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Grain growth in millimeter wave sintered silicon nitride ceramics

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Abstract

In this paper, to investigate the effect of millimeter wave heating on grain growth behavior in silicon nitride ceramics, specimens doped various rare earth sesquioxides as additives were sintered using a millimeter wave radiation 28 GHz. Comparative studies of densification, phase transformation, grain growth behavior of silicon nitride fabricated by millimeter wave and conventional sintering were carried out. Microstructure of the specimens was analyzed by scanning electron microscopy (SEM) and image analysis. Fully dense millimeter wave sintered silicon nitride presented a bimodal microstructure exhibiting higher values of fracture toughness and fracture strength than materials processed by conventional heating techniques. Results indicate that millimeter wave sintering is more effective in enhancing the grain growth and in producing the bimodal microstructure than conventional heating. It is also confirmed that the localized heating by millimeter wave radiation is taking place within the samples.

Keywords: Grain growth; Microwave processing; Si_3N_4; Sintering

1. Introduction

Silicon nitride (Si_3N_4) ceramics have been widely recognized as high temperature structural materials having excellent performance, such as good mechanical properties, high resistance to corrosion and high creep resistance. For these reasons, silicon nitride is being used for applications where metals can not be used, for example in high temperature gas turbines, heat exchangers, automotive engine components and cutting tools. Currently, silicon nitride-based ceramics are sintered by uni-axial hot-pressing and pressureless sintering. In this method, however, it is difficult to prepare the complex shapes and to control the degree of microstructure.

On the other hand, microwave heating technology has already spread in many fields such as industry, chemical reaction, biological sciences, household applications. Microwave heating is often termed the ''internal heating'' against the conventional ''external heating'' like an electric oven. Temperature profile within the material is opposite to that of conventionally fired materials, with the centre being the location of highest temperature. The microwave heating system is quite different from the usual heating by radiant heat and heat transfer. When irradiating microwave on the object, the material couple with the microwaves and absorbs the electromagnetic energy, transforming it into heat. Microwave heating generally means dielectric heating which heats dielectric substances in microwave and electromagnetic field. It can be regarded dielectric substances as assembly of molecules carrying a positive and negative charge. Placing this dielectric in the electric field, the molecules are polarized, as shown in Fig. 1b and c, from electrically equilibrium state shown in Fig. 1a. Molecules switch the state between Fig. 1b and c repeatedly because of alternative high frequency electric field. Consequently, molecules cause friction and collision each other and material generates the heat by itself.

In ceramics field, microwave heating technology has already adopted practically in pre-sintering process and for drying process to remove moisture and organic binders from a green body. Microwave heating makes the heating period shorter and the densification seems to be completed at relatively low sintering temperatures (saving energy). Furthermore, microwave can heat the object selectively using the difference of energy absorption efficiency of the materials. In addition to these properties, the fact that microwave heating is capable of producing material microstructures and properties different to those produced by conventional heating. This phenomenon is often called the ''microwave effect.''

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Although processing of established ceramics using microwave heating started with the aim at energy saving at first, active studies concerning with the "microwave effects" are still at a developmental stage.

Absorption energy of dielectric substance P is given as following

$$P = 2\pi f\varepsilon_0\varepsilon_r \tan\delta E^2 V_S \Theta \quad (1.1)$$

$$= 2\pi f\varepsilon'' E^2 V_S \Theta \quad (1.2)$$

where f is the frequency, ε_0 is the dielectric constant of vacuum, ε_r is the relative dielectric constant, $\tan\delta$ is the loss tangent, E is the strength of electric field, V_S is the volume of sample, Θ is the shape factor, ε'' is dielectric loss factor. When E, V_S and Θ are constant, the absorption energy P depends on $f\varepsilon''$.[1,2] But many ceramics have a low dielectric loss factor and couple poorly with microwaves at low temperature. Silicon nitride is no exception to this fact, the heating in a microwave field has to be associated to the preferential microwave absorption of the oxide additives. It was generally said that the addition of rare earth oxide to ceramics changes electrical characteristics in some cases.[3,4] It can be expected that differences in the nature and/or in the absorption factor of the additive will influence the sintering process and hence the final microstructure. However, the dielectric loss tends to increase dramatically with temperature, and above a certain critical temperature the material will couple readily. But sometimes this can lead to sintering problem such as thermal runaway, whereby heating of the absorbing material leads to increase in its absorbing capability and thus further increases in temperature. Such phenomena can lead to sample cracking. The selection of the sintering additive is more important significance in microwave heating.

In order to solve various problems arising in microwave heating, the use of millimeter wave is very effective. Since the above mentioned absorption energy P is proportion to the frequency, the efficiency of heating of millimeter wave is higher than microwave. Sufficient uniformity of the wave field can be obtainable in a practical applicator size because of its shorter wave length. The temperature dependency of dielectric loss factor ε'' is smaller when the frequency of microwave is higher (millimeter wave). This is very important to prevent thermal runaway. Consequently, these advantages make it possible to heat ceramics homogeneously.[2] Remarkable works on millimeter wave sintering of ceramics have been made since the 1980s at Oak Ridge National Laboratory (USA), Institute of Applied Physics in Russia, Osaka University[3–8] (Japan), and others.

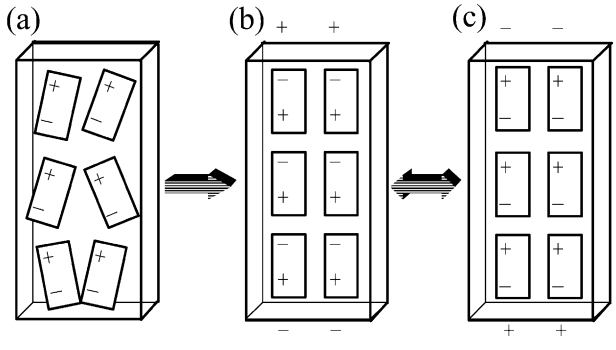

Fig. 1. Polarization of dielectric substance.

Our group has aggressively reported the studies on silicon nitride ceramics taking notice of the microstructures. In this paper, we report the comparative studies on grain growth behavior in silicon nitride ceramics heated by 28 GHz millimeter wave and by conventional heating.

2. Experimental

2.1. Preparation of specimen

Silicon nitride consisting of α-Si_3N_4 (E-10 grade, Ube Industries Ltd., Japan), 5 wt.% Al_2O_3 (Hokko Chemicals Ltd., Japan) and 5 wt.% Y_2O_3 (Nippon Yttrium Co., Ltd., Japan) was chosen as the reference sample of this study. Samples with various rare earth sesquioxides (La_2O_3, Gd_2O_3, Yb_2O_3; Nippon Yttrium Co., Ltd., Japan) as additives instead of Y_2O_3 were sintered by millimeter wave or conventional heating. The mole fractions of rare earth sesquioxide to alumina were set at the same values that of Y_2O_3 to Al_2O_3 in the reference sample. The volume percentages of additives (rare earth sesquioxide and Al_2O_3) were also adjusted to be the same as that of the reference sample. The nominal composition of each sample is given in Table 1. The α-Si_3N_4, Al_2O_3 and rare earth sesquioxide were mixed by a vibration mill using methanol as the mixing medium. After drying the slurry, the powder mixture was passed through a 60-mesh nylon sieve, pressed into a rectangular plate and then cold isostatically pressed under 500 MPa.

2.2. Sintering procedure

Millimeter wave sintering was carried out using a 28 GHz gyrotron source (FDS-10-28, Fuji Dempa Kogyo Ltd., Japan). The arrangement for heating the specimen

Table 1
Nominal composition of samples

Rare earth oxide	Al_2O_3 (wt.%)	Rare earth oxide (wt.%)	Si_3N_4 (wt.%)
Y_2O_3	5.00	5.00	90.00
La_2O_3	4.75	6.87	88.38
Gd_2O_3	4.76	7.65	87.59
Yb_2O_3	4.97	8.69	86.34

is shown in Fig. 2. When heating ceramics by millimeter wave, it is very important to minimize the heat loss from the surface of the material. It can be expected that the heat loss causes a thermal runaway, and cracking. Whole temperature of the applicator is not so high during the microwave heating that the heat loss is greater than the conventional one. This also means that it is difficult to keep the object at high temperature. In addition, because of the ubiquitous heat loss from the surface of a sample placed inside a "cold" microwave cavity the thermal gradient, once built up, does not disappear.[9–11] In order to prevent cracking of materials and to obtain homogeneous microstructures, thermal gradient should be avoided. These can be prevented by optimal use of sample insulation. The samples were placed top of a boron nitride plate in a silicon nitride crucible, which was further surrounded by alumina heat insulating material (Fibermax 18R, Toshiba Monofrax Co., Ltd., Japan). Temperature was measured by a W–Re thermocouple. The samples were sintered at 1700 °C and for 4 h under a nitrogen pressure of 0.1 MPa. For comparison, conventional gas pressure sinterings were also performed under the same conditions.

2.3. Analysis

Sintered samples were polished and plasma-etched (Plasma Reactor Model PR-41, Yamato Science Co. Ltd., Japan) for microstructure observation using scanning electron microscopy (SEM; JSM-T330AS, JEOL Ltd., Japan). Densities were measured by Archimedes' technique. In order to quantitatively characterize the microstructure of specimens, width, length and aspect ratio of grains were measured by using an image analyzer. Because β-Si_3N_4 has a hexagonal rod shape, its width and length were measured for each crystal appeared in the micrograph.

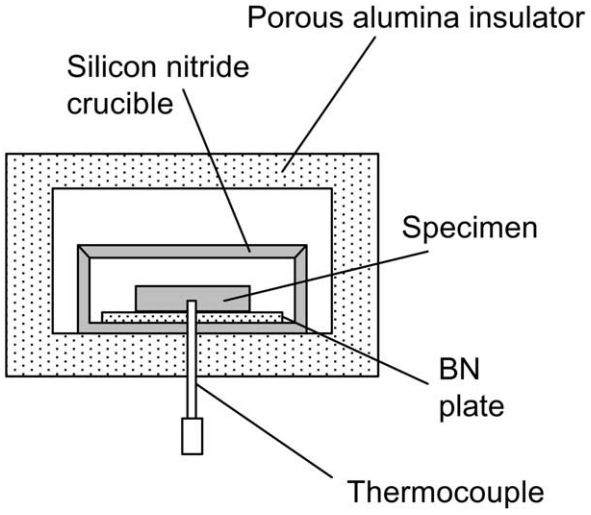

Fig. 2. Thermal insulation and setting of specimen.

3. Results and discussion

Table 2 shows differences of relative densities between millimeter wave and conventionally sintered samples and dielectric constants of each rare earth sesquioxide measured at 1 MHz for reference.[12] When millimeter wave fired at 1700 °C, the relative densities of silicon nitride with addition of Al_2O_3 and rare earth sesquioxide (La_2O_3, Gd_2O_3, Yb_2O_3) or Y_2O_3 was between 97.1–98.5%. On the other hand, conventional sintering at 1700 °C results in almost the same values of relative density as microwave sintering, 97.0–98.1%. Considering that they were sintered at 1700 °C under nitrogen pressure of 0.1 MPa, the millimeter wave sintering process presents clear advantages in comparison to conventional heating process, which requires a nitrogen pressure of 10 MPa.

Microstructural observation using SEM was carried out in this work. The La_2O_3 doped sample sintered by millimeter wave abnormally showed porosity with some pores as large as 3 μm in size as can be seen in Fig. 3. Brito et al.[13] has explained this is due to the presence of metallic silicon within the sample sintered by millimeter wave radiation. To analyze the similar microstructure in previously reported samples,[14] he carried out transmission electron microscopy (TEM) observation for specimen with Sm_2O_3. TEM micrograph of the Sm_2O_3 doped sample sintered by millimeter wave radiation shows the

Table 2
Relative densities of millimeter wave and conventionally sintered samples and dielectric constant of rare earth sesquioxide

Rare earth oxide	Relative density (%)		Dielectric constant
	Millimeter wave	Conventionally	
Y_2O_3	98.49	97.75	14.0
La_2O_3	98.14	96.95	20.8
Gd_2O_3	97.97	98.08	11.4
Yb_2O_3	97.09	97.80	12.6

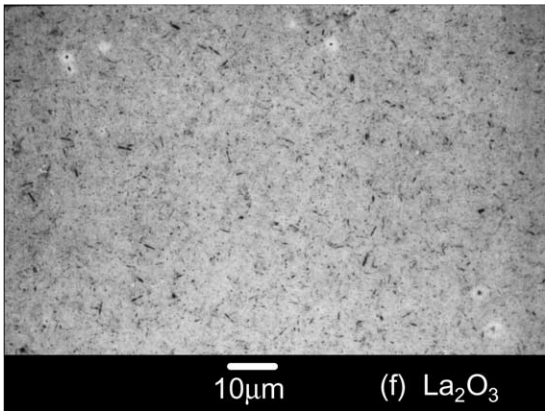

Fig. 3. SEM micrograph of specimen with La_2O_3 after millimeter wave firing at 1700 °C for 4 h.

presence of metallic silicon within the fine grained silicon nitride matrix. The silicon readily etched by the plasma produce contrast that can be interpreted as porous under SEM observation. The presence of metallic silicon is direct evidence that localized heating by millimeter wave radiation is taking place within the samples. Under the present environment conditions (nitrogen gas at 0.1 MPa) silicon nitride decomposes at temperatures higher than 1800 °C.

Fig. 4 shows microstructures of specimens with Y_2O_3, Gd_2O_3 and Yb_2O_3 after millimeter wave and conventional sintering. It can be seen in Fig. 4, the grains in the microwave sintered sample are larger than those of conventionally sintered. The effects of millimeter wave sintering on the microstructure homogenization and on grain growth are evident from the micrograph of Fig. 4. This trend can be also seen in other samples with rare earth sesquioxide. This seems to indicate that the use of millimeter waves for sintering enhances grain growth.[15–17] Silicon nitride having a well controlled bimodal microstructure indicates both high fracture toughness and high fracture strength.[18] SEM micrographs of Fig. 4

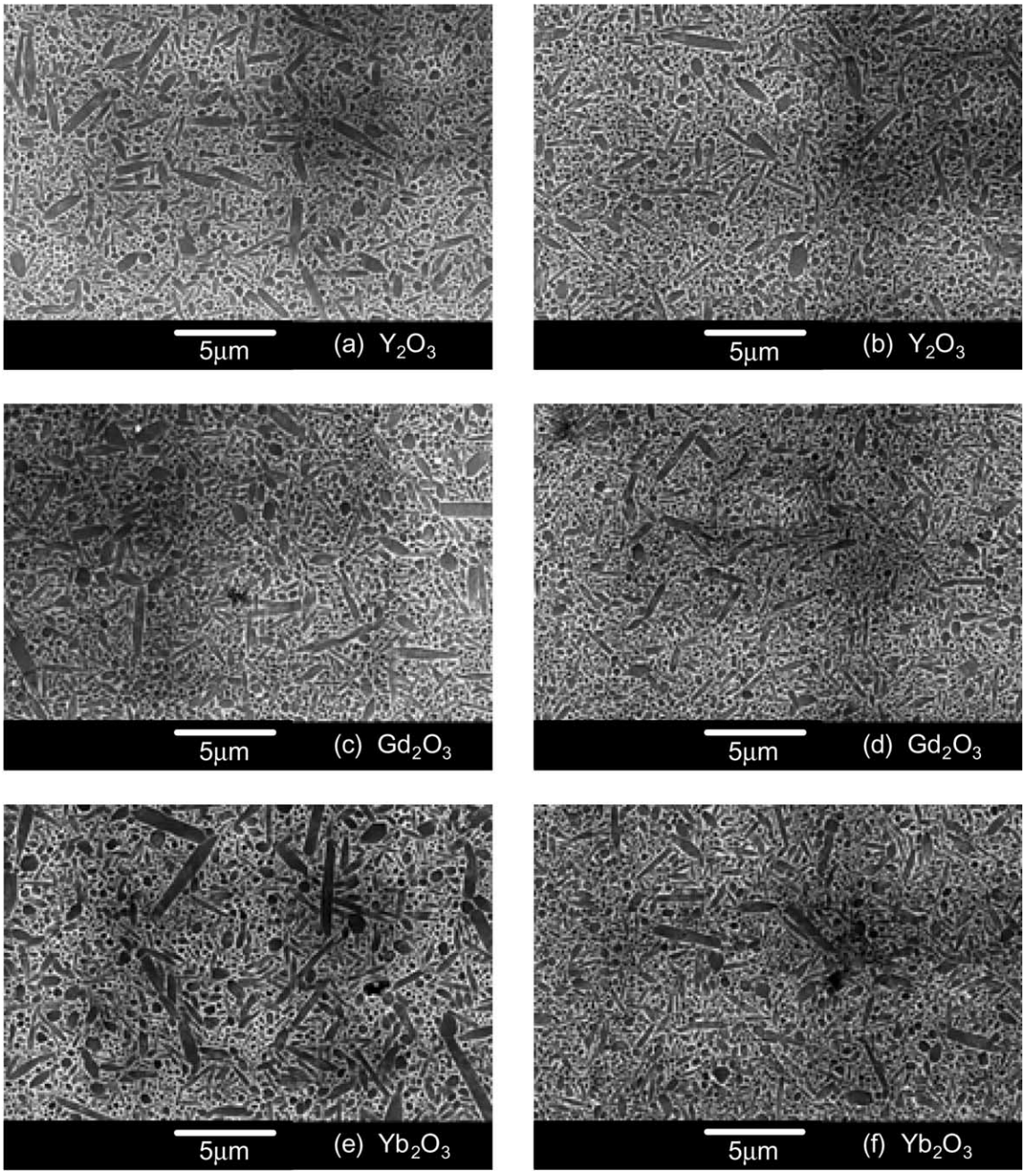

Fig. 4. SEM micrographs of specimens (a) with Y_2O_3 after millimeter wave sintered at 1700 °C for 4 h; (b) with Y_2O_3 after conventionally sintered at 1700 °C for 4 h; (c) with Gd_2O_3 after millimeter wave sintered at 1700 °C for 4 h; (d) with Gd_2O_3 after conventionally sintered at 1700 °C for 4 h; (e) with Yb_2O_3 after millimeter wave sintered at 1700 °C for 4 h; and (f) with Yb_2O_3 after conventionally sintered at 1700 °C for 4 h.

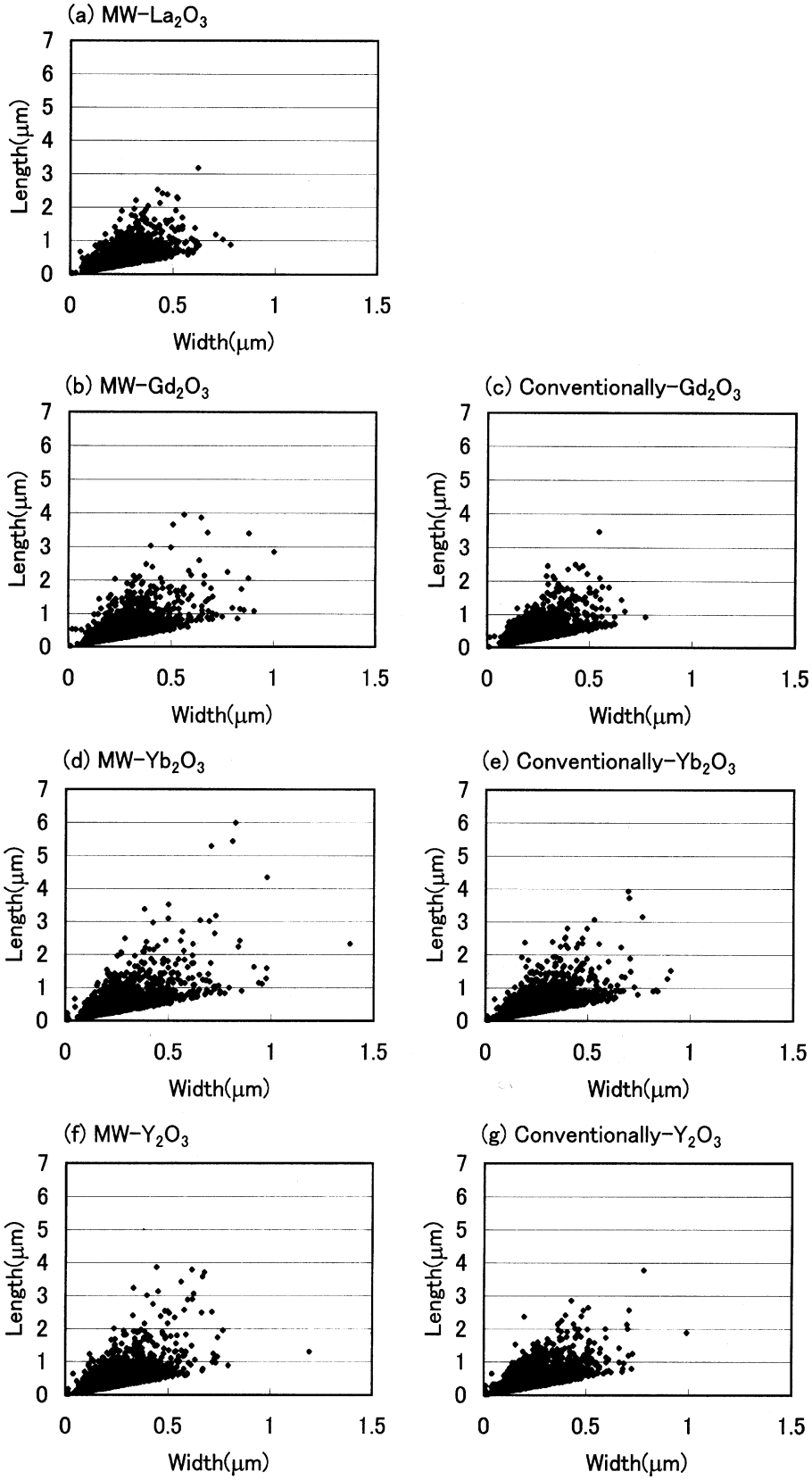

Fig. 5. Width-length distributions of grains in the specimens (a) with La_2O_3 after millimeter wave sintered at 1700 °C for 4 h; (b) with Gd_2O_3 after millimeter wave sintered at 1700 °C for 4 h; (c) with Gd_2O_3 after conventionally sintered at 1700 °C for 4 h; (d) with Yb_2O_3 after millimeter wave sintered at 1700 °C for 4 h; (e) with Yb_2O_3 after conventionally sintered at 1700 °C for 4 h; (f) with Y_2O_3 after millimeter wave sintered at 1700 °C for 4 h; and (g) with Y_2O_3 after conventionally sintered at 1700 °C for 4 h.

reveal the tendency to develop bimodal microstructures in millimeter wave sintered materials. This implies the possibility that the use of millimeter wave makes it possible to control the microstructure in silicon nitride ceramics.

In order to discuss quantitatively grain size distribution of specimens, measurement of width, length and mean aspect ratio of grains was conducted using an image analyzer. The width-length distributions and the mean aspect ratios of each specimen sintered at 1700 °C are shown in Figs. 5 and 6, respectively. In the case of specimens sintered by conventional heating, each additive makes little difference in distribution of grain size. Comparing with the distribution between millimeter wave sintered samples and conventionally sintered samples, however, it can be recognized remarkable differences. If compared with the same additive, grain growth of millimeter wave fired samples, especially in the length direction, is more significant than that of conventionally heated samples. This result means that the use of millimeter wave is very effective to enhance the grain growth and to promote the formation of a well controlled bimodal microstructure than conventional heating. Furthermore, when sintering specimens by millimeter wave, the radii of rare earth ions influence grain growth behavior. The number of elongated grains increases in the order of Yb_2O_3 > Gd_2O_3 > La_2O_3. Fig. 6 is also stated these tendencies very well. The fact that the aspect ratio of millimeter wave fired samples is greater than that of conventionally heated one indicates the advantage of millimeter wave for grain growth. And it can be also seen that the aspect ratio is increasing in the order of Yb_2O_3 > Gd_2O_3 > La_2O_3. Figs. 5 and 6 also indicate the characteristic grain growth behavior caused by the difference of additives. Although the aspect ratios of Yb_2O_3 and Y_2O_3 are almost the same value in Fig. 6, the distribution pattern of Yb_2O_3 is differ from that of Y_2O_3 in Fig. 5. Wider distributions are observed for Yb_2O_3 in Fig. 5. This can be concluded that the grains of the Yb_2O_3 doped specimen grew up in both width and length directions.

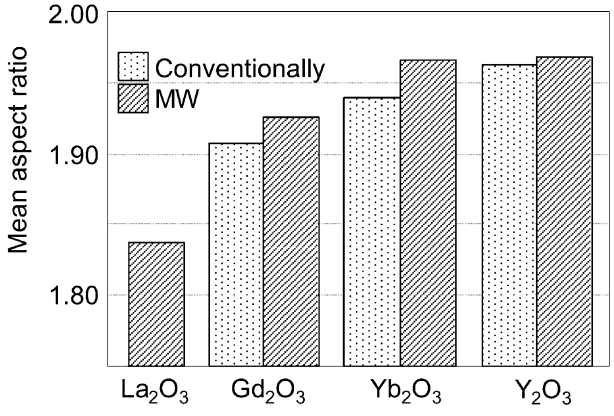

Fig. 6. Mean aspect ratio for particles of millimeter sintered specimens.

In order to discuss the difference in the microstructure between millimeter wave and conventionally sintered samples, it must be considered various parameters, e.g., melting points of the materials, formation of glassy phase, electric properties, particle size of the powders and so on. In this work, the dielectric constant and liquid formation temperature are considered to be very significant factor. Our literature survey could not yield any useful information on the dielectric constant of frequency 28 GHz. The dielectric constants for rare earth sesquioxide measured at 1 MHz[12] were used as guidance, assuming the oxinitride glasses containing different rare earths would present similar trends in dielectric properties.

Densification of silicon nitride is achieved by liquid-phase sintering process. The additives such as Y_2O_3 and Al_2O_3 are utilized to form a liquid phase during sintering. First, sintering additives form a liquid phase during sintering. Transformation from α-Si_3N_4 to β-Si_3N_4 proceeds according to solution-precipitation from the supersaturated liquid. This is why selection of the additives is very important role on silicon nitride ceramics. Gazza[19] has reported that liquid formation temperature lowers as increasing the ionic radius, when rare earths are used as additives for silicon nitride conventional sintering. For example, Scandium with an ionic radius of 0.73 Å presents a liquid formation temperature of 1700 °C while that for lanthanum (1.15 Å) is as low as 1500 °C. It was also reported that the radii of lanthanide (Ln) ions had a significant effect on grain growth behavior of β-Si_3N_4 in the Ln–Si–Al–O–N liquid phase during the α-β transformation.[20, 21] In addition to these factors, Booske et al.[22] claims that microwave fields exert a non-thermal ponderomotive force at surface or interfaces. This force can act as an additional driving force for ionic transport. Some groups have paid attention to this force but the details have not yet been identified.

Generally, it is supposed that the grain growth of silicon nitride to the width direction is controlled by the interfacial reaction, while that to the length direction is done by diffusion. Judging from selective growth to the length direction, millimeter wave heating enhances the diffusion controlled comparing with conventional heating. As mentioned above, densification of silicon nitride proceeds according to solution-precipitation from the supersaturated liquid and there are no useful data for dielectric constants of liquid phase at 28 GHz. Since liquid phase generally has a value high two or more figures, it can be considered that the selective grain growth to the length direction revealed in this work is owing to the selective millimeter wave absorption of the liquid phase. To determine plausible reasons for the enhanced grain growth observed in millimeter wave

sintered silicon nitride, detailed analysis of the glassy phase produced during sintering is underway and it will be subject of a future publication.

4. Conclusion

When Si_3N_4 with Al_2O_3 and rare earth sesquioxide as additives sintered by millimeter wave of 28 GHz, the samples could be densified up to 97.1% of their theoretical density. A clear difference in microstructure is observed between millimeter wave heated specimens and conventionally heated specimens all over the experiments performed in this report. Fully dense sintered silicon nitride presented a bimodal microstructure exhibiting excellent mechanical properties. From the sintering experimental results, the following conclusions can be drawn: (1) Grain growth of silicon nitride seems to be enhanced by millimeter wave heating. (2) Considering the relatively mild sintering conditions (nitrogen pressure of 0.1 MPa at 1700 °C), the use of microwave is very effective to obtain bimodal microstructures. During the present millimeter wave sintering conditions additives with slightly larger dielectric constants are selectively and rapidly heated causing localized decomposition of the silicon nitride. Although we mentioned at the beginning of this paper that the millimeter wave studies in sintering process are still at developmental stage, it is clear that millimeter wave sintering of ceramic materials will allow the production of a ceramic with a controlled microstructure that will yield an ideal combination of high strength and high toughness in a material.

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