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Compositional Effects of Ytterbia-Alumina Additives on Millimeter-Wave Sintering of Silicon Nitride†

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Abstract

Millimeter-wave sintering of silicon nitrides was performed by using several oxide aids based on alumina and ytterbia. Densification behavior of millimeter-wave sintered silicon nitrides does not simply depend on the chemical composition of the sintering aids, that is on the alumina content. It was found that the oxide aids with 6.4wt%Yb_2O_3-1.6wt%Al_2O_3 enhance the densification of silicon nitride even at a low temperature below 1600°C, and irrespective of the small amount of alumina. The rapid densification below 1600°C suggests a new sintering aid with a small amount of alumina available for the fabrication of silicon nitride by the millimeter-wave method.

KEY WORDS: (Millimeter-wave sintering) (Silicon nitride) (Yb_2O_3)

1. Introduction

Recently millimeter-wave heating has been considered as an attractive sintering method for ceramic fabrication. It has been reported that millimeter-wave heating can densify dielectric compacts using short times at lower temperatures compared with conventional methods using an electric furnace[1)]. It is believed that the characteristics of millimeter-wave heating arise from the electromagnetic effect known as the "non-thermal effect"[2,3)]. So far millimeter-wave heating has been attempted for sintering of materials and compositions such as alumina, zirconia, alumina-zirconia and silicon nitride[4-8)].

Silicon nitride is attractive as a structural material for high temperature usages[9)]. Silicon nitride has a good thermal shock resistance and mechanical properties such as high strength and high fracture toughness. However silicon nitride shows difficulty on densification, compared with oxide ceramics, because silicon nitride has a low diffusion coefficient and its decomposition is severely accelerated during sintering at high temperatures (more than 1700°C). Usually these problems of densification of silicon nitride are improved by adding sintering aids, such as Al_2O_3, MgO, Y_2O_3 and so on[10,11)]. The additives and SiO_2, which is originally on the surface of Si_3N_4, form a liquid phase and the liquid phase promotes diffusion of silicon nitride to achieve sufficient densification. The choice of the sintering aid is also important for mechanical properties because an oxynitride solid solution remains on the surface of the Si_3N_4 grain.

In this study millimeter-wave sintering was performed for silicon nitride. Yb_2O_3+Al_2O_3 was selected as a sintering aid because ytterbia is an additive expected to improve mechanical properties of silicon nitride[12-14)] and an ytterbia-alumina complex can lower the sintering temperature in the millimeter-wave heating process. The one possible reason to sinter silicon nitride at a lower temperature is the eutectic effect of the ytterbia-alumina complex additive, another reason is that the coupling of additive with millimeter-wave can be varied to promote the non-thermal effect. In this study, an optimum composition of Yb_2O_3+Al_2O_3 additive for silicon nitride in the millimeter-wave sintering process was established by fixing the Yb_2O_3+Al_2O_3 content at 8wt%

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Table 1 Composition and theoretical density of experimental silicon nitrides.

Sample name	Composition (wt%)			Composition of additives (wt%) (vol%)	Theoretical density (g/cm^3)	note
	Yb_2O_3	Al_2O_3	Si_3N_4			
7Yb-1Al	7	1	92	8 3.41	3.36	
6.4Yb-1.6Al	6.4	1.6	92	8 3.69	3.35	Eutectic point of $Yb_2O_3+Al_2O_3$ system
6Yb-2Al	6	2	92	8 3.88	3.34	
5Yb-3Al	5	3	92	8 4.34	3.33	

2. Experimental procedures

2-1. Green body preparation

A powder specimen of α-Si_3N_4 (Ube Co. Ltd., SN-E10) was used as the starting material. Yb_2O_3 (Shin-Etsu Chemical Co., RU grade) and α-Al_2O_3 (Sumitomo Chemical Co., AKP-20) powders were added as sintering aids. The mean grain sizes of these powders were 0.55μm, 1.04μm and 0.57μm respectively. The components of additives were selected as shown in **Table 1**. After mixing these powders at a desired composition, the mixed powder was milled in distilled water for 16hr with ammonium polycarboxy acid as dispersant. Alumina balls and pots were used for milling. These slurries were formed to 52mm diameter and 8mm thickness sizes by slip casting. The green bodies were made by calcining these slurries at 800°C for 1hr in air. The surfaces of green bodies were polished with #220 and #400 emery papers before sintering.

2-2. 28GHz millimeter-wave sintering

The green bodies were sintered using 28GHz millimeter-wave heating equipment (Fuji Denpa Kogyo, FGS-10-28). Sintering time was fixed at 1hr and sintering temperature was varied according to the contents of additives (**Table 2**). Heating and cooling rates were fixed at 10°C/min and 60°C/min respectively. Nitrogen gas was used as the atmosphere. Before sintering, the vacuum chamber (reactor for millimeter-wave sintering) was evacuated to 5Pa and

Table 2 Sintering temperature for 28GHz millimeter-wave heating experiment of silicon nitride.

Sample	Millimeter-wave sintering temperature (°C)					
	1500	1550	1600	1650	1700	1750
7Al-1Yb			●	●	●	●
6.4Yb-1.6Al	●	●	●	●		
6Yb-2Al		●	●	●	●	
5Yb-3Al	●	●	●			

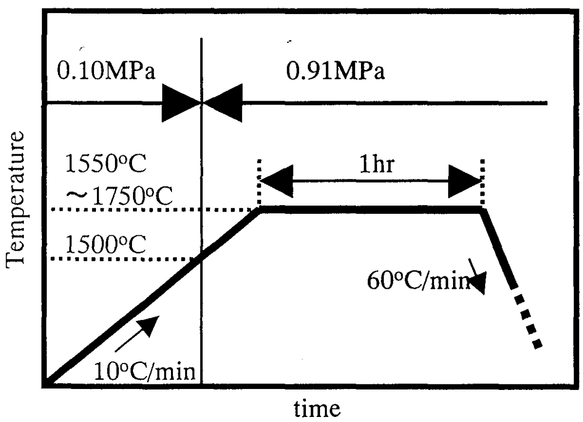

Fig.1 Time schedule of temperature and nitrogen pressure for sintering silicon nitride with 28GHz millimeter-wave heating.

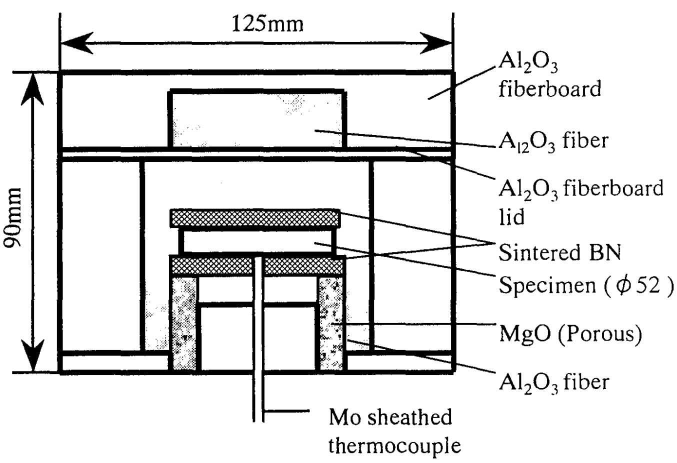

Fig.2 Schematic illustration of heat insulating arrangement for 28GHz millimeter-wave heating.

then nitrogen was introduced to a pressure at 0.10MPa. The nitrogen pressure was held at 0.10MPa until the sintering temperature reached 1500°C, then nitrogen pressure was increased to 0.91Mpa (**Fig.1**). The insulation of the sample was achieved using alumina fiber board (Nichias Co., 17LD) alumina wool (Isolite Co., isowool), porous magnesia (Nikkato Co., MG-1) and boron nitride plate (Denki Kagaku Kogyo, BN HC grade) as shown in **Fig.2**. The temperature of the specimen during sintering was measured by a Mo-sheathed W/W-Re thermocouple in contact with the specimen surface.

2-3. Characterization of sintered bodies

Densities of sintered bodies were measured by the Archimedean method. Densification was estimated by the ratio of relative density to the theoretical density (Table 1). Weight losses of sintered bodies were measured by weighing the samples before and after sintering. Before observing microstructure, the polished surface of silicon nitride was etched by using heated NaOH (300°C) for 40sec. Microstructures were obtained by observing these silicon nitrides with a field emission type scanning electron microscope (FE-SEM; Hitachi, S-4500).

3. Results and Discussions

First, densifications of millimeter-wave sintered silicon nitrides are shown in **Figure 3**. Except for the silicon nitride containing 7wt%Yb_2O_3-1wt%Al_2O_3 (7Yb-1Al), relative densities were obtained larger than 97%TD at 1600°C and it was found that 6.4Yb-1.6Al and 5Yb-3Al silicon nitrides densified more rapidly than 6Yb-2Al. On the other hand, the relative density of 7Yb-1Al silicon nitride increased with sintering temperature. Its relative density, however, reached only 95%TD even at 1750°C. The rapid densification of 6.4Yb-1.6Al silicon nitride is quite interesting, despite its lower volume fraction of sintering aids compared with 6Yb-2Al silicon nitride. The densification behavior of millimeter-wave sintered silicon nitrides can be explained from the phase diagram of the Yb_2O_3+Al_2O_3 system (**Fig.4**). The melting point of the Yb_2O_3+Al_2O_3 compound changes with composition, and a eutectic point appears at 1850°C between Yb_2O_3 and $(Yb_2O_3)_3(5Al_2O_3)_5$ solid solution. The composition of the eutectic point is about 20wt% Al_2O_3, and the composition of 6.4wt%Yb_2O_3- 1.6wt%Al_2O_3 sintering aid is close to 20wt%Al_2O_3. As shown in Fig.3, the necessary millimeter-wave power for holding the temperature of 6.4Yb-1.6Al silicon nitride at 1600°C was slightly lower than those for other silicon nitrides. This suggests that millimeter-wave absorption for the 6.4Yb-1.6Al sample is higher than for other samples.

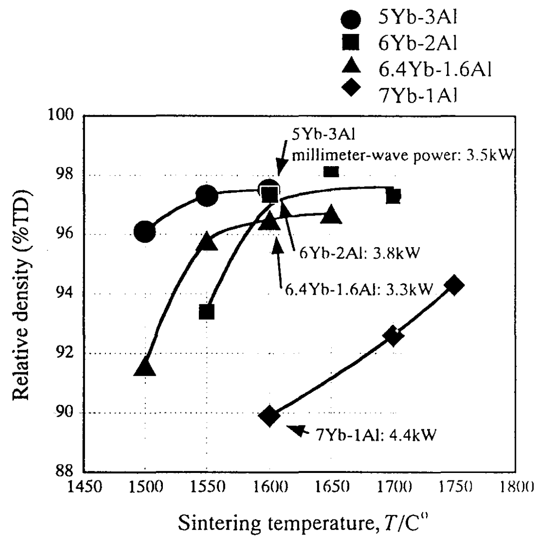

Fig.3 Relative density of silicon nitrides containing several components of Yb_2O_3+Al_2O_3 additives sintered by 28GHz millimeter-wave heating.

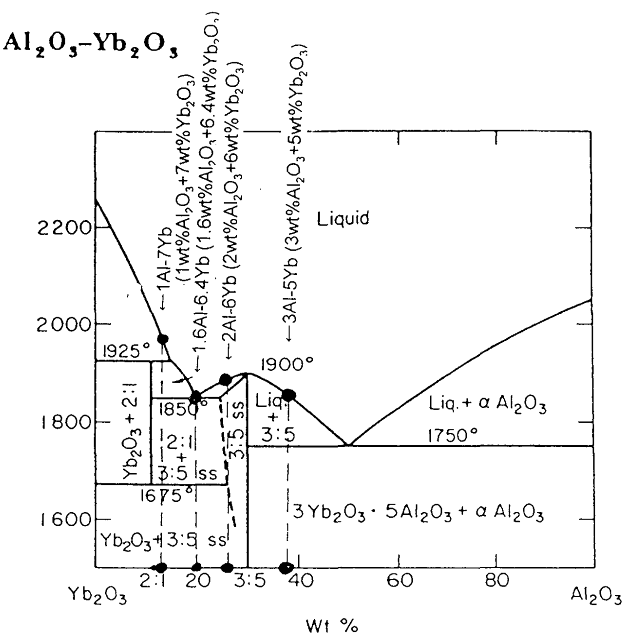

Fig.4 System Yb_2O_3+Al_2O_3. Compound ratios are given in the order Yb_2O_3:Al_2O_3.

R. S. Roth, T. Negas and L. P. Cook, "Phase Diagrams for Ceramists Volume V", Ed., American Ceramic Society, 1983

Easier absorption of millimeter-wave in 6.4Yb-1.6Al silicon nitrides enhances atomic diffusion between silicon nitride and the sintering aids, and contributes to the rapid densification.

Weight losses of millimeter-wave sintered silicon nitrides are shown in **Figure 5**. Weight loss in the sintering of silicon nitride usually arises from its decomposition but weight loss due to the sintering aid cannot be ignored because of decomposition of Yb_2O_3 to YbO and its sublimation. The weight loss for 7Yb-1Al silicon nitride was much higher than those of other silicon nitrides. The higher weight loss of 7Yb-1Al silicon nitride may be attributed to insufficient densification at 1600°C and even at higher sintering temperatures because a larger surface area still remains in the insufficiently densified state.

FE-SEM observations were made on the etched surfaces of millimeter-wave sintered silicon nitrides. The microstructures of four sorts of silicon nitride at several sintering temperatures are shown in **Figure 6.** With increasing temperature, grain growth is observed and unidirectional grain growth, with rod-like shapes,

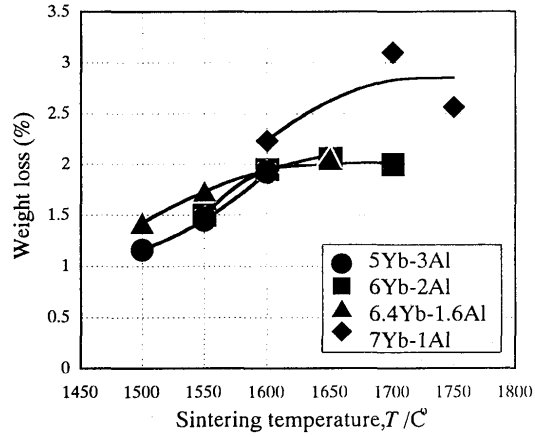

Fig.5 Weight loss of silicon nitrides containing several components of Yb_2O_3+Al_2O_3 additives sintered by 28GHz millimeter-wave heating.

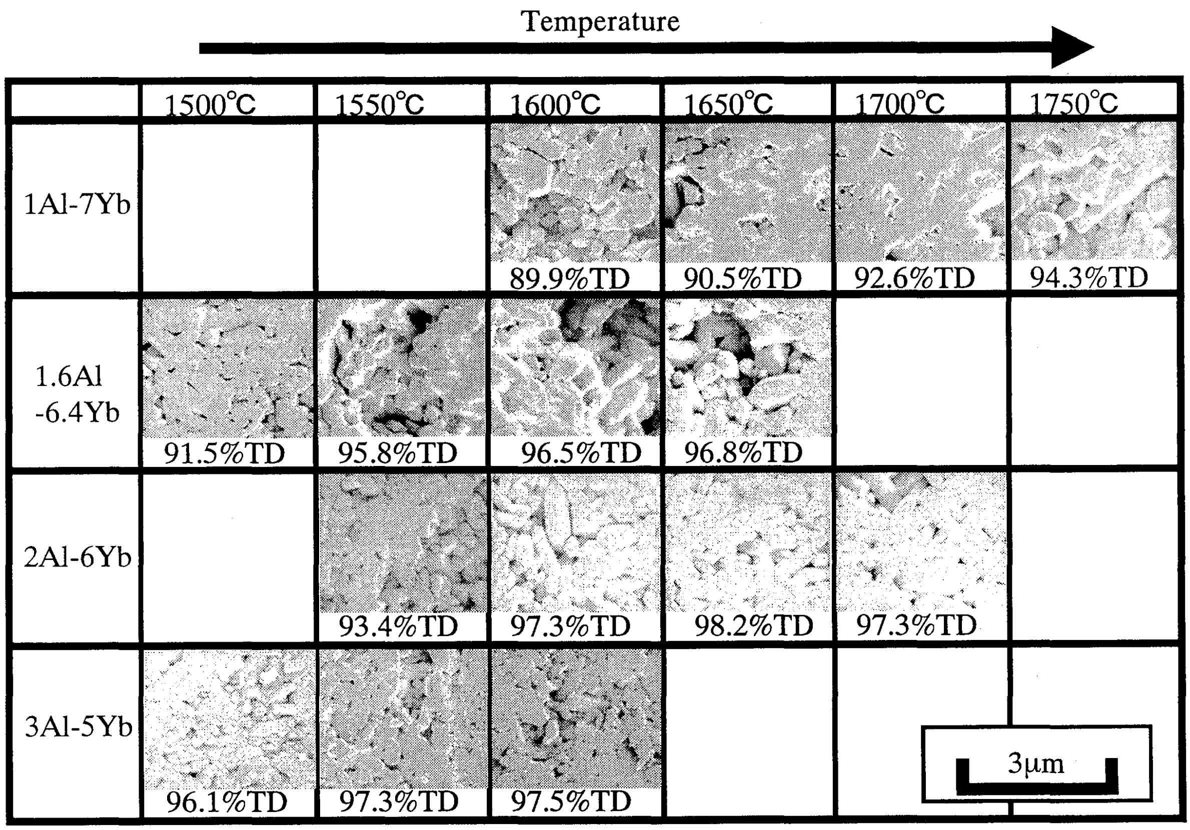

Fig.6 Microstructures of silicon nitride containing several components of Yb_2O_3+Al_2O_3 additives sintered by 28GHz millimeter-wave heating.

can also be observed in microstructures for higher temperature. Well-grown grains of 2μm to 3μm length are observed in the 7Yb-1Al silicon nitride sintered at 1750°C. On the other hand, rod-like grains only under 1μm in length are observed in the 5Yb-3Al silicon nitride sintered at 1600°C. Though relative densities of 7Yb-1Al silicon nitride sintered at 1750°C and 5Yb-3Al sintered at 1600°C are 94.3%TD and 97.5%TD respectively, the grain growth in 7Yb-1Al silicon nitride is more rapid than in 5Yb-3Al one. In the millimeter-wave sintering of silicon nitride, it appears that the increase of alumina content in the sintering aid of the Yb_2O_3+Al_2O_3 system can suppress the grain growth. Thus the usage of Yb_2O_3 as one component of sintering aids promotes more finely grained and dense silicon nitrides if Yb_2O_3+Al_2O_3 sintering aids with suitable compositions are selected.

4. Summary

It was found that highly dense silicon nitrides containing several components of Yb_2O_3+Al_2O_3 additives were sintered by 28GHz millimeter-wave heating. The silicon nitrides of 5Yb-3Al, 6Yb-2Al and 6.4Yb-1.6Al (the last one especially contains large amount of Yb_2O_3) were densified to around 97%TD by sintering at 1600°C. But the densification of 7Yb-1Al silicon nitride was not sufficient at 95%TD even after sintering at 1750°C. The microstructures of millimeter-wave sintered silicon nitrides were observed by FE-SEM and fine grained microstructures were obtained in 6.4Yb-1.6Al, 6Yb-2Al and 5Yb-3Al silicon nitrides. Also the microstructures of silicon nitrides sintered at 1600°C show that grain sizes become large with increasing alumina contents.

This study reveals the 28GHz millimeter-wave sintering can densify fine grained silicon nitride using suitable selected Yb_2O_3+Al_2O_3 additives. So the 28 GHz millimeter-wave sintering is expected to improve processing for high strengthened silicon nitride.

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