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Grain growth in microwave sintered Si_3N_4 ceramics sintered from different starting powders

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Abstract

Silicon nitride ceramics have been produced by microwave sintering at 28 GHz with Y_2O_3, Al_2O_3 and MgO as sintering additives. The effect of initial β content of the Si_3N_4 starting powder on the microstructural development has been assessed by scanning electron microscopy (SEM) and quantitative image analysis. Phase transformation behaviour was assessed by X-ray diffraction. Mechanical properties of the sintered bodies were determined through assessment of hardness and fracture toughness. It was found that the samples sintered from powders with lower initial β content developed larger grains than those from higher β content powders, due to fewer nucleation sites during the $\alpha \rightarrow \beta$ transformation. However, attempts to develop a more bimodal microstructure by using a mixture of the two grades of powder, in an effort to increase both fracture toughness and fracture strength, were unsuccessful. In this case the microstructure was similar to that developed in the materials produced from higher β content powders. The mechanical properties of the sintered bodies were very similar, despite differences in microstructure. This was attributed to the strong bonding between the grains and grain boundary phase resulting in crack paths in all the materials that were predominantly transgranular, with little debonding or crack deflection. Under these circumstances the effect of larger grains is eliminated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Grain growth; Mechanical properties; Microwave processing; Si_3N_4; Sintering

1. Introduction

Silicon nitride, of which there are two crystalline forms; α and β, is one of the most promising ceramics for use in high temperature, tribological and structural applications, due to its excellent thermal, wear resistance and mechanical properties.[1] Although sintering of silicon nitride has been carried out from β-Si_3N_4 powders,[2] dense Si_3N_4 ceramics are most commonly produced from α starting powders, which during sintering transform to the β phase, with a rod-like morphology, via a solution re-precipitation mechanism. This transformation occurs when the oxide additives, used to aid densification, react with the SiO_2 present on the surface of the Si_3N_4 particles to form a eutectic liquid. Small α particles dissolve in this liquid and re-precipitate on β nuclei present in the starting powders. The development of these β grains during the transformation, and their growth by Ostwald ripening following its completion, control the final microstructure and therefore properties. This microstructural development in silicon nitride ceramics is recognised as one of the most important factors in achieving high strength, high toughness materials.[3,4]

One method of developing a suitable microstructure is to seed the starting powder with additional β-Si_3N_4 grains.[5] The growth of these grains during sintering leads to a bimodal microstructure containing large rod-like grains within a finer grained matrix, and can lead to concomitant improvements in both strength and toughness.[6] However, the process complicates the sintering of the ceramics by including the time consuming step of developing and extracting the grains to be used as seed.

There exist numerous commercial grades of α-Si_3N_4 powder, which have different amounts of residual β content. There has been little work carried out on the effect of using these different powders on the microstructural development in silicon nitride ceramics,[7] although they may provide an easy and less time consuming method of controlling the microstructural development.

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Unlike conventional heating techniques, where the heat is generated at the surface of the sample by radiation and then conducted to the centre, microwave heating is applied volumetrically due to interactions within the bulk of the material. Most of the reported work on microwave sintering of silicon nitride has been carried out at a frequency of 2.45 GHz.[8–10] Although, for oxide ceramics, sintering at higher frequencies has been reported to result in reductions in the inherent temperature gradients associated with microwave heating,[11] silicon nitride produced by microwave sintering at frequencies greater than 2.45 GHz has received very little attention.[12,13] Since silicon nitride is a poor microwave absorber at low temperatures, the heating is associated with heating of the oxide additives,[14] and our group has recently reported that one of the advantages of microwave sintering of silicon nitride is the enhanced development of β grains at a very early stage in the transformation process.[15] It is thought that this is due to localised heating with the grain boundary phase, and the possibility of dissolution of some of the pre-existing β nuclei.

It was, therefore, envisaged that microwave sintering from powders possessing different characteristics in terms of residual β content, would lead to differences in the microstructural development of these materials, and possibly to improved mechanical properties. In this work we report on the effect of initial β content on the grain growth in silicon nitride ceramics following the α→β transformation stage.

2. Experimental

2.1. Powder preparation

Specimens were prepared from different blends of α-Si_3N_4 starting powders; (Grades E-5 and E-10 Ube Industries Ltd, Japan). The characteristics of these powders are given in Table 1. In addition a series of samples were produced from a 50:50 mixture by weight of these two grades. The additives used in all cases were 5.00 mass% Y_2O_3 (RU-P, Shin-Etsu Rare Earth Ltd., Japan), 3.58 mass% Al_2O_3 (AKP-50, Sumitomo Chemical Ltd., Japan) and 1.42 mass% MgO (1000A, Ube Industries Ltd, Japan). The relative amounts of Al_2O_3 and MgO were chosen so as to give an overall composition of 5% by mass of the spinel ($MgAl_2O_4$). The powders were mixed and planetary milled in methanol, before being dried by evaporation and vacuum oven heating. The dried powders were sieved through a 250 μm mesh and uniaxially pressed under a pressure of 7.6 MPa before being cold isostatically pressed under 500 MPa.

2.2. Microwave sintering

The pressed samples were sintered in a nitrogen atmosphere of 0.1 MPa, in an applicator fed by a 28 GHz Gyrotron source (FDS-10-i28, Fuji Dempa Kogyo Ltd. Japan) as reported previously.[16] The samples were buried in a 50:50 Si_3N_4:BN powder bed and located inside the chamber within a double walled boron nitride crucible. The experimental configuration was surrounded by porous Al_2O_3 insulation. Sintering was carried out at temperatures ranging from 1450 to 1850 °C with 1 h holding at the sintering temperature. The temperature was monitored by a W-Re thermocouple embedded in the centre of the sample. The heating rate was approximately 10 °C min^{-1}, and following the holding period the samples were allowed to cool in the applicator at an average cooling rate of 20 °C min^{-1}. Identical samples were sintered conventionally under the same heating cycle for comparison purposes.

2.3. Characterisation

Sintered specimens for microstructural analysis were polished through successive grades of silicon carbide and finished with 1 μm diamond slurry. Plasma etching was carried out in CF_4 (Plasma reactor PR-41, Yamato Science Co. Ltd. Japan). The etched samples were gold coated for electron conductivity and microstructural characterisation was carried out by scanning electron microscopy (JSM-6340, Jeol Ltd, Japan) and quantitative image analysis.

Phase analysis was carried out by X-ray diffraction (Model RAD-RB, Rigaku Ltd, Japan), and the relative amounts of α and β Si_3N_4 were determined following the method reported by Gazzara and Messier.[17] Bulk density was measured by the Archimedes method. Grain size distributions were assessed by image analysis of the polished and etched surfaces. In all cases, a minimum of 1000 grains was counted for each specimen. Mechanical property analysis was carried out on polished specimens. Hardness was determined by Vickers indentation, Hv, under a load of 98 N. Fracture toughness was assessed by the indentation fracture method (JIS R1607), under the same load.

Table 1
Characteristics of the starting powders. The number of β nuclei in the E5 powder is an order of magnitude lower than that of the E10

Starting powder	Specific surface area (BET) ($m^2\ g^{-1}$)	Mean particle diameter (μm)	β Si_3N_4 content (mass%)	β Particle density ($N\ \mu m^{-3}$)
E5	5.3	0.36	1.5	0.6
E10	11.2	0.17	4.0	15.5

3. Results and discussion

The mechanical properties of sintered silicon nitride are closely linked to the β-Si_3N_4 content, with both fracture strength and fracture toughness increasing with β content due to the contribution to mechanisms such as crack bridging and crack deflection.[18] In order to assess the effect of grain growth on mechanical properties, as opposed to assessing the effect of increasing β content, it is therefore necessary to sinter the samples at temperatures sufficient to produce full transformation. Fig. 1 shows the microstructure of the samples sintered from the E5 and E10 powders by both conventional and microwave sintering, at the lowest temperature at which full transformation to β-Si_3N_4 had been achieved. In the case of microwave sintering, this was at an indicated temperature of 1450 °C, whereas in the conventionally sintered material the temperature was 1750 °C for the E10 sample, and full transformation was not achieved in the E5 sample until 1850 °C. The densification of the samples sintered by both sintering techniques was complete before the end of the transformation to β-Si_3N_4 such that the densities of all these samples were comparable, at around 98% of theoretical density.

Comparison of these samples showed that the microstructures of the microwave and conventionally sintered materials were very similar for both the E5 and the E10 powders. In both cases the E5 sintered body showed a much larger grain size the one sintered from E10 powder. Quantification of the grain growth behaviour in the sintered samples was carried out by image analysis of the polished and etched surfaces. The grain size distribution of these samples is shown in Fig. 2, and confirms that the microstructures were very similar at the end of the transformation process in terms of maximum grain size and grain size distribution.

The fact that silicon nitride ceramics readily decompose at temperatures around 1900 °C under conventional pressureless sintering,[19] meant that there was little opportunity to assess further grain growth in the conventionally sintered bodies, without resorting to longer holding periods at high temperature, or sintering under high nitrogen pressures in order to suppress the decomposition. In contrast, the $\alpha \rightarrow \beta$ transformation in the microwave sintered materials was complete at 1450 °C for both the E5 and E10 samples, thus providing the opportunity to study the effect of further heating on the grain growth and mechanical properties, under the same sintering conditions.

The reason for such reductions in temperature during microwave sintering is still the focus of much debate, with claims of non-thermal "microwave effects".[20]

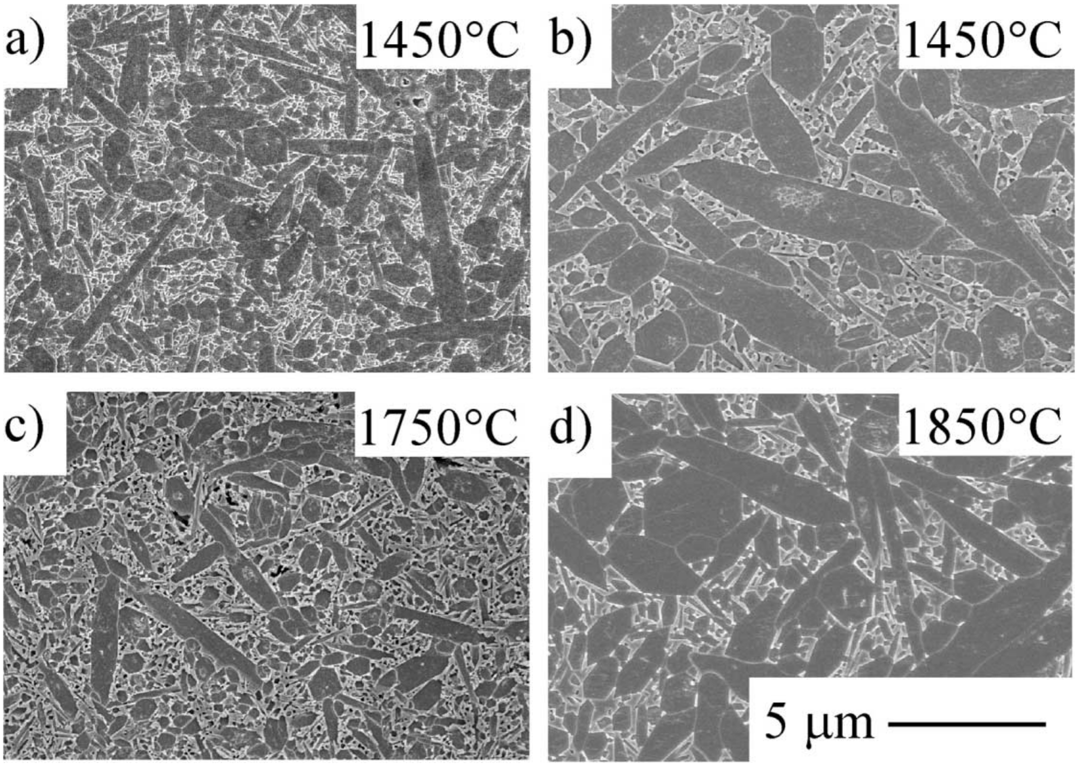

Fig. 1. Microstructures of microwave sintered (a and b) and conventionally sintered (c and d) silicon nitride ceramics from different starting powders. (a) And (c) show microstructures of samples sintered from E10 starting powder, and (b) and (d) show E5 sintered bodies. The microstructures shown are at the lowest temperature at which full β Si_3N_4 was achieved. Microwave and conventionally sintered samples show similar microstructures for both powders.

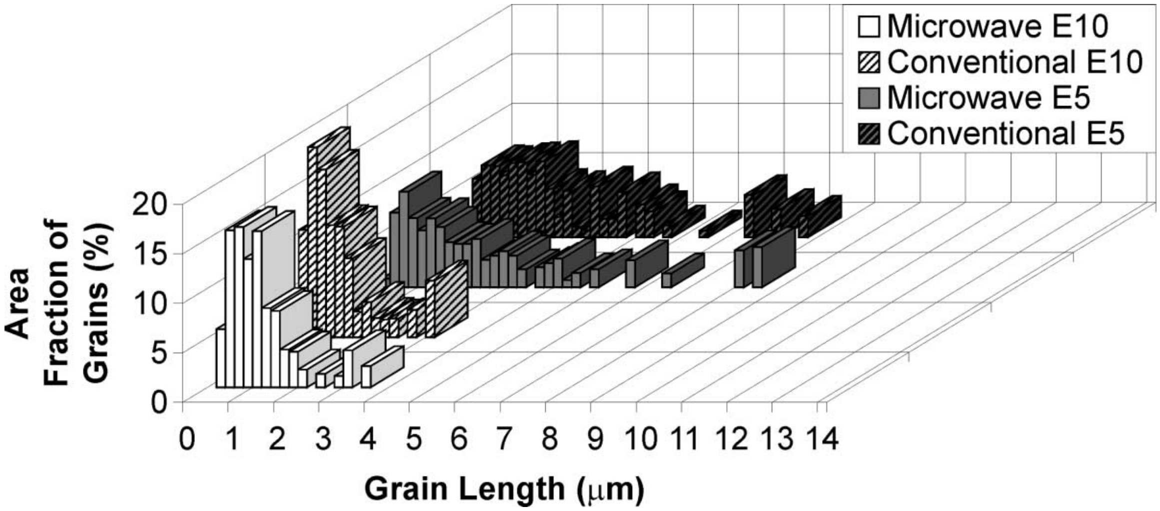

Fig. 2. Grain size analysis at the end of the α→β transformation (temperatures given in text). At this stage of sintering the grain size distribution of samples sintered by both microwave and conventional sintering were similar. E5 sintered powders show wider grain size distributions and a larger area fraction of large grains than the E10.

Other researchers suggest that reported temperatures are simply underestimated due to the difficulty in temperature measurement.[21] In the current work, the fact that the ceramics could be sintered up to indicated temperatures of 1850 °C without any decomposition, is an indication that the bulk temperature was not significantly underestimated. However, because microwave heating of silicon nitride ceramics is associated with adsorption by the oxide additives, there may be the possibility of localised temperature differences within the green body. Our group has recently reported that such differences could be responsible for the enhanced grain growth observed during the α→β transformation stage of microwave sintered silicon nitride.[22] The fact that the microstructures of both conventional and microwave sintered samples at the end of the transformation process were similar, is attributed to greater grain impingement in the case of the latter restricting further growth.

The microstructures of the microwave sintered E5 and E10 samples as a function of sintering temperature are shown in Fig. 3. As can be seen from this figure, all the samples showed grain growth with increased sintering temperature. The samples sintered from the E5 powder showed much larger grains than those from E10 powder at all temperatures. The samples sintered from the mixture of E5 and E10 powders are shown in Fig. 4. It was expected that the microstructures in these samples would consist of a mixture of those produced from the two sets of individual samples. That is a more bimodal microstructure consisting of fewer large grains than the E5 powder in a matrix of finer grains. However, this was not the case. The microstructures in this case were very similar to those produced from the E10 powder, with none of the large grains, seen in the E5 samples, observed.

Fig. 5 shows the area fraction of grains plotted against grain length for all the microwave sintered samples at temperatures of 1450 °C, corresponding to the end of the α→β transformation, and at 1750 °C. With increasing sintering temperature, all the samples showed grain growth, with an increase in the area fraction of larger grains, and also a widening of the grain size distributions, indicating a general coarsening of the matrix microstructure as smaller grains are consumed during Ostwald ripening.

The E5 sintered samples show wider grain size distributions and a larger area fraction of elongated grains when compared to the E10 and E5:E10 samples. This behaviour was observed at all sintering temperatures. The E10 and E5:E10 powders show very similar grain size distributions. These results show that large grained microstructures could be successfully obtained by sintering of powders containing a lower initial β-Si_3N_4 content. During the α→β transformation these grains act as nuclei for the precipitation of β-Si_3N_4. Table 1 shows that the number of β nuclei in the E10 powder is an order of magnitude greater than that of the E5 powder, and the reduced number of nucleation sites in the case of the E5 powder means that the precipitated grains can grow to a greater extent. However, attempts to produce a bimodal microstructure by combining mixtures of the two powders were unsuccessful. In this case, the microstructural development continued in the same way as in the case of the higher nuclei samples.

The fracture toughness and Vickers hardness of the sintered bodies are shown in Fig. 6. The hardness of the samples was constant at around 14 GPa, and the fracture toughness showed values of around 6 MPa $m^{1/2}$. It has been reported that the properties of silicon nitride, in particular fracture toughness, exhibit a maximum at sintering temperatures that correspond to the end of the

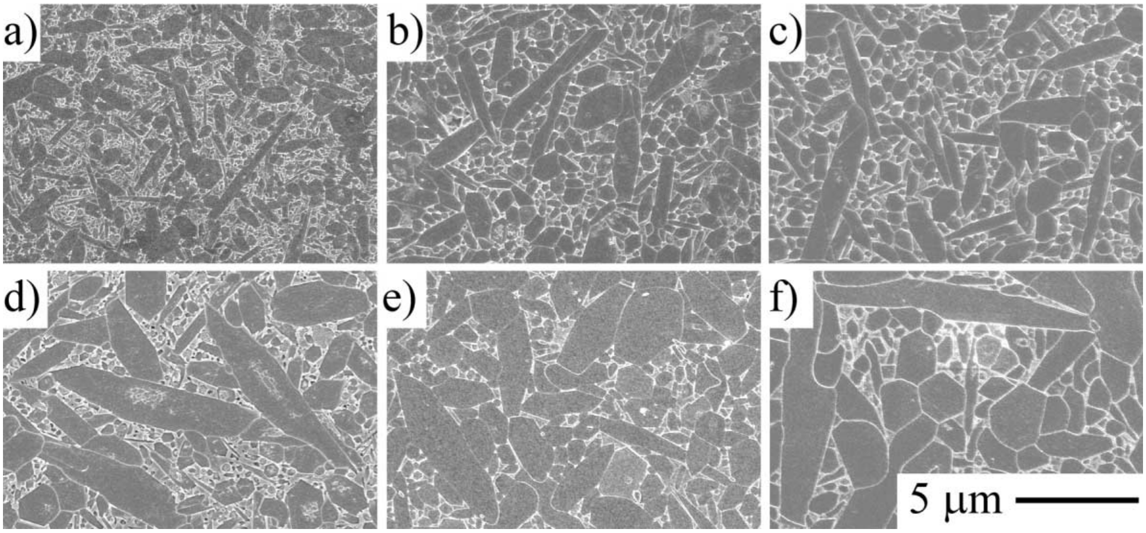

Fig. 3. Microstructures of silicon nitride ceramics microwave sintered from E10 (a–c) and E5 (d–f) starting powders. Sintering temperatures were (a and d) 1450 °C, (b and e) 1550 °C and (c and f) 1650 °C. Both sets of samples show increasing grain growth with sintering temperature, but the E5 sintered samples show much larger grains at all temperatures.

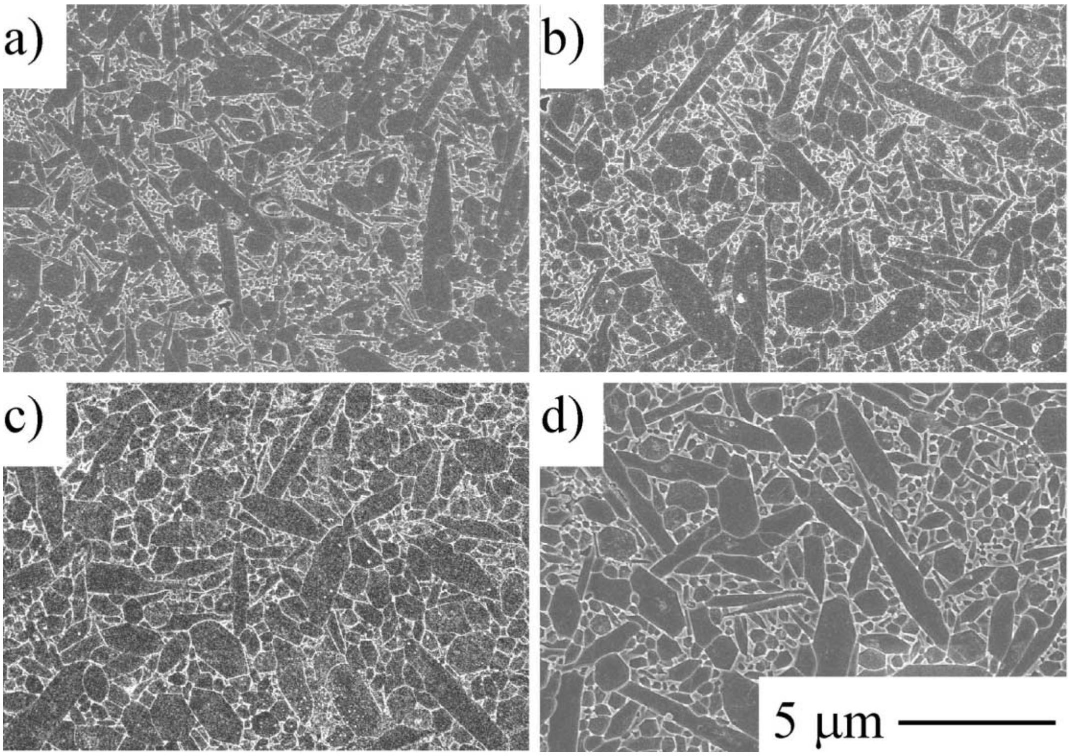

Fig. 4. Micrographs of samples microwave sintered from a 50:50 mixture of E5 and E10 starting powders. Sintering temperatures were (a) 1450, (b) 1550, (c) 1650 and (d) 1750 °C. The samples showed increasing grain size with temperature, but the microstructures were very similar to those sintered from E10 powder.

$\alpha \rightarrow \beta$ transformation process, and that further sintering results in reduced toughness due to reductions in aspect ratio of the β grains.[23] However, in this work this was not the case, there was no decrease in toughness with sintering temperatures beyond the completion of transformation.

Although the grain size of the E5 and E10 sintered samples was significantly different, with much larger grains in the case of the former, there was no significant effect on mechanical properties. Tiegs et al.[24] studied the effect of varying the β nucleation and growth kinetics of gas pressure sintered silicon nitride on the micro-

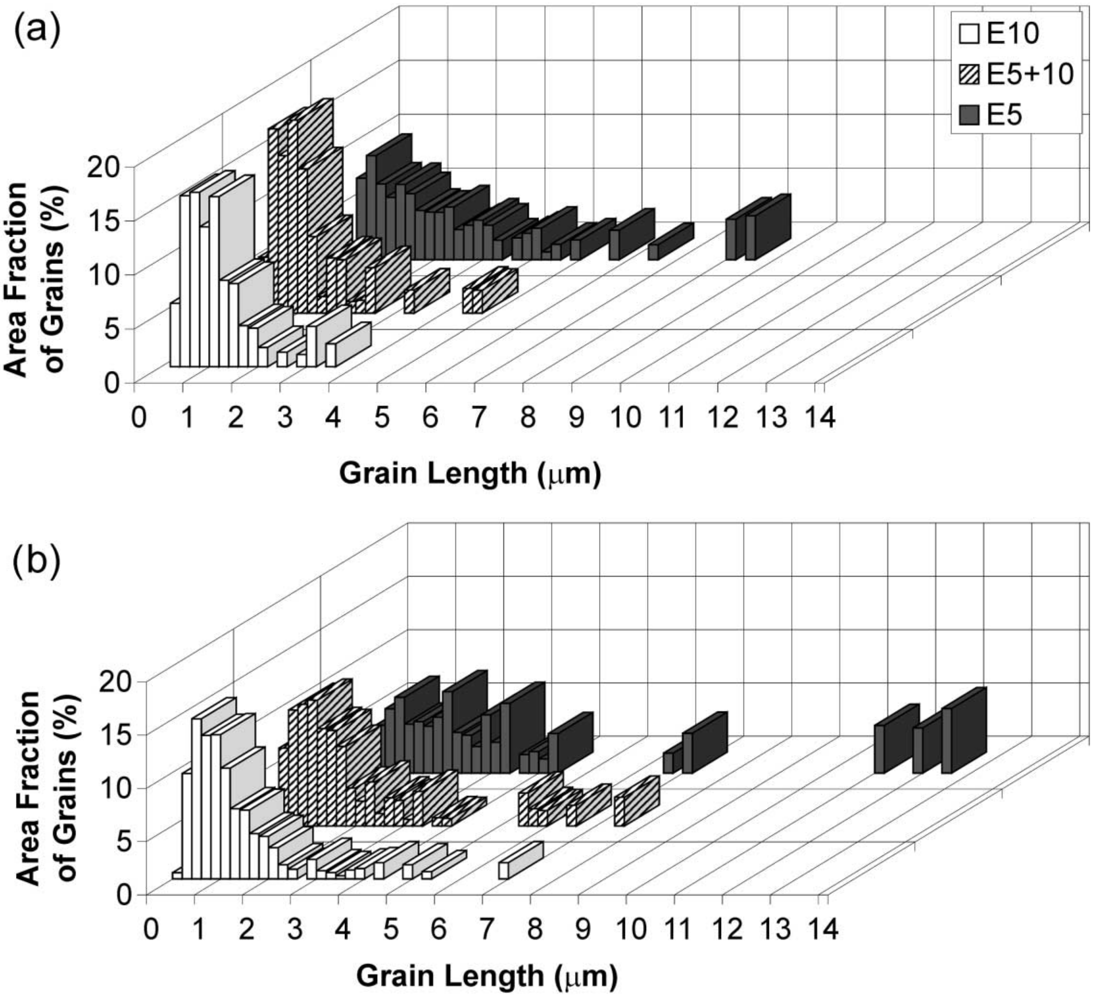

Fig. 5. Grain size analysis of the microwave sintered samples from different starting powders at (a) 1450 °C, the end of the $\alpha \rightarrow \beta$ transformation, and (b) 1750 °C. All samples showed grain growth and wider grain size distributions with increasing temperature. The E5 sintered samples show wider grain size distributions and a larger area fraction of elongated grains than the other samples at all temperatures. The samples sintered from the E10 and the E5:E10 powders were very similar.

structure and mechanical properties. In their work, various β contents were produced by both a low temperature holding step in the sintering process prior to higher temperature sintering to complete the transformation, and by mixing of different starting powders. These authors also reported that although there were microstructural differences between the materials, there was no significant effect on fracture toughness, and indicated that the grain boundary phase may be the dominant factor for fracture toughness. It is known that in silicon nitride ceramics, improvements in mechanical properties, in particular fracture toughness, depend not only on the development of large grains within the microstructure, but also on the interfacial bonding between grains and grain boundary.[25] The presence of large grains can increase the fracture toughness providing that interfacial debonding occurs, which requires a suitably weak interfacial strength.[26] If the interfacial bonding is too strong then the crack propagation becomes more transgranular[27] and the effect of large grains is reduced. This bonding between grains and grain boundary is controlled by the chemistry of the glassy phase. The silicon nitride ceramics of Tiegs et al.[24] were produced with additives of 6% Y_2O_3 and 2% Al_2O_3. For this additive system, Sun et al.[27] showed that grain boundary debonding was promoted by increasing the Y_2O_3:Al_2O_3 ratio, leading to improved fracture toughness. Similarly, Pyzik et al.[28] reported that decreasing the Y_2O_3:MgO ratio led to decreased fracture toughness. In the current work, where the content of Al_2O_3 and MgO is relatively high (Y_2O_3:Al_2O_3/MgO = 1:1) it might then be expected that interfacial debonding is restricted.

Fig. 7 shows the crack paths in the E5 and E10 samples following Vickers indentation. It can be seen from this figure that the crack path is indeed predominantly transgranular, with little crack deflection or interfacial debonding, thus implying strong bonding between the grains and grain boundary phase. Under these circumstances, despite the larger grains in the E5 samples, their

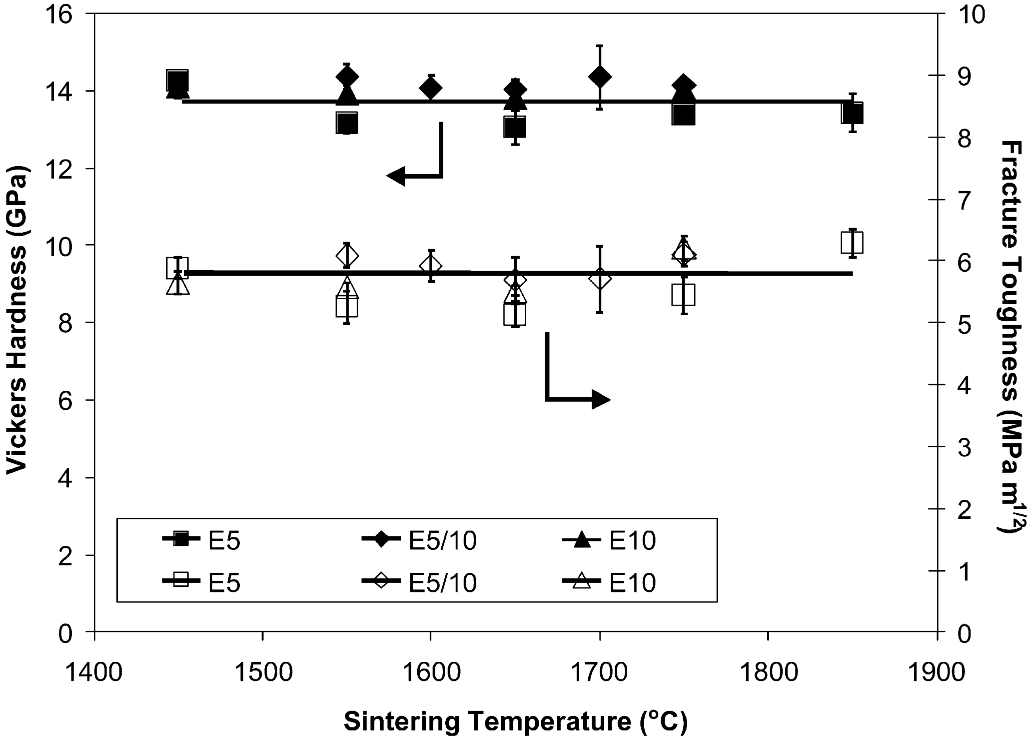

Fig. 6. Mechanical properties of the microwave sintered bodies. All the samples show similar properties, in terms of hardness and fracture toughness, despite the differences in microstructure.

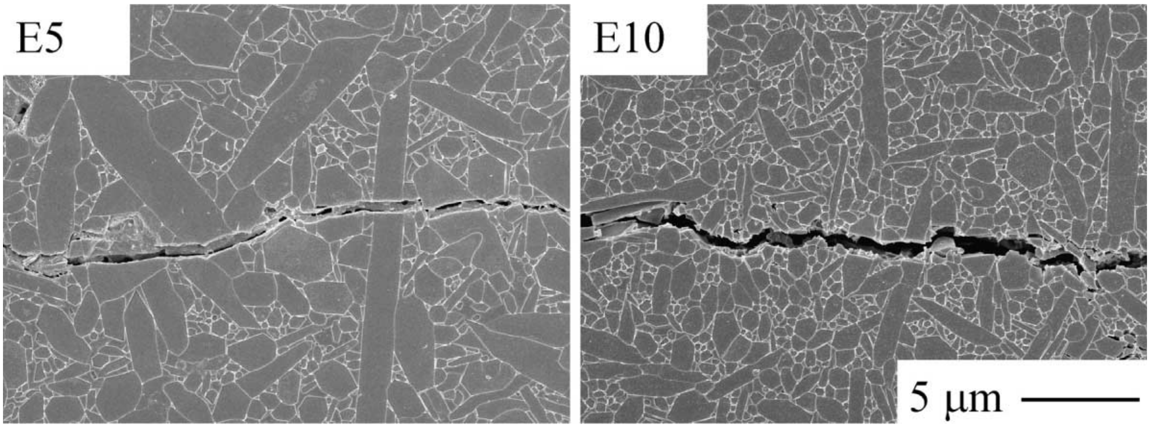

Fig. 7. Indentation crack paths in the E5 and E10 microwave sintered materials. Sintering temperature in both cases was 1650 °C. Although the microstructure of the E5 sample showed much larger grain size, the crack path in both cases was predominantly transgranular. In this case the effect of larger grains on mechanical properties is reduced.

effect on the mechanical properties is negligible, since the toughening mechanisms in silicon nitride rely to a large extent on developing a tortuous crack path with high degree of intergranular fracture.

4. Summary

Silicon nitride ceramics have been produced by microwave sintering of α-Si_3N_4 powders with different characteristics, in particular initial β-Si_3N_4 content, and the effect on microstructural development and mechanical properties has been assessed. It was found that the powder with a lower initial β content resulted in the development of a microstructure characterised by larger grain size than the powder with higher content, due to a lower number of nucleation sites. Attempts to develop a more bimodal microstructure by mixing of the powders were unsuccessful, with the microstructure in this case resembling that from the higher nuclei powder.

The mechanical properties were very similar despite the differences in microstructure. This was attributed to strong bonding between the grains and grain boundary, resulting in crack paths that were predominantly transgranular, with little crack deflection.

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