodies using Al_2O_3–Y_2O_3 additives, those using Al_2O_3–Yb_2O_3 additives exhibited a narrower temperature zone for α–β transformation, which is attributed to the finer structure for the sintered body. This is affected by the difference in solubility of Si_3N_4 in the two kinds of glasses phases.

(5) High room temperature strength of 900–1000 MPa was obtained for sintered bodies with a 10.0 mass% addition of additives, and this is considered to be due to the finer micro-structure. The high-temperature strength of sintered bodies having a Yb_2O_3/Al_2O_3 ratio in the range of 1.0–1.5 was about 300–400 MPa, and no improvement in high-temperature strength was observed.

(6) For sintered bodies obtained by using additives with a Yb_2O_3/Al_2O_3 ratio of 20 (with 22.9 mass% Yb_2O_3 and 1.17 mass% Al_2O_3), high-temperature strength improved to 620MPa for 1300 °C strength and 480 MPa for 1400 °C strength. The improvement in the high-temperature strength of Si_3N_4 using Al_2O_3–Yb_2O_3 additives is considered to be due to the fact that the high-temperature viscosity coefficient of Al_2O_3–Yb_2O_3–SiO_2 based glass is higher than that of Al_2O_3–Y_2O_3–SiO_2 based glass.

(7) Precipitation of a $Yb_4Si_2N_2O_7$ phase at the grain boundary glass phase, as induced by crystallization processing, enables the improvement of 1300 °C strength to about 650–720 MPa.

(8) Crystallization processing resulted in a 30% reduction in the amount of weight change during oxidation (from

3.42 to 2.46 mg/cm^2), demonstrating the effectiveness in improving oxidation resistance.

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