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Microwave Sintering of α/β-Si_3N_4

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Abstract

Dense silicon nitride from α- *and* β-Si_3N_4 *powders with 6 wt% (Y_2O_3+Al_2O_3) additives were fabricated in a TE_{103} single mode cavity microwave sintering system operating at 2·45 GHz. Packing powders were used. The sintering behaviour was investigated with special interest in the evolution of the* α- *to* β-Si_3N_4 *phase transformation, densification and microstructure development. Densities of about 96·7% TD and 95% TD were achieved by microwave sintering of* α- *and* β-Si_3N_4 *powders; the* α *to* β *conversion is more rapid than densification in the microwave heating of* α-Si_3N_4. © *1997 Elsevier Science Limited.*

1 Introduction

Microwave sintering is an emerging technology challenging traditional sintering methods. Volumetric and internal heating leads not only to rapid heating and sintering velocity, but also to improved microstructure and properties.[1] At present, rapid sintering of ceramics materials shows promise of enhanced densification, this being attributed to the rapid passage of a specimen through the low-temperature regime where grain coarsening dominates into the regions where densification mechanisms prevail.[2] Many reports[3–5] show that ceramics have been successfully sintered and fine grain size, uniform microstructure, high density, and significant energy savings are achieved by microwave heating. A rapid heating rate and short processing time are responsible for these benefits.[3]

Silicon nitride ceramics are the leading candidates for high-temperature structural applications because of their combination of properties. But extremely low self diffusion coefficients cause difficulty in fabricating fully dense products. Sintering aids have to be used to react with the SiO_2 existing at the surface of the Si_3N_4 particles to form a liquid phase and to achieve densification; diffusion through the liquid phase determines the densification behavior, the resulting grain size and the extent of α to β conversion.[6] The mixture of Al_2O_3 + Y_2O_3 is a common additives and Al_2O_3 addition to the Si_3N_4+Y_2O_3 system enhances densification by decreasing the viscosity and liquefaction temperature of the glassy phase.[7,8] At present, the few reports about microwave sintering of Si_3N_4 ceramics centre on using a multi-mode cavity microwave sintering system. Tiegs[9] shows coupling to the Si_3N_4 materials by way of the sintering additives; sintered Si_3N_4 materials showed improved densification and enhanced grain growth as compared to samples heated conventionally under similar conditions. Patterson and his coworkers[10] obtained uniformly sintered Si_3N_4 tools using powder bed technology and greatly economized in energy and time. In our study, we used a single mode cavity microwave sintering oven with designed insulation configuration to heat the specimen to the sintering temperature by hybrid heating and to obtain a uniformly sintered specimen with high density and good mechanical properties.

2 Experimental Procedure

The α-Si_3N_4 and β-Si_3N_4 powder characteristics are listed in Table 1; Y_2O_3 and Al_2O_3 are 99·9% purity.

The starting powders used were 94 wt% α-Si_3N_4 + 3 wt% Y_2O_3 + 3 wt% Al_2O_3, 94 wt% β-Si_3N_4 + 3 wt% Y_2O_3 + 3 wt% Al_2O_3. The mixtures of powders were milled in absolute alcohol for 24 h. After drying, the powder mixtures were die-pressed into bars, and then cold isostatically pressed under a pressure of 200 MPa. The sintering experiment were carried out in a single mode cavity microwave sintering system (TE_{103}) operating at 2·45 GHz. Since the silicon nitride is a poor coupler at room temperature, insulation and

Table 1. α-Si_3N_4 and β-Si_3N_4 powder characteristics

Powder source	Si_{free} (%)	*N* (%)	*O* (%)	Si_{total} (%)	d(μm)
α-Si_3N_4	0·5	38·09	1·01	59·58	0·72
β-Si_3N_4	0·11	38·07	0·33	61·05	0·51

preheating are used to help silicon nitride absorb microwave energy and to reach sintering temperature. Figures 1(a)–(c) show the insulation configuration. The specimens were presintered at 1100°C for 5 min in flowing nitrogen gas with the insulation configuration shown in Fig. 1 (a), then rapidly heated to 1740°C with a soaking time of 5 min in the insulation configuration shown in Fig. 1 (b). Figure 1 (c) shows a plan view of Fig. 1 (a). Packing powders are 30 wt%Si_3N_4+ 10 wt%BN+60 wt%SiC in Fig. 1 (b).

Density and linear shrinkage rates of the samples were measured at several predetermined temperatures. Densities were measured after cooling by the water immersion method and the surface temperatures were measured by an optical pyrometer. The phase compositions of specimens were determined by X-ray diffraction. The α and β contents were determined quantitatively by comparing the intensities of the strongest X-ray diffraction lines. Microstructures were observed at fractured surfaces by SEM techniques. Three-point bending strength was measured with a span of 20 mm; fracture toughness was determined by indent methods. HR_A were measured by hardness equipment [Akashi(AVK-A)].

3 Results and Discussion

3.1 Microwave sintering and densification behaviour

Figures 2 (a) and (b) show the relative density of α- and β-Si_3N_4 versus sintering temperature. Figures 3 (a) and (b) shows linear shrinkage of α- and β-Si_3N_4 versus sintering temperature. As can be seen in the two figures, initial densification proceeded slowly, then increased rapidly above 1400°C. This initial densification temperature corresponded to the lowest eutectic temperature of 1350°C in the SiO_2–Y_2O_3–Al_2O_3 system. Dense products from α-Si_3N_4 (above 96·7%TD) were attained after sintering at 1740°C with a soaking time of 5 min while dense products from β-Si_3N_4 have a maximum relative density of 95%TD at 1700°C. From the two figures, the densification of α-Si_3N_4 is more rapid than that of β-Si_3N_4, and the linear shrinkage of α-Si_3N_4 is more evident than that of β-Si_3N_4. This difference may affect the phase conversion of α-Si_3N_4.

3.2 Phase transformation in microwave sintered α-Si_3N_4

Variation in the β-phase fraction for the sintering temperatures studied is shown in Fig. 2 (c). Between 1200 and 1300°C, the β-phase fraction remains constant and at higher temperature α to β conversion begins and the extent of transformation increases with sintering temperature until completion is reached between 1700 and 1740°C. Processed conventionally, α-to-β conversion begins near 1400°C and finishes near 1800°C.[11] In our study, the intergranular eutectic liquid temperatures

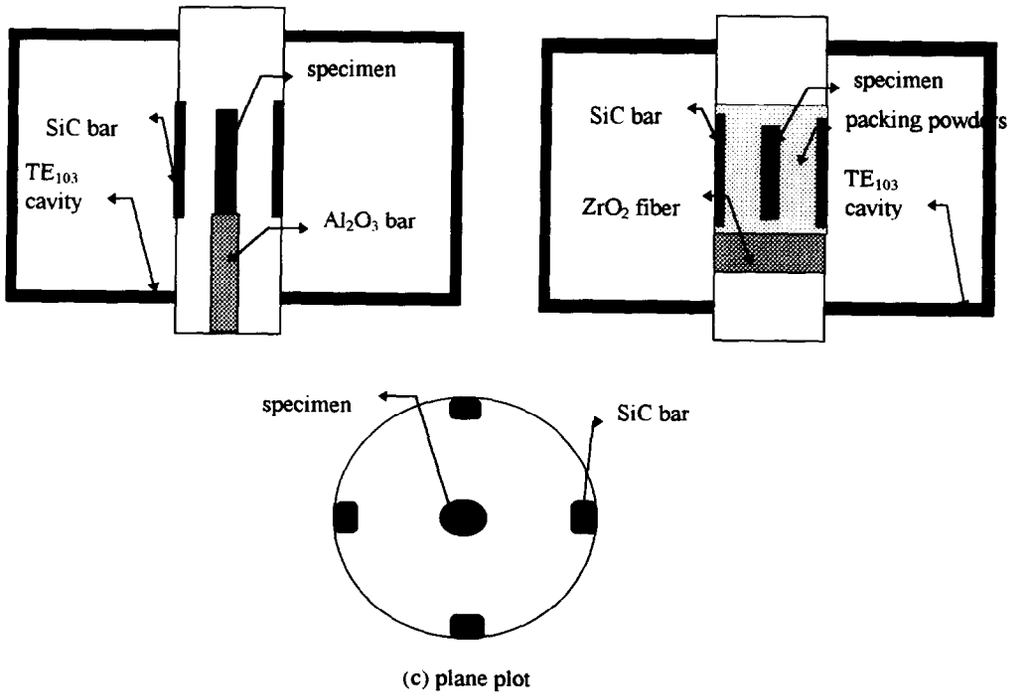

Fig. 1. Hybrid heating methods used in (a) microwave presintering of silicon nitride, (b) microwave sintering of silicon nitride, (c) plane view.

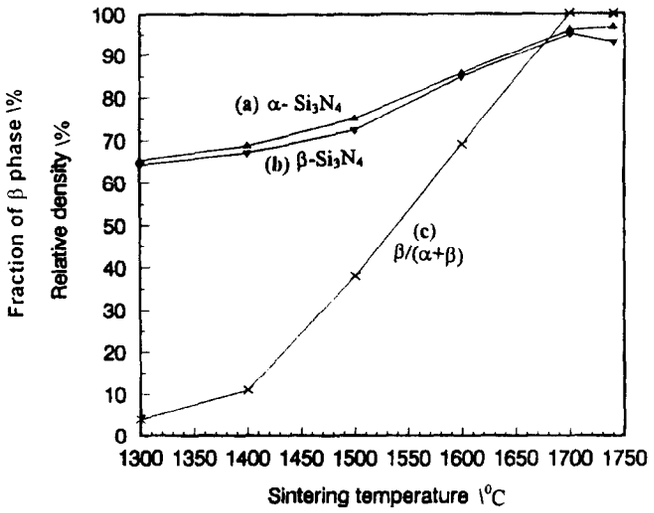

Fig. 2. Relative density of α and β-Si_3N_4, β phase fraction versus sintering temperature. (a) α-Si_3N_4, (b) β-Si_3N_4 and (c) β phase fraction.

are 1350°C for the Y–Si–Al–O–N system.[12] Usually, a sintering temperature above 1750°C is required to obtain complete densification. It is evident that microwave heating shows enhanced sintering behaviour. Since α-Si_3N_4 densifies in the study more rapidly than β-Si_3N_4 under the same conditions, and $\alpha \rightarrow \beta$ transformation occurs over the same temperature range, it is possible to attribute the more rapid densification of α-Si_3N_4 to the influence of the transformation.

3.3 Densification progess and microstructure development

Microstructural observation of the microwave sintered specimens shows a considerable inhomogeneity. This can schematically be seen in Fig. 4 which shows surface layers which do not fully densify while full densification is achieved at the centre. By measuring the density of the whole sample and that of the sample with the surface removed by grinding, the density at the surface

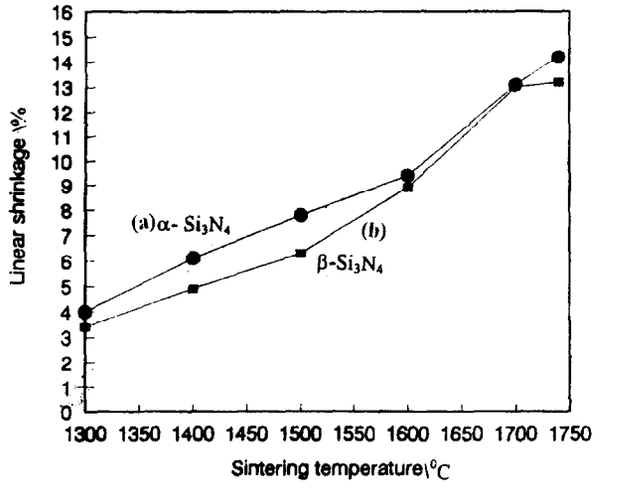

Fig. 3. Linear shrinkage versus sintering temperature. (a) α-Si_3N_4 and (b) β-Si_3N_4.

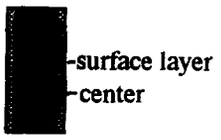

Fig. 4. Different densities of microwave sintered sample between the surface and the centre parts.

Fig. 5. SEM fractograph of surface layer shows a large degree of porosity.

can be shown to be lower than that at the centre. A large degree of porosity in the surface layer was also observed under SEM of a fracture surface as shown in Fig. 5. The difference between the surface and the centre can be associated with the character of microwave heating. As shown in Fig. 6, there exists a lower temperature at the surface than at the centre in microwave heating, thus it is possible that the centre part is fully dense while the surface part is incompletely densified.

The progress of sintering is then as shown in Fig. 7. When the centre part begins to densify and

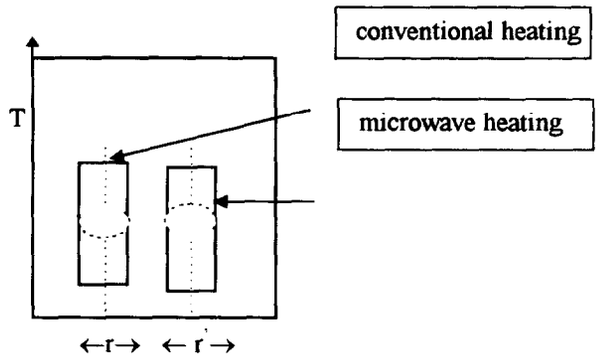

Fig. 6. Contrary temperature gradient between conventional and microwave heating.

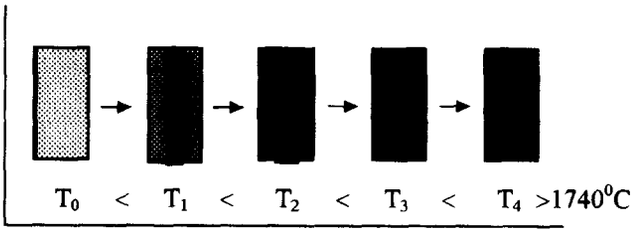

Fig. 7. Densification progress of sintered samples.

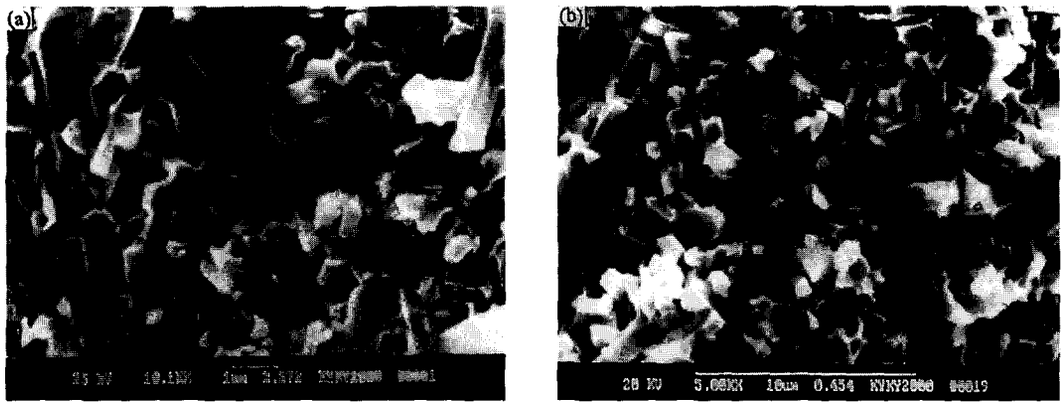

Fig. 8. SEM fractograph of microwave sintered sample from α-Si_3N_4 at different sintering temperatures. (a) 1650°C and (b) 1740°C.

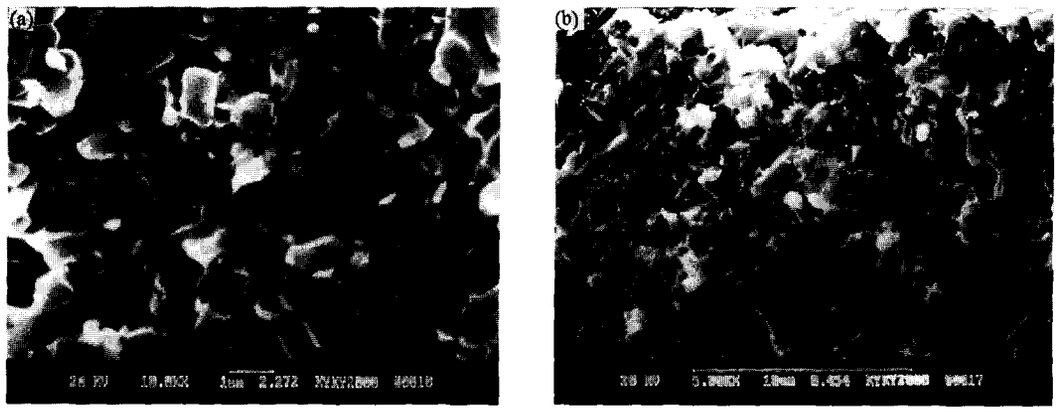

Fig. 9. SEM fractograph of microwave sintered sample from β-Si_3N_4 at different sintering temperatures. (a) 1650°C and (b) 1740°C.

shrink, transient stresses arise due to the shrinkage mismatch between the dense centre and the porous surface; according to Braudeau *et al.*[13] and Searcy,[14] temperature gradients and transient stresses play an important role in the rapid densification of materials. With longer soaking time, the whole sample will be fully dense, but longer holding times or higher sintering temperatures often result in abnormal growth at the centre grain or in lowering of the density.

SEM fractrographs of microwave sintered samples from α-Si_3N_4 powders and β-Si_3N_4 powders at 1650°C and 1740°C are shown in Figs 8 (a) and (b) and Figs 9 (a) and (b). The specimen from the α-Si_3N_4 powder fractured in both the intergranular mode and the transgranular fracture mode; the transgranular fracture mode is thought to be associated with the interlocking arrangement of newly formed β-Si_3N_4 grains. The elongated β-Si_3N_4 grain morphology also is evident and some grain pull-out or partial pull-out is observed. Such pull-out would increase fracture energy thus resulting in an increase in fracture strength. The values of mechanical properties of sintered samples are listed in Table 2.

Table 2. Mechanical properties of microwave sintered Si_3N_4 samples

Powder source	*Relative density (%)*	*HR_A*	*Bending strength*	*Fracture toughness*
α-Si_3N_4	96·7	91·4	600 MPa	6·1 MPa $m^{1/2}$
β-Si_3N_4	95	90·3	510 MPa	5·3 MPa $m^{1/2}$

4 Conclusions

(1) α and β-Si_3N_4 powders doped with 6 wt%(Y_2O_3+Al_2O_3) were sintered to 96·7% TD at 1740°C for 5 min and 95% TD at 1700°C for 5 min, respectively in a TE_{103} single mode cavity microwave sintering system operating at 2·45 Ghz. Uniform microstructures and good mechanical properties were obtained.

(2) The results show $\alpha \rightarrow \beta$ transformation occurs between 1300 and 1700°C.

(3) α-Si_3N_4 powders densify more rapidly than β-Si_3N_4 powders in microwave sintering, perhaps as a result of the phase transformation of α-Si_3N_4 powders.

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