Journal of the European Ceramic Society 22 (2002) 271–278
www.elsevier.com/locate/jeurceramsoc

Microstructural designing of silicon nitride related to toughness☆

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Received 16 January 2001; received in revised form 13 April 2001; accepted 21 April 2001

Abstract

Two ways of microstructural control were investigated with the intention to improve fracture toughness of gas pressure sintered silicon nitride : seeding and optimisation of sintering time. In order to study the effect of seeding, different amounts of large β-Si_3N_4 whiskers were added to different silicon nitride powders. Seeding can lead to a low toughening improvement, providing that the initial powder is free from large pre-existing β nuclei. If not, seeding has a negligible effect on the microstructure because of nuclei interaction and an unfavourable effect on densification, hence on toughness. The effect of the sintering time was studied in a case of abnormal nuclei growth. Toughness can be improved by increasing the sintering time, providing that the composition of the intergranular phase remains stable. Correlations between microstructural parameters and toughness are consistent with the reinforcing mechanisms in composites (crack bridging and crack deviation): toughness is proportional to the grain diameter square root and increases as the fraction of the large grains increases.

Keywords: Design of microstructure; Seeding; Si_3N_4; Toughness

1. Introduction

Silicon nitride's toughness can be improved by the in situ growth of elongated grains. These large elongated grains can indeed act as whiskers in ceramic composites, i.e. they can activate toughening mechanisms such as crack deflection and crack bridging. Because larger grains can act as strength determining defects too, grain growth has to be controlled. Two ways are possible. One way is to control the sintering time. The other way consists in seeding with rod-like single βSi_3N_4. Several studies showed that seeding could enhance mechanical properties.[1–3] Nevertheless, this effect has not been systematically observed. In particular, seeding in αSNE05 powder does not improve toughness.[4] The conditions for which seeding leads to an improved reinforcement are not well established.

This report is divided into two parts. In the first one, seeds were added in three different silicon nitride powders in order to clarify the effect of seeding on microstructure and toughness of silicon nitride. In the second part, the effect of sintering time has been studied on one interesting powder:αSN10 without seeds.

2. Experimental procedure

βSi_3N_4 particles (0–10 wt.%, Bayer, Fig. 1) were ultrasonically dispersed and then planetary milled with Si_3N_4 powder and with the sintering aids (Y_2O_3, 5 wt.%, Meldform Metals and Al_2O_3, 2 wt.%, Pechiney) using butanone (66 vol.%) and ethanol (34 vol.%) as the mixing medium. The powder mixture was dried and passed through a 200 μm mesh sieve before isostatically pressing. Three different powders containing different α/β ratios, but the same grain size, were tested (see Table 1).

The pellets were sintered by nitrogen gas pressure sintering following a two-stage process optimised in a recent work (1800 °C, 0.1 MPa, 1 h 30 min/1950 °C, 4 MPa, t_2).[5] Different sintering times were tested: t_2 = 10, 45, 90, 180, 540 min.

☆ This work is a part of the PhD thesis of F. Cluzel Peillon (Saint Etienne, 29 March 2001).

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00290-4

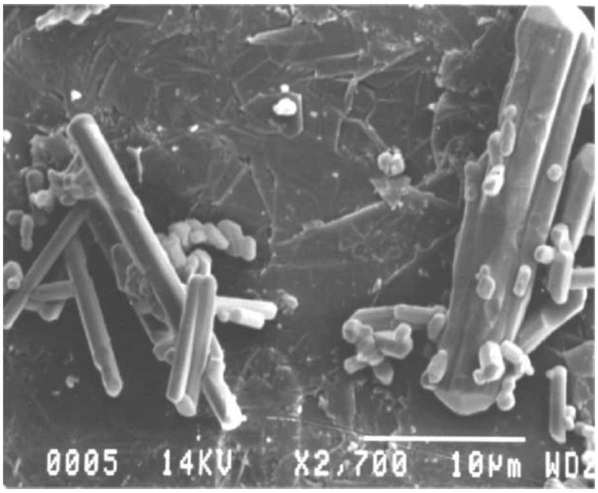


Fig. 1. βSi_3N_4 seeds (Bayer).

Table 1
Si_3N_4 powders characteristics

Powder	βAldrich	αSN-E05	αSN-E10	β Seeds
Provider	Aldrich	UBE	UBE	Bayer
α/β	≈0/100	95/5	98/2	0/100
Specific area (m^2/g)	Unknown	4.1	9–13	1–1.5
d_{90} (μm)[a]	0.2	0.2	0.2	1
d_{50} (μm)[a]	0.6	0.8	0.6	8
d_{10} (μm)[a]	1.7	1.7	1.3	70–80

[a] Measures from laser granulometer Coulter.

Bulk density was measured by the Archimedes method. Densification was studied with a high temperature dilatometer (SETARAM). Microstructural characterisation was carried out by SEM on polished and plasma etched sections. An image analyser (CUE SERIES, Olympus) was used to characterise the microstructure. The grain diameter was defined as the minimum Feret diameter and the aspect ratio R_{95} as the mean aspect ratio of the 10% largest grains.[6] Fracture toughness was obtained by the surface indentation technique following Evans derivation.[7] *R*-curve behaviour was determined by the indentation strength method.[8]

3. Results and discussion

3.1. Seeding

3.1.1. Densification

Fig. 2 shows shrinkage curves of materials with different initial Si_3N_4 powders during the first sintering stage under 0.1 MPa. Densification starts at 1300–1400 °C. At these temperatures, the chemical reaction between the sintering aids and the silica layer on Si_3N_4 is initiated. The first maximum (1300–1400 °C) in the densification rate corresponds to the rearrangement of the particles. At 1600–1800 °C, densification by the solution/diffusion/precipitation mechanism takes place. The phase transition α/β occurs simultaneously. Densification is slightly enhanced when the α/β ratio is high, due to the higher solubility of αSi_3N_4 powder compared to the βSi_3N_4 solubility. The lower densification of the αSNE05 powder compared to the αSNE10 powder may be due to its lower specific area (see Table 1).

Seeding βSi_3N_4 single particles slightly hinders densification, as shown in Fig. 3: after the first sintering stage under 0.1 MPa nitrogen pressure, densification decreases as the concentration of seeds increases, because of steric hindrance and the low specific area of the seeds. The state of closed porosity (~92% TD) is hence not reached when the pressure is applied. High pressured gas trapped in the pores prevents complete final densification, which decreases down to 95% TD after the second sintering stage in samples seeded with 10 wt.% of nuclei.

3.1.2. Microstructure

SEM micrographs are reported in Fig. 4. It is noteworthy that unseeded microstructures contain acicular grains even in the initial βSi_3N_4 powder ($R_{95}=2.8$). Anisotropy is hence not linked to the crystallographic nature of the initial silicon nitride powder. It can be explained by different growth mechanisms in the different directions of the βSi_3N_4 crystals.[9,10] On the contrary, grain size and its distribution (cf. Fig. 5) depend on the α/β ratio in the initial powder : the distribution is narrow for a low ratio (0/100) whereas it is broad and multimodal for a very high ratio (98/2, 95/5). It is inferred that βSi_3N_4 grains originated from the silicon nitride powder act as seeds because of their low solubility in the liquid phase during sintering.

The effect of seeding on microstructure is illustrated on Figs. 4 and 5. This effect depends on the α/β ratio in the initial silicon nitride powder. With a high α/β ratio (98/2), the bimodal grain size distribution is modified as the concentration of seeds increases. When seeding with a low amount of βSi_3N_4 (2.5 wt.%), the population of large grains ($d_{min} > 2.5$μm) increases, because the number of nucleation sites increases. Above 5 wt.% of seeds, the grain size distribution becomes almost monomodal. On the contrary, the effect of seeding is negligible on microstructure with a lower α/β ratio (95/5 and 0/100).

It seems that there is a critical amount of nuclei beyond which nuclei growth is slowed down. This idea has been developed by Emoto and Mitomo.[11] According to them, nuclei addition exceeding 10 wt.% decreases the driving force for abnormal grain growth because of nuclei interaction. In the present study, this critical amount is about 5 wt.% βSi_3N_4 (originated either from initial powder or adding seeds). Below this value, abnormal grain growth

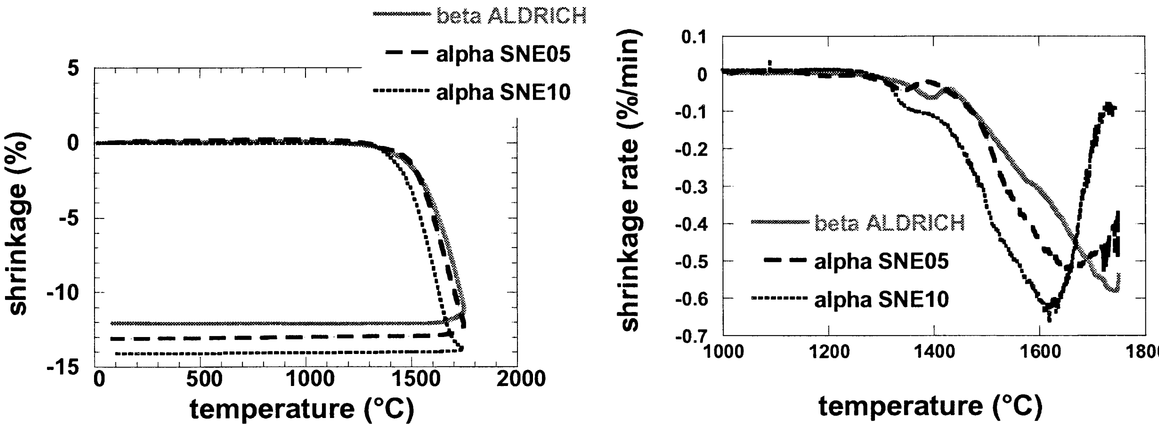


Fig. 2. Densification curves of the different silicon nitride powders.

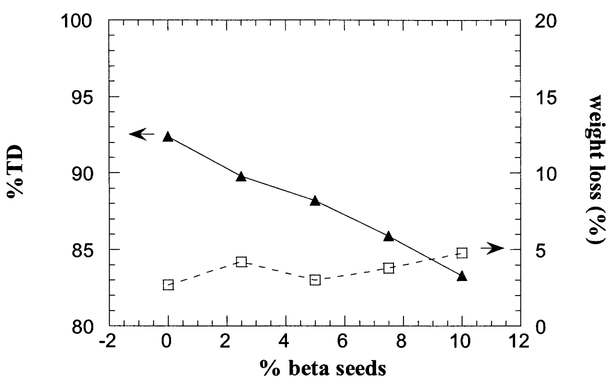
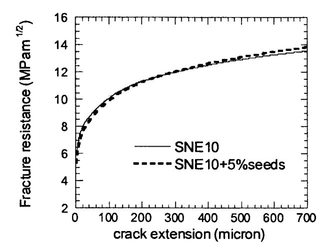
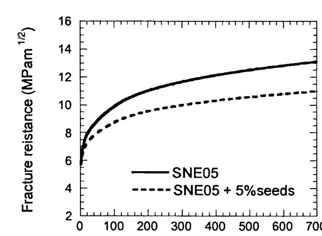
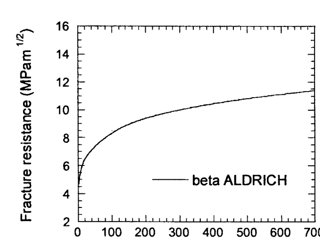


Fig. 3. Densification and weight loss after the first stage of the two-stage process as a function of the concentration of the seeds.

Table 2
Fracture toughness and *R*-curve behaviour

Initial powder	Toughness (MPa $m^{1/2}$)	*R*-curve
αSNE10 without seeds	8.1±0.3	
αSNE10 +2.5% seeds	8.4±0.4	
αSNE10 +5% seeds	7.9±0.3	
αSNE05 without seeds	8.5±0.5	
αSNE05 +5% seeds	7.9±0.6	
αSNE05 +10% seeds	7.7±0.4	
βaldrich without seeds	7.3±0.2	
βaldrich +2.5%seeds	7.5±0.3	

occurs so the large-grains amount increases when seeding. Above this value, the driving force for nuclei growth is not high enough to favour abnormal growth. Nuclei growth becomes normal as the amount of nuclei increases. Besides, growth rate is low, as shown further. Adding a few more nuclei by seeding has a negligible effect on the final microstructure.

Seeding can hence be an efficient technique to modify significantly the silicon nitride microstructure, but providing that the initial silicon nitride powder contains a low content of pre-existing β nuclei i.e. a very high α/β ratio ($>95/5$).

3.1.3. Toughness

Results on toughness are reported in Table 2. Every type of microstructure shows a *R*-curve behaviour, indicating that toughening mechanisms are activated in all cases, with or without seeds. The highest toughness values correspond to microstructure containing one or several populations of large grains, in agreement with reinforcement enhancement by large elongated grains.[12] Nevertheless, the toughness range when modifying microstructure is narrow (7.3–8.4 MPa $m^{1/2}$). Except for the case of αSNE10 ($\alpha/\beta = 98/2$), seeding does not improve toughness because its effect on microstructure is negligible. Moreover, seeding can decrease toughness because of porosity due to a lower densification rate (SNE05's case). For an engineering point of view, seeding can hence be unsuccessful. Seeding is efficient to get

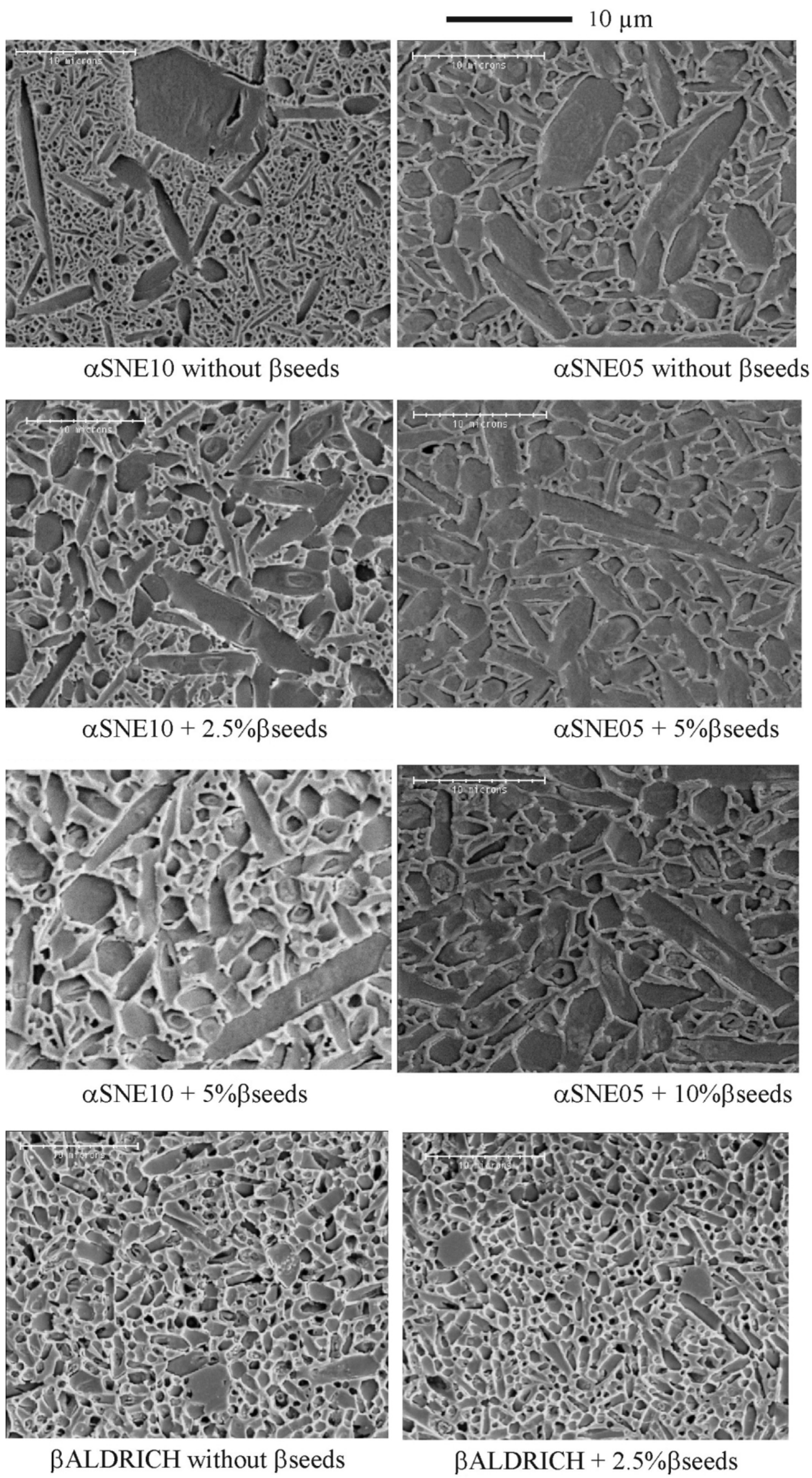


Fig. 4. SEM micrographs (×3500) on polished and plasma etched surface.

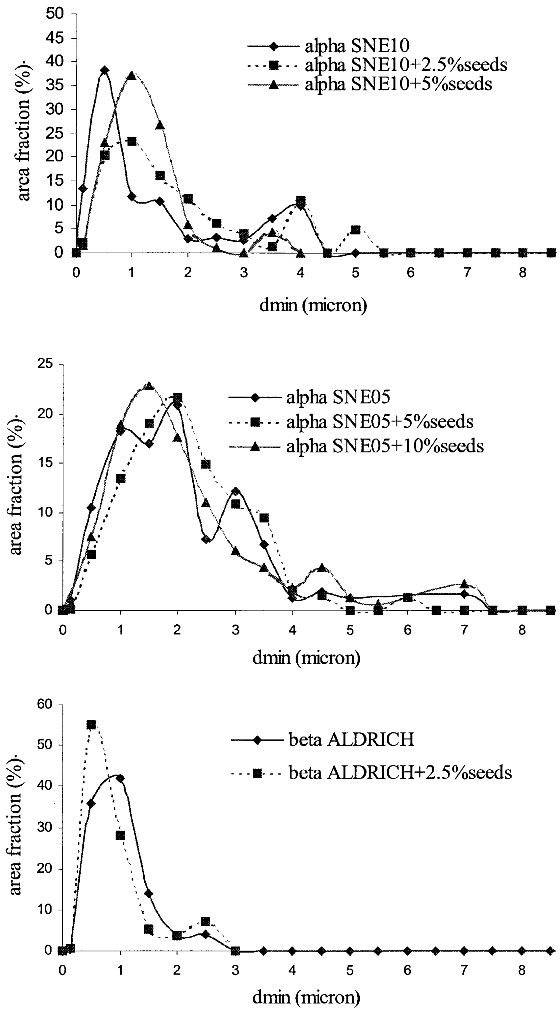


Fig. 5. Area fraction distribution of diameter.

a reinforcing improvement if the Si_3N_4 powder is fine and free from large pre-existing β nuclei.

3.2. Sintering time

The effect of sintering time has been studied with the unseeded αSNE10 powder because its driving force for abnormal grain growth is high due to its low β content.

3.2.1. Densification

A high densification rate was obtained for all samples (97–98%TD). It is noteworthy that the weight loss slightly increases as the time increases. X-ray diffraction study reveals the presence of crystallised phases after $t_2=9$ h, suggesting that a partial crystallisation of the intergranular phase occurs during the sintering.

3.2.2. Microstructure

At short sintering times ($t_2=10$–45 min), the grain size distribution is monomodal (see Fig. 6). As time increases, the distribution becomes multimodal ($t_2=1$ h 30 min, 3 h, 9 h). In another report,[13] we show that the slow growth of the matrix grains can be assimilated to a normal growth with interface reaction control. This slow growth is associated with the abnormal grain growth of few large grains.

3.2.3. Toughness

Toughness variation with sintering time is reported in Table 3. Toughness increases as sintering time increases. The low toughness at $t_2=9$ h can be explained by the chemical modification of the intergranular phase (partial crystallisation).

Reinforcement by crack bridging and crack deflection is theoretically favoured by the increase of grain size, aspect ratio and proportion of large elongated grains. The study of the effect of these three parameters on toughness confirms the occurrence of such mechanisms in our sample. Fig. 7 shows that toughness values increase and then reach a plateau as the proportion of large grains (diameter > 1 μm) increases. This observation is in good agreement with Faber's theory, according to which the toughening increment due to crack deflection around rod-shaped particles becomes volume fraction independent above 0.2.[14] Besides, this toughness is proportional to the square root of mean grain diameter, as shown in Fig. 7. This observation is consistent with the model proposed by Becher,[15] which describes the crack bridging reinforcement by noncubic matrix grains in composites. Only the aspect ratio could not be correlated with toughness because of the high dispersion of the experimental measures. It is worthy of note that the two-dimensional models used for crack bridging do not take into account the effect of the crack front bowing between grains. It could be interesting to study thoroughly the correlation microstructure/toughness by using a three-dimensional model based on the Green[16] and Bower[17] works.

The strength-determining-defect size a_c can be evaluated from the equation $K_{IC}=Y\sigma_r(a_c)^{1/2}$. For $t_2=3$ h, which leads to the highest toughness (8.1 MPa $m^{1/2}$) and to a strength value of 945 MPa, the critical-defect-size supposed being elliptic ($Y=1.3$) is 43 μm. This value is higher than that of large elongated grains : large grains population (diameter > 1 μm) has a mean diameter of 1.7 μm and a mean aspect ratio R_{95} of 2.0. Providing that the intergranular phase composition remains stable, increasing the sintering time can hence be an interesting way to reach both high strength and high toughness.

Table 3
Toughness values as a function of sintering time

t_2 (min)	10	45	90	180	540
Toughness (MPa $m^{1/2}$)	6.7±0.2	7.6±0.2	7.9±0.3	8.1±0.3	6.9±0.2

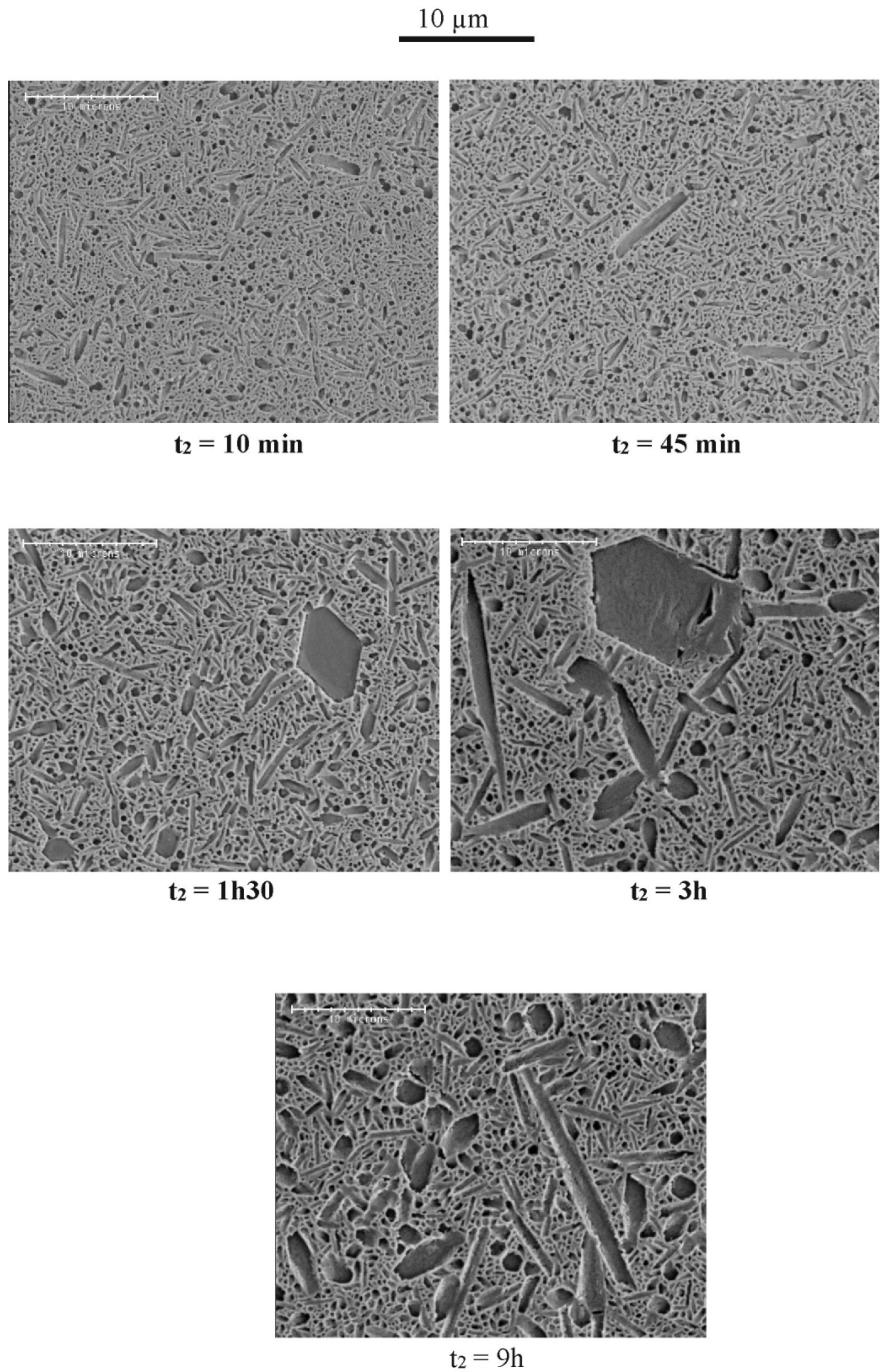


Fig. 6. Microstructure evolution as a function of sintering time (αSNE10, SEM $\times$3500).

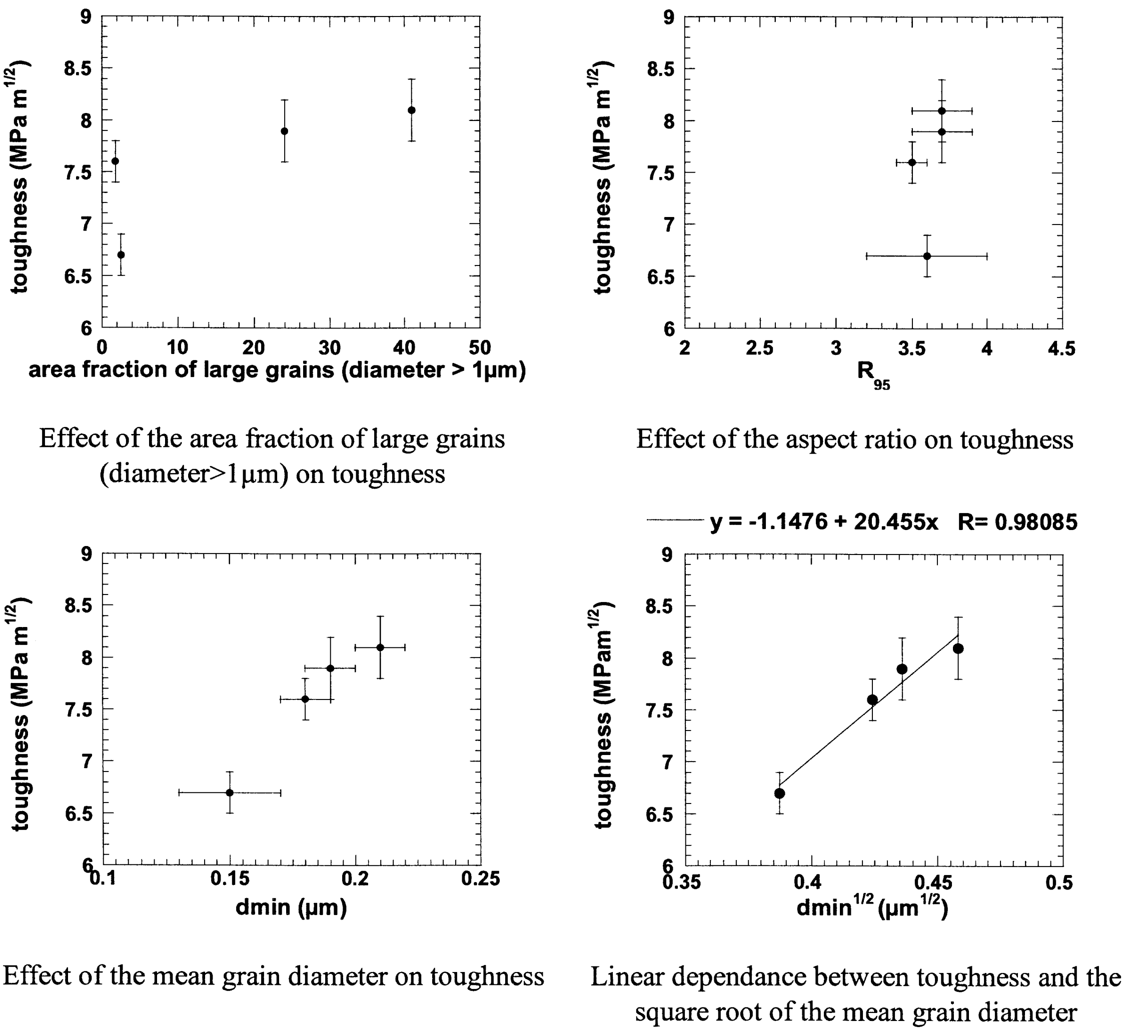


Fig. 7. Correlation between microstructural parameters and toughness.

4. Conclusion

Two ways of microstructural control have been studied in order to improve fracture toughness in silicon nitride : seeding and optimisation of the sintering time.

Seeding with single large β-Si_3N_4 whiskers leads to a low improvement providing that the initial Si_3N_4 powder is free from large pre-existing β nuclei (increase of ~4% for αSNE10 + 2.5% seeds). If not, seeding has a negligible effect on microstructure because of nuclei interaction and an unfavourable effect on densification. In that case, large β seeds addition contributes to decrease toughness (decrease of ~10% for αSNE05 + 10% seeds).

The increase of the sintering time in a case of abnormal nuclei growth leads to an increase of toughness, providing that the composition of the intergranular phase remains constant (increase of ~30% for $\Delta t = 3$ h). Correlation between microstructural parameters and toughness are consistent with the reinforcing mechanisms in composites (crack bridging and crack deviation) : toughness is proportional to the grain diameter square root and increases as the fraction of the large grains increases.

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