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Correlation between microstructure and toughness of hot pressed Si_3N_4 ceramics seeded with β-Si_3N_4 particles

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Abstract

Silicon nitride materials with distinct microstructures have been prepared by hot-pressing mixtures of α-Si_3N_4 powders plus oxide additives and β-Si_3N_4 seeds. These seeds were β crystals obtained by the SHS technology. The presence of these β-Si_3N_4 particles retarded the densification rate. The influence of the holding time at the sintering temperature on the microstructure and mechanical properties has been analysed in the β-seeded Si_3N_4 materials, in comparison with the non-seeded materials. These β-seeds were effective in enhancing α→β transformation and the general coarsening of the microstructure. The toughness has been discussed as a function of microstructural parameters, such as average grain size, average aspect ratio and area fraction of elongated grains.
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Keywords: B. Microstructure; C. Toughness; $HPSi_3N_4$; β-Si_3N_4 seed

1. Introduction

The mechanical properties of silicon nitride materials are greatly marked by their microstructure [1–3]. Generally, microstructures with elongated β phase grains of high aspect ratio, homogeneously distributed in a finer matrix, are the optima for developing high toughness and strength Si_3N_4 materials [4,5].

In practice, silicon nitride densifies by a liquid phase sintering process, which takes place by dissolution of the α phase into a melt and subsequent precipitation of the β phase. This oxide melt is formed on heating by reaction between the additives and the SiO_2 layer existent on the surface of silicon nitride particles. The kinetics of the sintering process and therefore, the final microstructure are in part determined by the composition of this liquid phase and the sintering technique.

Many studies have been dedicated to achieve control over the microstructure of silicon nitride materials and hence its mechanical behaviour [1–7]. In this way, attempts have been made to govern the microstructure of Si_3N_4 materials through the use of seeding particles [4,5,8], i.e. β-Si_3N_4 crystals that act as nuclei for the growth of β-Si_3N_4 grains during the sintering process [4,8]. In general, these seeds are prepared for the purpose by sintering of α powders with oxide additives, leaching afterwards the secondary phases, although other methods have also been reported [9]. Therefore, there is a wide range in size and morphology of seeding particles [5,7,9].

Silicon nitride materials with excellent mechanical properties have been described [4,5,10] for seeded compounds processed by tape casting and gas pressure sintering at temperatures above 1800 °C. In these cases, microstructures consisting of elongated and highly oriented grains developed. Furthermore, these highly oriented Si_3N_4 ceramics presented a greatly enhanced thermal conductivity, which is very interesting for some applications [11,12].

In general, these type of materials were processed from fine grained α-Si_3N_4 powders using a little amount of additives (<8 wt.%), being Al_2O_3 always employed to promote liquid formation and therefore densification. Part of that alumina enters in solid solution within the Si_3N_4 crystals and part remains in the residual glassy phase [1], and it can be harmful for some properties such as high temperature mechanical resistance or thermal conductivity [11,12].

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The effect of the β-seed particles on the densification/transformation of α-Si_3N_4 powders, hot-pressed using yttrium oxide and silica as additives, is analysed in this paper. The repercussion of the seeding on the microstructure has been quantitatively evaluated comparing to the non-seeded materials. The toughness of these materials is discussed as a function of microstructural parameters such as α/β ratio, porosity, average aspect ratio and area fraction of elongated grains.

2. Experimental

The silicon nitride powder employed was a commercial α-Si_3N_4 (E05, UBE Corp. Japan) with 0.6 μm average particle size, 4.8 m^2/g specific surface area, percentage of β-phase lower than 5 wt.% and an initial oxygen content of 1.1 wt.%. An 8 wt.% of submicronic Y_2O_3 powders (H.C. Starck, Germany), with 0.31 μm average particle size and 14 m^2/g specific surface area, and 5 wt.% of fumed silica (Cab-O-Sil, Cabot Corp., USA), with 0.007 μm average particle size and 380 m^2/g specific surface area, were used as additives. This composition was homogenised by attrition milling in isopropanol during 3 h using Si_3N_4 balls as milling media.

The β-Si_3N_4 powders were developed by SHS España (Madrid, Spain), using a proprietary technology based on the Self-Propagating-High-Temperature-Synthesis (SHS) method. They were disentangled using mortar and pestle as they were agglomerated. The percentage of β phase was 85 wt.%, the main impurities were 0.11 wt.% Al_2O_3 and 0.04 wt.% of TiO_2, determined by Inductively Coupled Plasma (ICP) spectroscopy. The prismatic morphology of the β crystals and the presence of particle aggregates are evidenced in Fig. 1. The particle size distribution measured by laser scattering is depicted in Fig. 2, showing an average agglomerate size of 30 μm and a 5 wt.% of agglomerates higher than 100 μm.

The β-Si_3N_4 seeded composition was prepared by adding 5 wt.% of β particles to the base composition and milling the whole mixture for another 3 h, to break down the agglomerates. Particle size distribution of the β-seeded milled mixture was then measured.

Silicon nitride bodies were fabricated by hot pressing at 1750 °C, under a nitrogen atmosphere of 0.1 MPa, using 50 MPa of uniaxial pressure. Different silicon nitride specimens were attained varying the holding time for 15, 30 and 90 min. The base composition, i.e. with no seeds added, was sintered under the same conditions and holding times. X-ray diffraction (XRD) procedures were used for identification of the main crystalline phases and for measuring the α/β phase ratio using the relative intensities of selected XRD peaks [13].

For the mechanical tests, dense billets were machined into prismatic bars with the tensile surface perpendicular to the hot-pressing axis. Bars were finished by longitudinal grinding using a 400-grit metal bonded diamond wheel at a depth of cut of 6 μm/pass. The edges of each traction surface were chamfered with 600 grit SiC paper prior to testing. Fracture toughness, K_{IC}, was measured by the indentation-strength method [14] with a four-point bending test rig, a Vickers indentation load of 490 N was applied in the middle of the traction surface previously to flexure testing. Values represent an average of 3–4 tests. In some specimens, K_{IC} was measured by the direct indentation method [15] on mirror polished specimens using a load of 490 N.

Vickers hardness, H, was estimated by indentation using an average of five indentations (49 N) per sample. They were done on a polished surface perpendicular to the hot pressing axis. Elastic modulus, E, was calculated from measurements of the resonance frequency and density in the prismatic bars.

Samples were polished with 6, 3 and 1 μm diamond suspensions and etched in a CF_4-5 vol.% O_2 plasma during 1–3 min, for microstructural observation in the scanning electron microscope (SEM). The quantitative evaluation of the microstructure was accomplished using image analysis techniques on the SEM micrographs. The imaged surface was always perpendicular to the hot-pressing axis and the number of grains measured was around 1500 for each specimen. The diameter was defined as the shortest of the 12 directed diameters (i.e., projections on 12 lines spaced every 15° around a half-circle), and the aspect ratio as the greatest of the ratios between each directed diameter and its perpendicular. The average aspect ratio was calculated using the 10% highest apparent aspect ratios [16] and the corresponding area percentage they occupied was

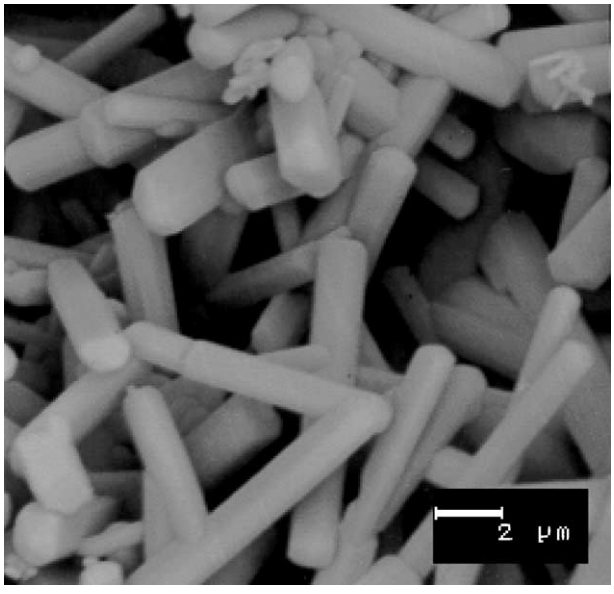

Fig. 1. SEM micrograph of β-Si_3N_4 seeding particles produced by SHS technology.

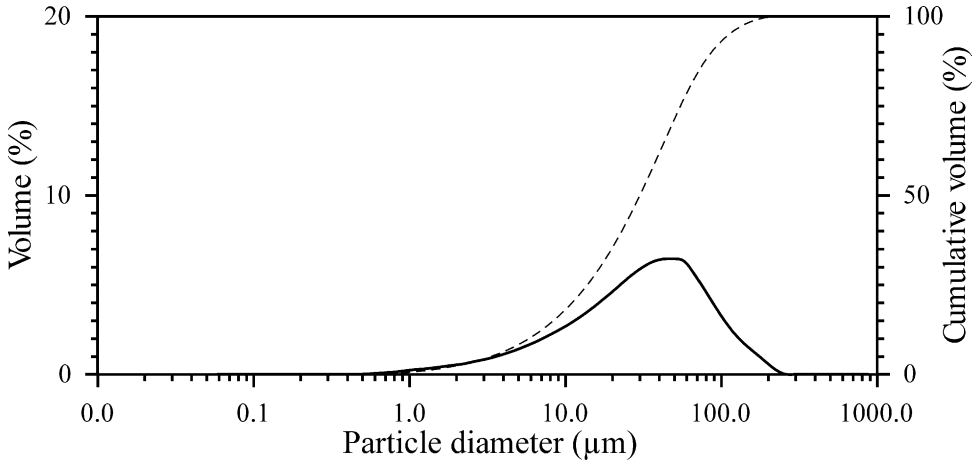

Fig. 2. Particle size distribution of the seeding particles.

also measured. Grain size distributions were depicted as histograms in area percentage.

3. Results

The as received β-Si_3N_4 seed particles were formed by agglomerates of crystals with high aspect ratios, which size and length can be estimated around 1 and 5 μm, respectively (Fig. 1). Therefore, these particles seem well suited to act as seed particles [4]. The particle size distribution for the seeded composition (Fig. 3) indicates that the milling procedure was effective in breaking agglomerates larger than 30 μm in the initial β-seeds as is seen in Fig. 2. The small peak centred at 8–10 μm in the distribution of Fig. 3 must then correspond to the seeds, which average size remains more than one order of magnitude higher than that of Si_3N_4 powders (0.6 μm).

The Si_3N_4 base composition began shrinkage at 1500 °C, whereas the addition of β particles retarded in about 200 °C this temperature (Fig. 4). After 90-min of holding, density was slightly higher in the non-seeded composition (Table 1), as the theoretical density calculated from the rule of mixtures from the initial composition was the same for both compositions. For lower holding times, densities were similar to that of the 90-min sample in the non-seeded specimens while in the seeded samples, the densities increased with holding time.

A similar amount of α phase was detected in both seeded and non-seeded materials for the longest holding time. Nevertheless, significant differences between seeded and non-seeded materials were observed for shorter holding times, where transformation was uncompleted. In fact, the amounts of α phase were 68 and 86 wt.% for the 15-min seeded and non-seeded specimens, respectively. At 30 min, the quantity of β phase lowered down to 14 wt.% in the seeded sample but it remained quite high in the non-seeded specimen (74 wt.%). XRD analyses confirmed that the secondary crystalline phases were the same in all the samples ($Y_2Si_2O_7$ and Si_2N_2O).

The mechanical parameters are summarised in Table 1. A wide variation in K_{IC} values, from 8.5 to 2.4

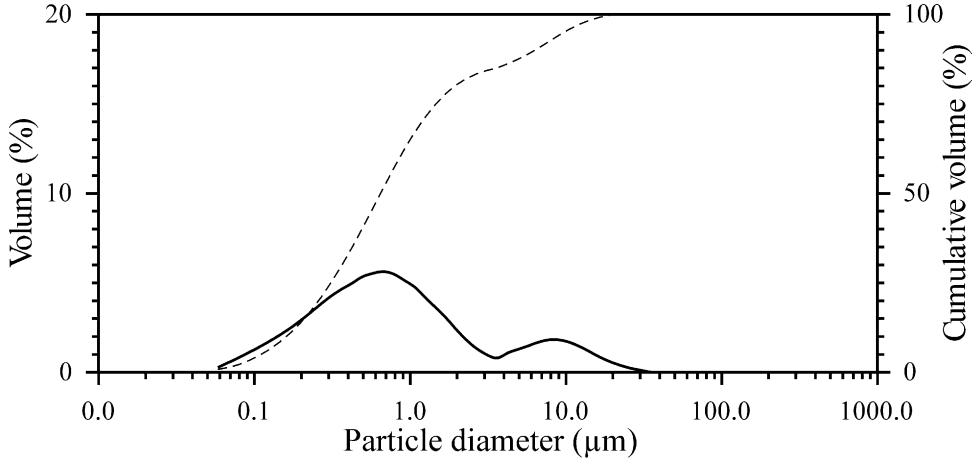

Fig. 3. Particle size distribution of attrition milled β-seeded composition.

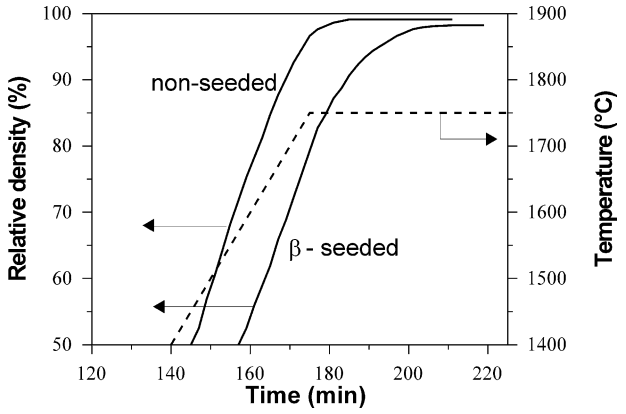

Fig. 4. Densification behaviour for seeded and non-seeded materials as a function of temperature.

MPa $m^{1/2}$, was observed where the highest value corresponded to the non-seeded material (90-min) and the lowest to the 15-min holding seeded sample. For both materials a toughness increase with holding time was observed.

Hardness ranged from 13 to 18 GPa (Table 1) and had a perfect agreement with the percentage of remnant α phase, except for the 15-min seeded sample that had a lower hardness than expected because its relatively low density (Table 1). On the other hand, the elastic modulus of these silicon nitride materials correlated perfectly with density achieved in each sample (Table 1).

Representative microstructures of each polished specimen are shown in Fig. 5. In the 15-min seeded sample (Fig. 5a), a homogeneous microstructure of isometric fine non-transformed α-Si_3N_4 grains with few isolated larger β grains was developed. In the 30-min seeded sample (Fig. 5b), a bimodal distribution with some grains of high aspect ratio embedded in a smaller grained matrix was observed. And for the 90-min seeded material (Fig. 5c), a general coarsening in the microstructure with substantial diminution of elongated grains was appreciable. Conversely, the non-seeded materials displayed a stronger bimodal microstructure for the 30-min and 90-min specimens (Fig. 5e,f) and an isometric fine microstructure for the 15-min holding time (Fig. 5d). These results can be seen quantitatively in the histograms represented in Fig. 6.

4. Discussion

The addition of seeds in the shape of elongated β crystals to the Si_3N_4 base composition resulted in a decrease of the sintering rate and limited the final density (see Fig. 4 and Table 1). Even though the milling step was effective for reduction in the seed agglomerate size, their size remained much larger than the α powders and retarded sintering. This sintering behaviour is in agreement with studies on constraint densification [17] and it can be explained by the development of localised regions of compressive strain in the matrix around the β crystals. In these regions, densification and grain growth will occur forming a solid network that constraints the shrinkage. Similar densities for the seeded and non-seeded samples were accomplished only for the 90-min holding time, both attaining almost a complete transformation (Table 1). Hirao et al. [4] also observed a retard in sintering rate with seeding, and they only achieved full density for holding times of 6 h at temperatures of 1850 °C.

Significant differences in the amount of α phase between seeded and non-seeded materials were observed for holding times shorter than 90 min. For those holding times, transformation kinetics was faster in the seeded specimens. Therefore, these particles were effective seeds in the sense that they acted as nuclei for the α→β transformation.

The β seeds also acted as nuclei for particle growth [4,11] because they caused a general coarsening in the microstructure and decreased the average aspect ratio. These effects are clearly seen in Fig. 7 that shows how the average diameter remained almost constant in the non-seeded specimens while it gradually increased with holding time in the seeded materials (Fig. 7a). Besides, average aspect ratio in seeded samples reached its maximum for the 30-min sample and then started to decrease but in the non-seeded samples it increased steadily (Fig. 7b). Furthermore, according to Fig. 7c, the area fraction of elongated grains in the seeded specimens seemed to reach its maximum value (~8%) for the 30-min holding time, while in the non-seeded samples no limit was observed for the given holding times. This decrease in the aspect ratio of large elongated

Table 1
Properties of HP-Si_3N_4 materials with and without seed added as a function of the holding time at 1750 °C

Sample	Holding time (min)	Density (g/cm^3)	α-Si_3N_4 (wt.%)	K_{IC} (MPa $m^{1/2}$)	E (GPa)	H (GPa)
Si_3N_4 non-seeded	15	3.21	86	3.3±0.3[a]	–	17.9±0.2
	30	3.22	74	5.0±0.4[a]	311±19	15.5±0.4
	90	3.23	3	8.5±0.2	312±4	13.6±0.2
β-Seeded	15	2.89	68	2.4±0.8	254±9	13.1±0.4
	30	3.15	14	5.6±0.3	303±22	15.1±0.1
	90	3.17	6	6.2±0.4	305±2	14.0±0.2

[a] Direct indentation method.

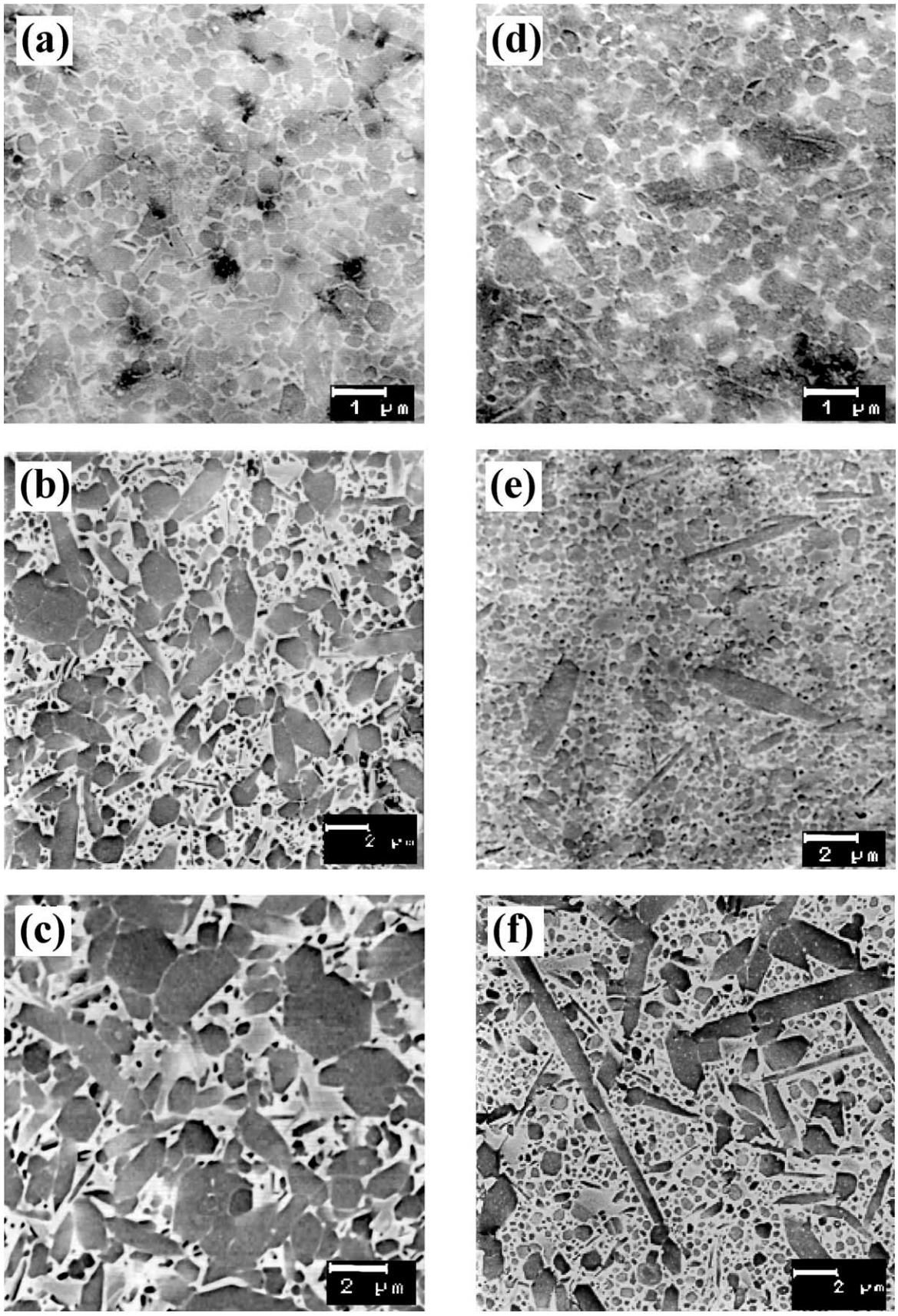

Fig. 5. SEM microstructure of the β-seeded Si_3N_4 for 15 min (a), 30 min (b), and 90 min (c) holding times and corresponding non-seeded materials 15 min (d), 30 min (e) and 90 min (f).

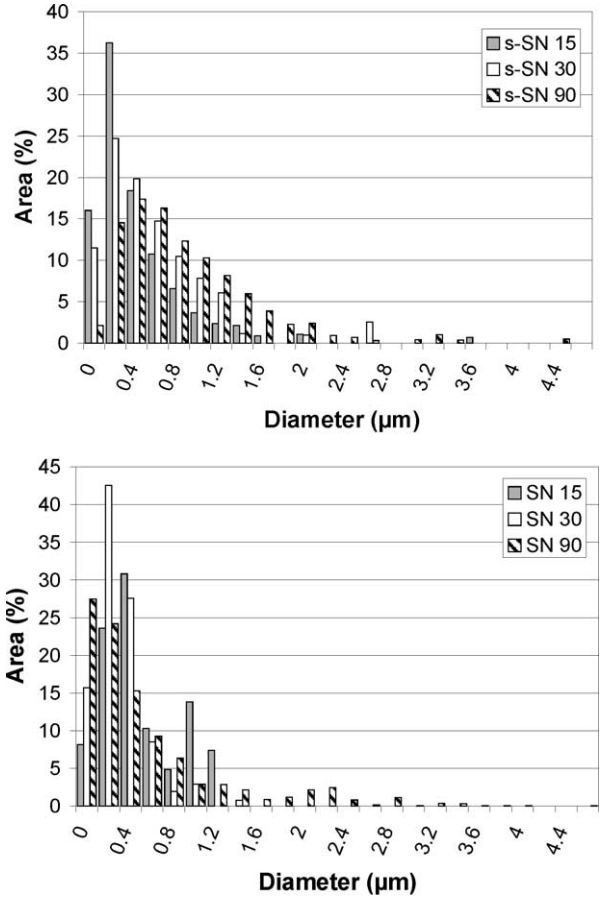

Fig. 6. Grain size distributions for the seeded and non-seeded samples held for 15, 30 and 90 min at the maximum sintering temperature.

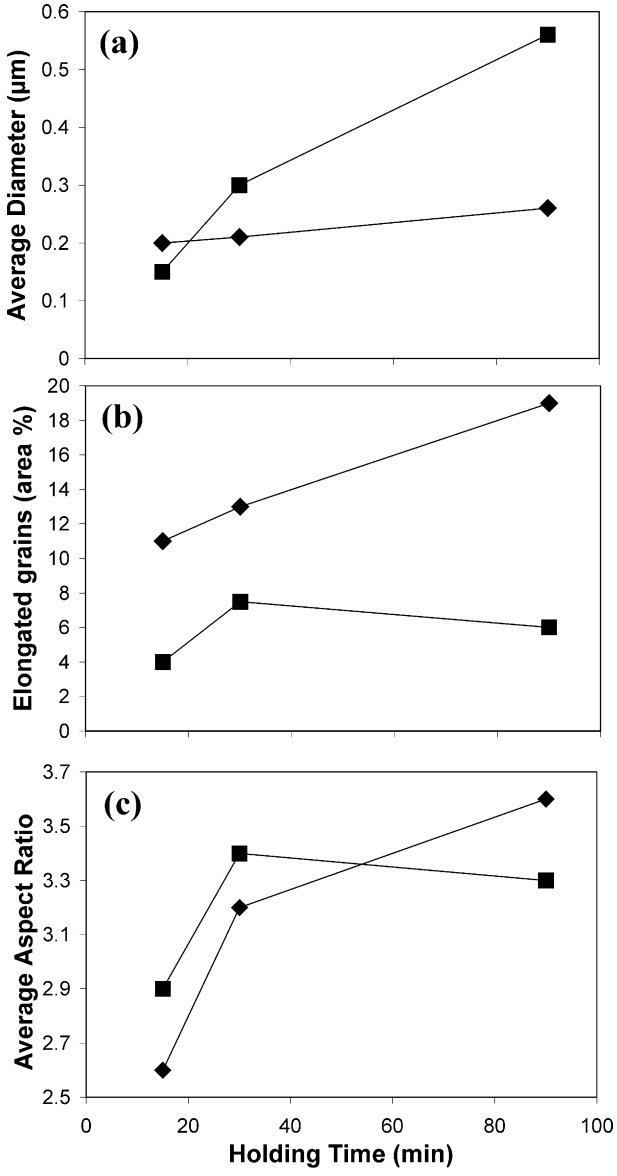

Fig. 7. Average diameter (a), area fraction of elongated grains (b) and average aspect ratio (c) as a function of holding time at the maximum sintering temperature, for seeded (■) and non-seeded specimens (◆).

grains with holding time, observed for seeded samples, is consistent with flattening of grain junctions (or shape accommodation) in an Ostwald ripening coalescence process. Therefore, seeds did not enhance abnormal grain growth of the elongated grains or highly bimodal microstructures, as observed by other authors [4,5,9], and they did not seem to create the required microstructures for improved mechanical performance.

Emoto and Mitomo [18], using fine β-Si_3N_4 powders as starting materials,showed that when the number of β nuclei was above 30% monomodal microstructures developed. A similar effect seems to occur in the present study although in this case the α⇒β transformation and grain growth effects superpose. Then, the observed microstructural evolution can be partly connected to the number of β nuclei present in the starting powders. For the base non-seeded composition, the number of β nuclei could be estimated as 5 wt.%, which is the fraction of coarser particles (>2 μm) in the starting α powders [19]. In the seeded composition, the number of β nuclei was of course larger (~10 wt.%, the sum of these nuclei to the β-seed addition) and seemed to be enough to avoid abnormal grain growth in this powder. Furthermore, this effect is in concordance with findings of Dressler et al. [20], which argued how the presence of many β nuclei produced a sterical hindrance for particles grow, reducing the heterogeneity in the microstructure.

When few seed particles are partially aligned along the *c*-axis, as it probably occurs in tape caste or extruded Si_3N_4 materials [4,5,21], elongated β grains can freely grow by epitaxy on the seed particles [22], and the effect of seeds is greatly enhanced. Results on gas pressure sintered Si_3N_4 materials with seeds added, and formed by die-pressing [22], also displayed a general coarsening on the microstructure but without a bimodal behavior. It is known that hot pressing produces Si_3N_4 materials with some degree of alignment in the β grains

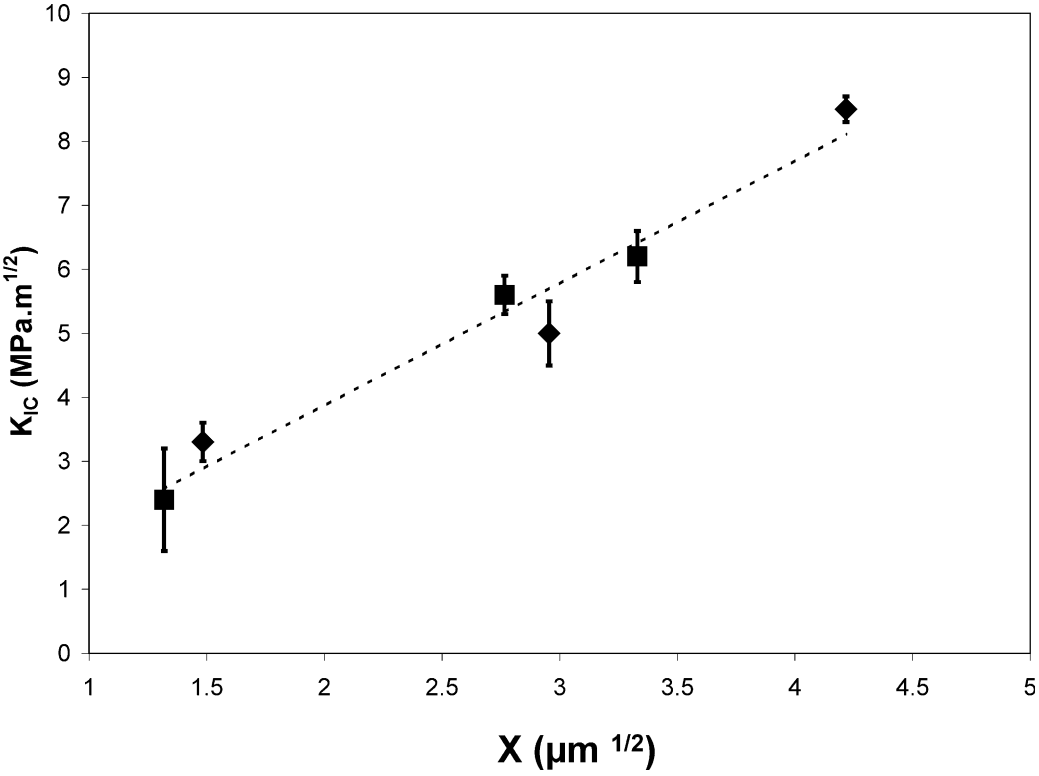

Fig. 8. Fracture toughness versus the parameter X defined by Eq. (1) (see text in Discussion). The symbol ascription is the same as in Fig. 7.

[23,24], nevertheless with the seeding procedure here described this effect was not enhanced.

It should be pointed out that besides the number of β nuclei and their adequate alignment, other variables, such as the use of high temperatures, low amount of oxide additives and high Nitrogen pressures, seem to be key requisites [16–21] to get remarkably bimodal microstructures in Si_3N_4 materials. In the same sense, works on alumina materials [25] showed that highly bimodal microstructures were developed only when a little amount of additives was used. For the additive system used in our materials, the liquid phase formed has a relatively low viscosity and therefore, the amount of additive cannot be substantially reduced without compromising density or else increasing the sintering temperature and applying Nitrogen pressure to avoid decomposition of the nitride phase.

The fracture toughness of the studied materials increased when bimodal microstructures developed. According to the bridging reinforcing model [26], the fracture toughness depends on the area fraction of bridging grains as well as on the debonding length, which can be related to the average aspect ratio and the average diameter of the β grains. In Fig. 8, the fracture toughness data for all specimens are plotted as a function of the parameter X, which contains all the involved microstructural parameters and is defined as:

$$X = \sqrt{\Phi \bullet \mathrm{AR} \bullet D} \quad (1)$$

where Φ is the area fraction of elongated grains, AR its average aspect ratio and D its average diameter. As it can be cleary observed in this plot, K_{IC} shows a linear increase with X in agreement with the model predictions [26]. Therefore, the low fracture toughness (<3.5 MPa m$^{1/2}$) of the 15-min seeded and non-seeded samples is due to the lack of β-Si_3N_4 bridging grains, as these samples showed homogeneous microstructures mainly formed by isometric α-Si_3N_4 grains (Fig. 6a,d). For the 30-min and 90-min holding times, the number and size of the elongated β-Si_3N_4 grains raised leading to materials with a more heterogeneous microstructure (Fig. 6). In these types of materials, toughening mechanisms such as deflection, de-bonding, bridging and pullout occurred and fracture toughness higher than 6 MPa m$^{1/2}$ were measured. This effect was more pronounced in the 90-min non-seeded material and the highest fracture toughness (8 MPa m$^{1/2}$) was achieved.

As expected, hardness increases with the α/β ratio in the samples [27], except for the 15-min seeded sample that showed low hardness due to its relatively low density (Table 1). As shown in this table, the elastic modulus of the silicon nitride materials mainly depended on densification degree.

5. Conclusions

The addition of seeds in the shape of elongated β crystals fabricated by SHS to the Si_3N_4 base composition resulted in an important decrease in sintering rate together with an increase in the α→β transformation kinetics of the hot pressed Si_3N_4 materials.

The addition of 5 wt.% β seeds produced a general coarsening in the microstructure of the material and decreased the average aspect ratio of the β grains, acting as nuclei for particle growth and leading to a more homogeneous microstructure. Moreover, the area percentage of elongated grains reached a maximum value of ~8% in the seeded samples.

The fracture toughness of the studied materials increased with the area fraction of bridging grains as well as with the β grain size, in agreement with predictions of the bridging toughening mechanism. Maximum toughness was achieved in the sample with the highest fraction of elongated grains, which corresponded to the 90-min non-seeded material.

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