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Effect of Microwave Heating on Densification and $\alpha \rightarrow \beta$ Phase Transformation of Silicon Nitride

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Abstract

Silicon nitride compacts doped with Al_2O_3 and Y_2O_3 were sintered by microwave heating in a multimode cylindrical cavity applicator operating at 2·45 GHz. The densification and the $\alpha \rightarrow \beta$ phase transformation behavior of the microwave-sintered silicon nitride were investigated and compared with those of conventionally sintered materials. Microwave heating enhanced the densification and the $\alpha \rightarrow \beta$ phase transformation. The silicon nitride containing 12 wt% additives showed more enhanced densification and $\alpha \rightarrow \beta$ phase transformation than that containing 8 wt% additives. © 1997 Elsevier Science Limited.

1 Introduction

Silicon nitride is one of the most promising non-oxide ceramics for structural applications at high temperature. However, it is difficult to consolidate Si_3N_4 into dense ceramics because of its high degree of covalent bonding and low self-diffusivity. Manufacturing a dense Si_3N_4 ceramics requires sintering additives that provide a liquid phase during sintering and enhance the densification.[1] Currently, hot isostatic pressing and gas pressure sintering in the presence of additives are common fabrication methods for producing a fully dense Si_3N_4, but these methods are expensive. Since the high manufacturing cost limits the introduction of silicon nitride into the market place, it is required to develop new processing techniques capable of achieving high densities and excellent properties at reasonable cost.

In recent years, microwave processing has received attention in the preparation of ceramic materials. Microwave processing is a novel technique which differs fundamentally from conventional heating methods in that heat is generated internally within the material. Among the applications of microwave heating, microwave sintering has been claimed to have several advantages over conventional sintering techniques, such as a reduction in manufacturing cost and in sintering temperature, and an improvement in material properties.[2,3] Many efforts have been made over the last decade to develop the technique for various oxide ceramics. Less work has been reported on the microwave sintering of non-oxide ceramics which requires high sintering temperatures of over 1700°C.

In this work, the microwave sintering of Si_3N_4 with Y_2O_3 and Al_2O_3 as additives was carried out in a 2·45 GHz microwave furnace. Conventional pressureless sintering was performed using the same sintering schedule. The rates of the densification and of the $\alpha \rightarrow \beta$ phase transformation were compared and the effect of microwave heating was investigated.

2 Experimental procedure

High purity α-Si_3N_4 (E-10, UBE Industrial Ltd., Tokyo, Japan) powder was used as a starting material. As sintering additives, Al_2O_3 (AKP-50, Sumitomo Chemical Co., Ltd., Tokyo, Japan) and Y_2O_3 (Grade Fine, H. C. Stark GmbH, Goslar, Germany) powders were used. Alpha-Si_3N_4 and 8, 12 wt% additives (1 : 3 mixture of Al_2O_3 and Y_2O_3) were mixed by ball milling in ethanol for 24 h using Al_2O_3 balls and a polypropylene container. For convenience, the silicon nitride specimens with

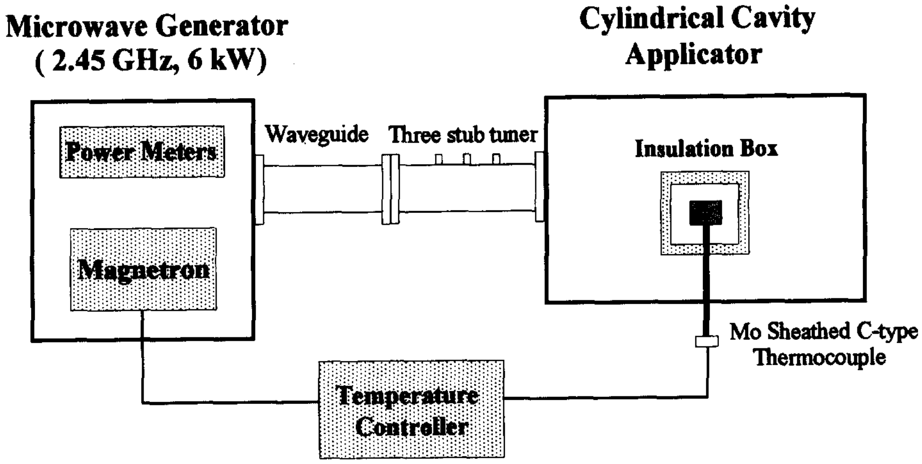

Fig. 1. Schematic of the microwave furnace used in this study.

8 and 12 wt% additives are designated as 2A6Y and 3A9Y, respectively. After mixing, the powder mixture was dried. The softly agglomerated powder was then crushed and sieved through a 60 mesh sieve. The sieved powder was die-pressed at 30 MPa and isostatically pressed at 200 MPa. The size of the resultant pressed specimens was about $\phi 24 \times 6$ mm for microwave sintering and $\phi 10 \times 5$ mm for conventional pressureless sintering.

Microwave sintering was carried out in a 2·45 GHz, 6 kW microwave furnace using an insulation box designed for this study. Figures 1 and 2 show the microwave furnace and the insulation box, respectively. The microwave furnace was built in-house and the insulation box was composed of a BN crucible, alumina fiber boards, and a SiC plate. The SiC plate functioned as a preheater. The specimen was placed in the insulation box and then heated to sintering temperature with a heating rate of 25°C/min in a nitrogen atmosphere. During the heating cycle, the temperature was monitored using a molybdenum-sheathed C-type thermocouple in contact with the specimen and controlled automatically through feedback control from a programmable controller. Conventional pressureless sintering was performed in a graphite resistance furnace (Astro Industries Inc., CA, USA) using the same sintering schedule. Pure Si_3N_4 powder was used as a powder bed to suppress the decomposition of the specimen in both cases.

The bulk densities of the sintered specimens were measured in distilled water by the Archimedes method. The polished and plasma-etched surfaces of the sintered specimens were observed by scanning electron microscopy (SEM). The crystalline phases were identified using X-ray diffractometry (XRD) and their amounts were calculated by the method proposed by Gazzara *et al.*[4]

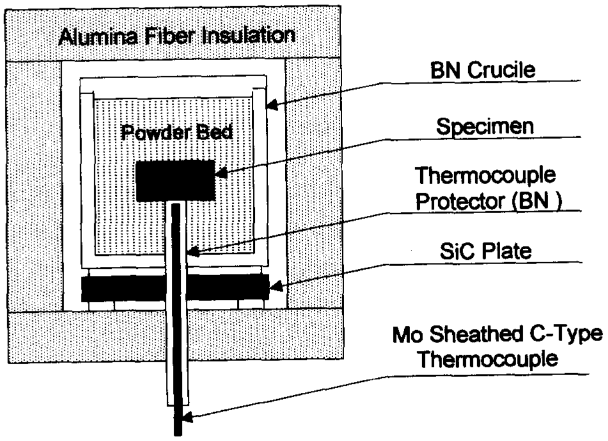

Fig. 2. Schematic of the insulation box.

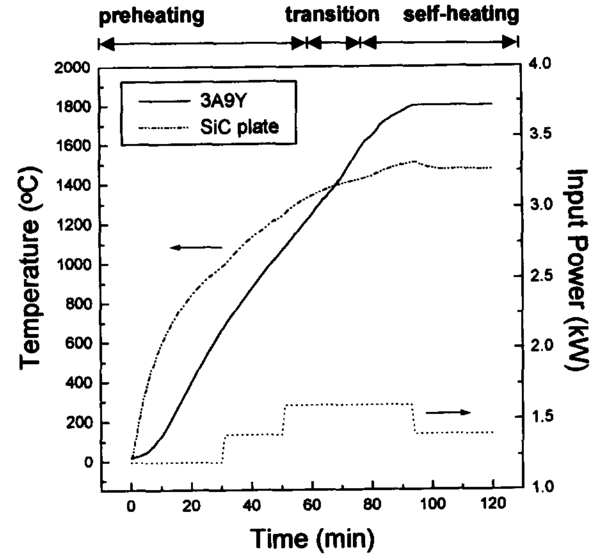

Fig. 3. Temperature of the specimen and of the SiC preheater during the microwave heating process.

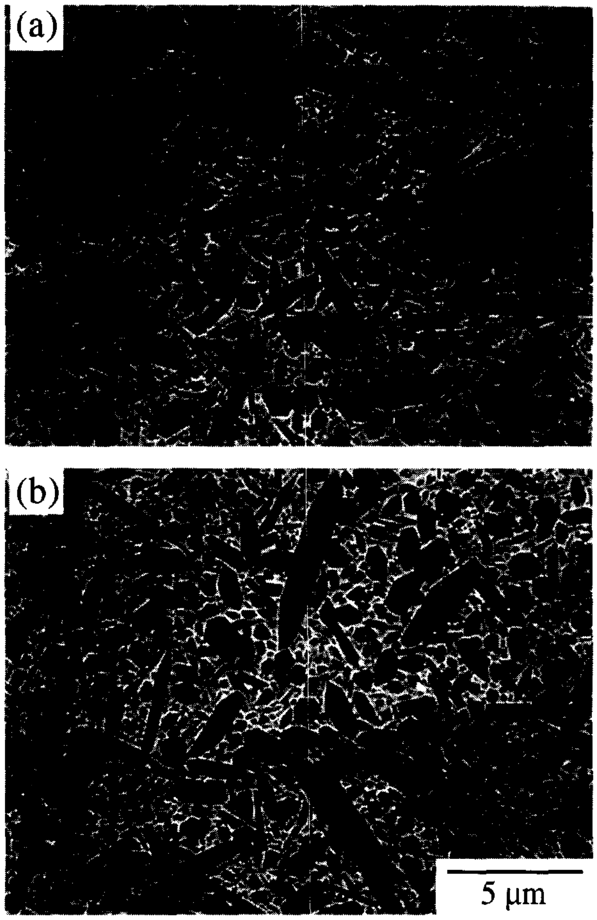

Fig. 4. SEM micrographs showing the parts of the (a) center and (b) near surface of 3A9Y microwave-sintered at 1750°C for 30 min.

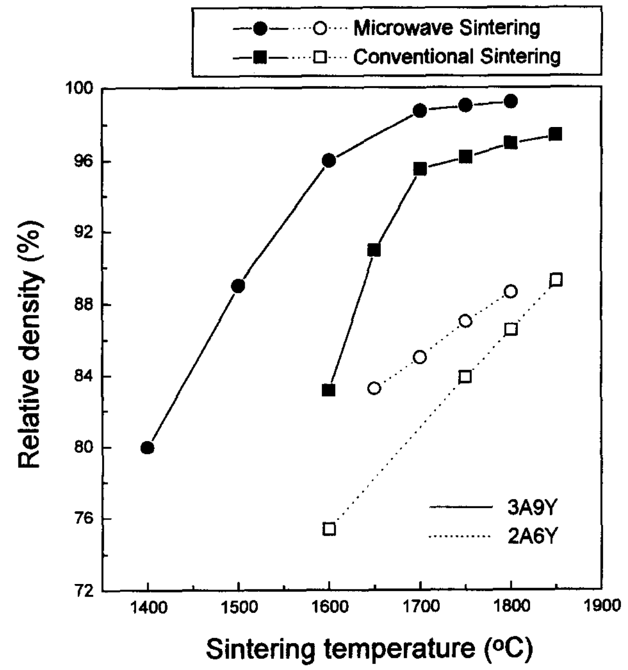

Fig. 5. Variation of relative density with sintering temperature for 2A6Y and 3A9Y. The isothermal holding time was 30 min.

3 Results and discussion

A characteristic of the insulation box in Fig. 2 is the use of the SiC plate as a preheater. Silicon nitride is a low loss ceramics that has a low effective loss tangent, tanδ_e, at room temperature. But above a critical temperature, T_{cr}, tanδ_e rises rapidly, resulting in a more effective heating. Due to this loss tangent behavior, direct microwave heating from room temperature is not easy and thermal runaway can occur when a large temperature difference happens within the specimen. Therefore, uniform preheating to the critical temperature of the specimen is needed if the specimen is to be heated efficiently without thermal runaway.

Figure 3 shows the temperature of the specimen and of the SiC preheater, measured simultaneously during the microwave sintering process. The temperature of the SiC preheater was higher than that of the specimen at lower temperature, but above 1390°C the specimen temperature became higher than that of the preheater. This suggests that the SiC plate preheated the specimen until the transition at about 1390°C.

Figure 4 shows the microstructure of the center and of the near surface region of the 3A9Y specimen microwave-sintered at 1750°C for 30 min. No differences are observed, thus indicating the absence of significant thermal gradients within the sintered specimen.

Figure 5 shows the variation of relative density with sintering temperature for 2A6Y and 3A9Y. The microwave-sintered specimens exhibited higher relative density than the conventionally sintered specimens at all sintering temperatures. The microwave-sintered 3A9Y reached more than 99% of theoretical density at a sintering temperature of 1600°C. In the case of conventionally sintered 3A9Y, such a high density could not be obtained even at a sintering temperature of 1850°C.

The microstructures of the microwave-sintered and the conventionally sintered 3A9Y were compared in Fig. 6. In the case of the microwave-sintered specimen, the average grain size was larger at all sintering temperatures and the interlocked microstructure with elongated grains was already formed at 1700°C. Abnormal grain growth of the elongated grains can be seen with the increase of the sintering temperature. On the other hand, in the case of conventionally sintered specimens, most of the grains were equiaxed at 1700°C and these equiaxed grains transformed into elongated grains

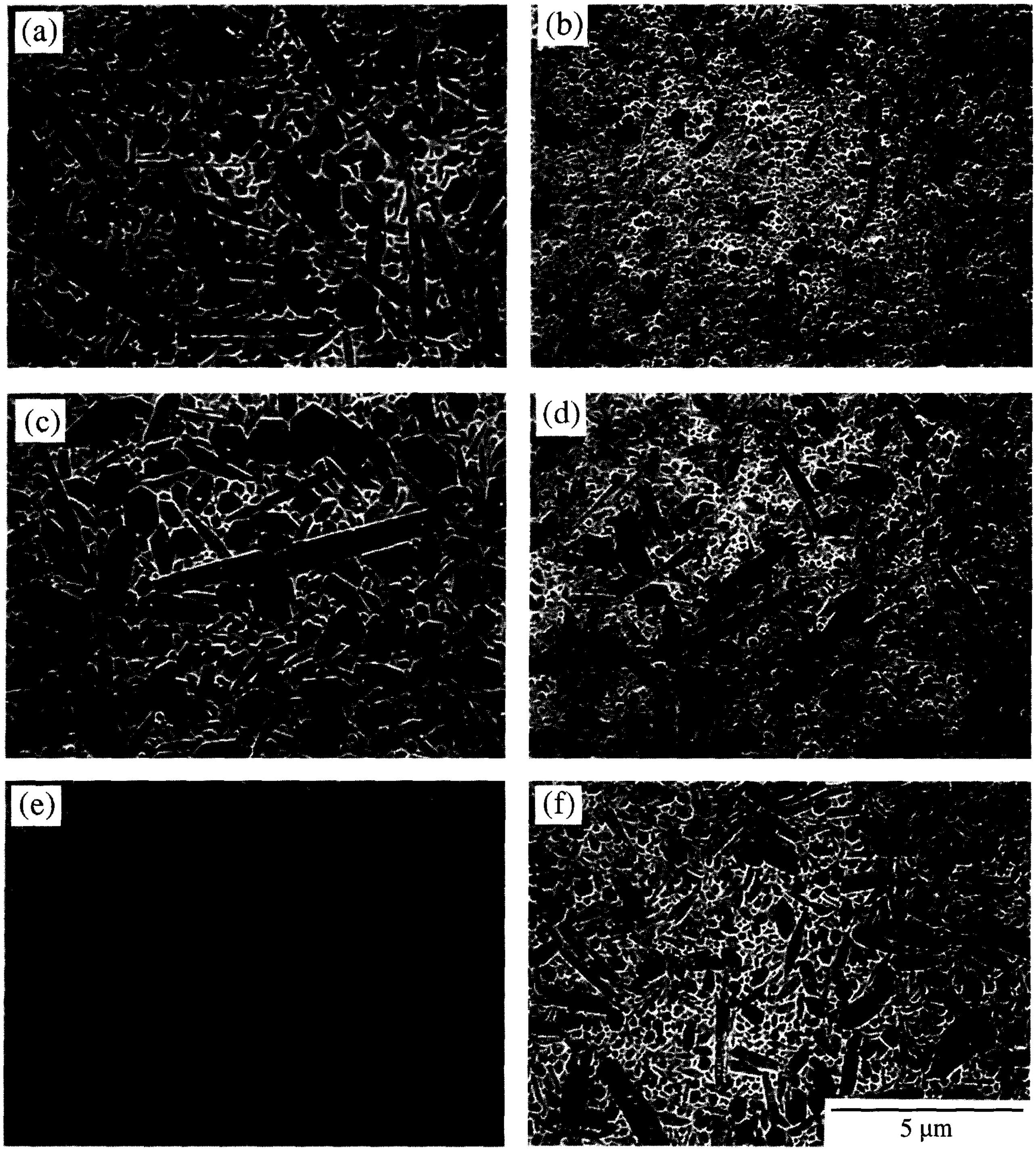

Fig. 6. SEM micrographs of 3A9Y sintered by (a, c, e) microwave and (b, d, f) conventional heating. The sintering temperatures were (a, b) 1700°C, (c, d) 1750°C, and (e, f) 1800°C.

as the sintering temperature increased. The development of grain morphology in silicon nitride ceramics depends directly on the $\alpha \rightarrow \beta$ phase transformation.[5] Therefore, different behavior in the $\alpha \rightarrow \beta$ phase transformation is expected between the two heating methods.

The variation in the β-phase fraction for the sintered specimens is shown in Fig. 7. This figure clearly demonstrates the presence of an effect of microwave heating on the $\alpha \rightarrow \beta$ phase transformation.

The results in Figs 5 and 7 showed that the densification and the $\alpha \rightarrow \beta$ phase transformation were enhanced by microwave heating and the magnitude of the enhancement was higher in 3A9Y than in 2A6Y. This implies that there is a relation between the effect of microwave heating and the sintering additives.

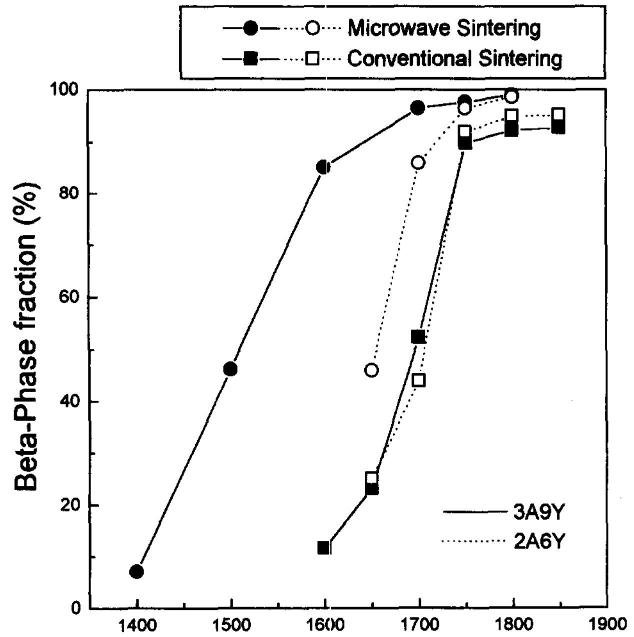

Fig. 7. Variation of β-phase fraction with sintering temperature for 2A6Y and 3A9Y.

In the present study, the following experiment was performed to investigate the effect of the microwave heating with respect to the sintering additives. Under constant microwave power of 1·1 kW, specimens with different amounts of additives (0, 4, 8, and 12 wt%) were heated and the variation of temperature with time was measured. The temperature profiles are shown in Fig. 8. In spite of the same microwave power, specimens containing larger amounts of additives reached higher temperatures with the same duration of heating time. This is evidence that the microwave heating of silicon nitride occurs predominantly by coupling between the microwaves and the sintering additives. To show the influence of sintering additives more clearly, the heating rate of the specimens (dT/dt) was derived as a function of temperature. Two peaks appeared as shown in Fig. 9. The first peak, at lower temperature, is due to the preheating of the SiC plate and the second peak is due to the coupling between the microwaves and the specimen. Accordingly, the influence of sintering additives can be seen in the second peak. The height of the second peak increased and the position shifted toward low temperature as the content of additives increased.

The microstructure of silicon nitride during sintering is made up of silicon nitride grains and the intergranular liquid phase. The liquid phase is formed by a reaction between sintering additives and surface silica on the silicon nitride starting powders.[6] In the SiO_2–Al_2O_3–Y_2O_3 ternary system, the liquid formation temperature (eutectic temperature) is 1345°C. It is, therefore, the intergranular liquid phase that absorbed the microwave preferentially after the transition step.

Since the microwave heating enhanced both the densification and the $\alpha \rightarrow \beta$ phase transformation, it seems that the kinetics of the solution-diffusion-precipitation mechanism[7,8] responsible for these processes was increased by the microwave heating.

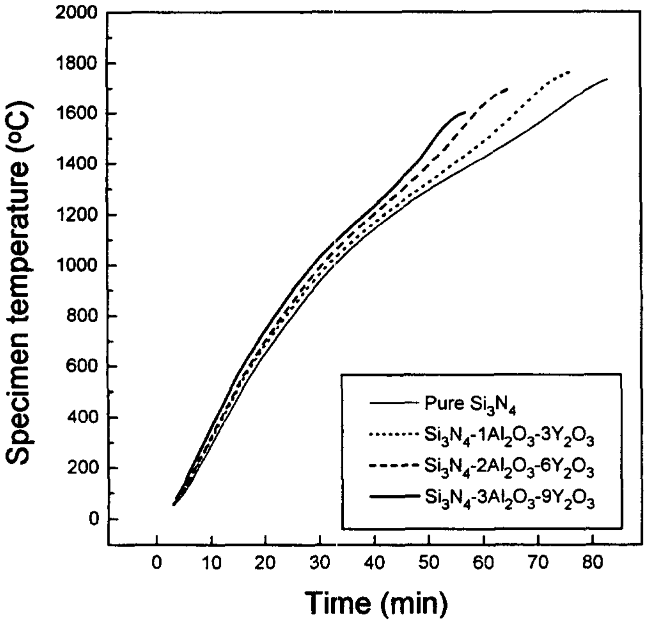

Fig. 8. Heating profiles of the specimens containing different amounts of additives (0, 4, 8, and 12 wt%). The specimens were heated under the constant microwave power of 1·1 kW.

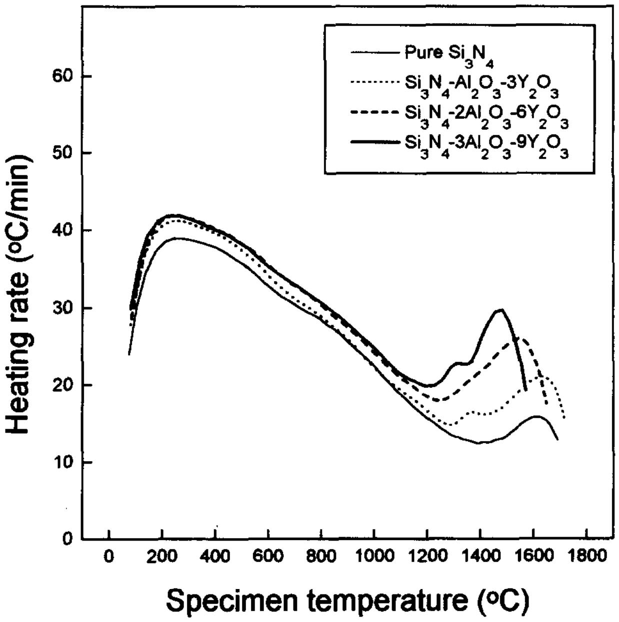

Fig. 9. Heating rate curves derived from the heating profiles in Fig. 8.

It is not clear yet whether the rate-determining mechanism is diffusion-controlled or reaction-controlled. Contradictory results have been reported for Si_3N_4–Al_2O_3–Y_2O_3 by Abe[9] (diffusion-controlled), and Boberski *et al.*[10] (reaction-controlled). A more detailed interpretation is accordingly not possible at this stage.

4 Conclusions

Silicon nitride with near theoretical density was obtained by the microwave sintering of α-Si_3N_4 with the addition of Al_2O_3 and Y_2O_3 as additives. The densification and $\alpha \rightarrow \beta$ phase transformation were enhanced by microwave heating as compared with conventional heating. It was shown that the microwave heating of silicon nitride occurs predominantly by coupling between the microwave and the sintering additives.

Acknowledgements

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