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Correlation between fracture toughness and microstructure of seeded silicon nitride ceramics

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Abstract Microstructure development and fracture toughness of Si_3N_4 composites were studied in the presence of seeds and Al_2O_3 + Y_2O_3 as sintering aids. The elongated β-Si_3N_4 seeds were introduced into two different α-Si_3N_4 matrix powders; one was the ultra fine powder matrix and the other was the coarse powder matrix. The amount of seeds varied from 0 to 6 wt%. The grain growth inhibition and the mechanism of toughening were discussed and correlated with microstructure. The maximum fracture toughness of 9.0 MPa $m^{1/2}$ was obtained for ultra fine powder with 5 wt% seeds hot pressed at 1,700 °C for 6 h.

Introduction

Silicon nitride is a promising structural material for room and high-temperature applications because of its excellent mechanical properties. However, a wider application of silicon nitride is still limited by the insufficient fracture toughness compared to that of most metals and alloys. One type of microstructure which is often used to enhance high fracture toughness in Si_3N_4 ceramics is the bimodal microstructure consisting of large, elongated β-Si_3N_4 grains in a matrix of smaller either slightly elongated or equiaxed grains [1]. The presence of seeds in silicon nitride matrix acts as nuclei for preferential materials deposition, resulting in a selective grain growth [2]. The seeds are permitted to grow to a much larger aspect ratio then the rest of the matrix grains thus leading to the creation of the bimodal microstructure [3]. So far, the preferable method of producing the seeds has been the gas pressure sintering [4]. In the present study, a different seeds fabrication technique was employed involving powder bad and pressureless firing instead of pressure. Two different α-Si_3N_4 matrix powders were used to affect the grain size in the sintered composite. In addition, TiN was added to the mix with an objective of imparting higher fracture toughness to the system [5, 6, 7]. It was hoped that, in this way, two different mechanisms of toughening would be operating simultaneously.

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Experimental procedure

In this study, two different α-Si_3N_4 powders were used to fabricate the samples. One powder had an average particle size of 0.3 µm, designated as LC 12-SX (H.C. Starck) and the other powder had an average particle size of 1.0 µm, designated as UBE SN E03 (Ube Industries Ltd., Japan). The SEM of the two powders is presented in Fig. 1.

The initial composition of the compact used to fabricate the seeds was 4.4 wt% Y_2O_3 (H.C. Starck P7/88), 8.3 wt% SiO_2 (Merck) and remaining α-Si_3N_4. The compacts were embedded in the powder bed (50 wt% Si_3N_4 and 50 wt% BN) and heated in a graphite resistance furnace (Astro 606) to 1,850 °C for 6 h in flowing nitrogen. After removing from the furnace, the fired samples were crushed and

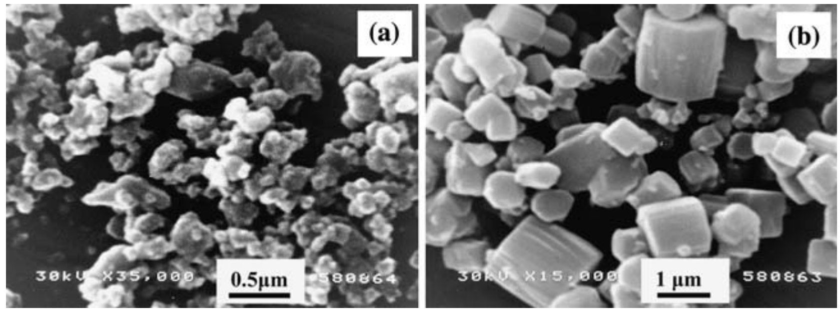

Fig. 1 SEM of the starting powders: (**a**) LC12-SX and (**b**) UBE SN E03

screened through 355-µm sieve to remove finer fractions of the seeds. The screened powder was subjected to an acid treatment to remove the un-reacted oxides components [8].

Examination of the SEM and optical images, it is found that the β-Si_3N_4 seeds have a broad size distribution consisting of elongated grains and equiaxed grains. The size and aspect ratio of the β-seeds were determined by measuring the length and diameter of the grains under transmission and optical microscopes Leika DC 350F (Fig. 2b) to which computer facility for measurement and determination of the seeds size was attached. The average aspect ratio of the seeds was ~3.7 which is close to 4.1, a value shown to be optimal for achieving high fracture toughness [9]. About 40% of large seeds had diameter lower than 1 µm. In the next step, the Si_3N_4 matrix powder with Al_2O_3/Y_2O_3 (70/30 wt%) as sintering additive was prepared. The total amount of additive used in this work was 10 wt%. Homogenization of the α-Si_3N_4 powder and additives was performed in a vibro mill (Fritsch Pulverisette 9) for 2 h using isopropanol as a solvent and alumina as a milling media. Another matrix mixture to which the seeds were added consisted of 36 wt% TiN with remaining being the Si_3N_4, Al_2O_3 and Y_2O_3.

In order to ensure homogeneous distribution of seeds within the matrix powders, the homogenization was performed in an attritor for 6 h with isopropanol as a solvent. The seeds concentration in the mixture was 0–6 wt%. The obtained powders were dried and sieved before hot pressing. Hot pressing was carried out in a graphite resistant furnace (Astro) at 1,700 °C under the pressure of 40 MPa in the flowing nitrogen. Isothermal heating time was varied from 1 to 6 h. Density was measured by Archimedes method. Microstructure development was studied on a polished and etched surfaces using scanning electron microscopy, JSM 5300 (JEOL–Japan). Samples were polished to prepare the surface for indentation fracture toughness measurements. Indentation load was 20 kg. Fracture toughness of the specimens was calculated from Tanaka's equation by measuring the crack length and indentation load [10].

Results and discussion

Silicon nitride seeds in silicon nitride matrix

The relative content of β-Si_3N_4 phase and relative density of the hot-pressed samples are displayed in Fig. 3 and Table 1. Similar results were obtained earlier [5] for TiN containing samples.

Unlike pressureless sintering [11], no reduction in hot-pressed density was observed with the increase of seeds content for all seed contents of up to 6 wt%. The same results were obtained for both fine and coarse powders (Fig. 3 and Table 1). As expected longer hot pressing time lead to a continuous increase in sintered density.

It is well known that Al_2O_3 and Y_2O_3 react with SiO_2 from the surface of the α-Si_3N_4 powder particles to form liquid phase which acts as a vehicle for mass transport. Another role of liquid phase is to facilitate early phase transformation from α-Si_3N_4 to β-Si_3N_4. This transformation is expected to be intensified farther by the presence of

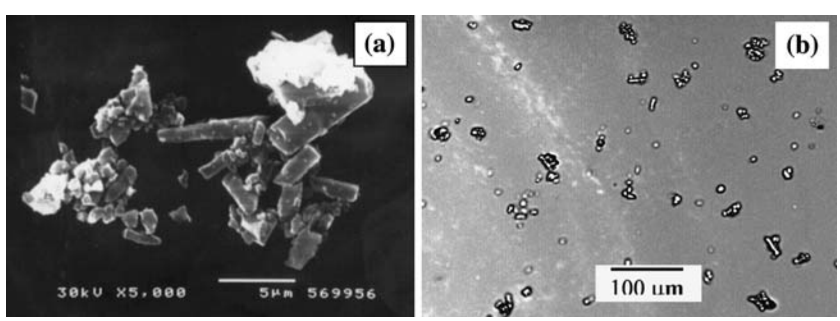

Fig. 2 Seeds images (**a**) SEM micrograph and (**b**) optical micrograph

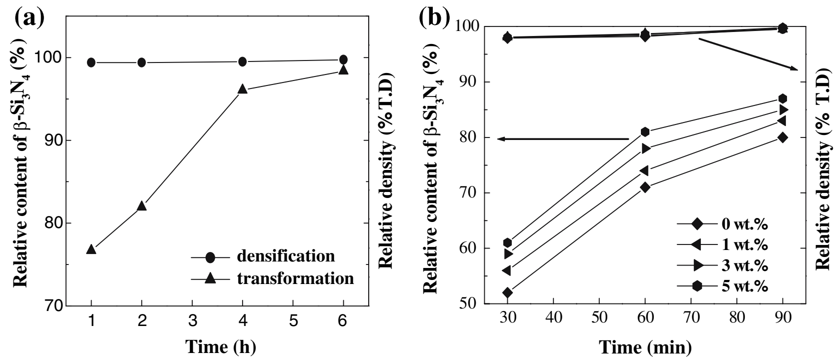

Fig. 3 Densification and the degree of $\alpha \rightarrow \beta$ phase transformation as a function of heating time in samples obtained from ultra fine LC 12-SX powder (**a**) non-seeded, 1,700 °C and (**b**) seeded, 1,500 °C

Table 1 Sintered densities (%TD) of UBE E03 powder vs. seeds content

1,700 °C	Seeds concentration (wt.%)				
Time (h)	0 wt%	1 wt%	3 wt%	5 wt%	6 wt%
1	97.6	97.6	98.2	97.6	98.2
2	98.2	98.4	98.2	98.4	98.8
4	99.1	99.1	99.4	99.7	99.9
6	99.9	99.9	99.9	99.9	99.9

seeds which act as the nucleation sites for the new phase, resulting in the selective grain growth [2]. In order to better understand the role of seeds in transforming the α-Si_3N_4 to β-Si_3N_4, the rate constant (K) and the activation energy (E_a) for transformation were calculated from the Arhenius equation:

$$K = A\ \exp(-E_a/RT) \quad (1)$$

where A is a constant, R the gas constant and T is the absolute temperature. The activation energies (E_a) for different seeds concentrations were determined from the slope of ln K vs. $1/T$, i.e.

$$\ln K = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad (2)$$

The results are summarized in Table 2 for three different temperatures and seeds contents. Inspection of Table 2 shows that the activation energy for transformation for ultra fine powder decreases with increasing seed content while the rate constant increases with increasing seeds content.

Inspection of Fig. 3a and b shows that while densification is practically complete after 1 h of sintering, phase transformation continues even after 6 h of sintering. It follows therefore that the grain growth is the dominant process taking place during the isothermal hold at hot pressing temperature. It is also found that the growth of the larger β-Si_3N_4 seeds proceeded faster than the smaller equiaxed beta grains leading to bimodal grain structure. While the length of the grains increases with seeds content up to 5 wt% seeds, the diameter does not change considerably. The change of seeds size with hot pressing time and seeds content determined by SEM is shown in Fig. 4. For ultra fine powder, the maximum aspect ratio was obtained at 5 wt% seeds. Further increase in seeds content, above 5 wt%, lead to a decrease in both the grain length and the aspect ratio of β-Si_3N_4 grains. During the hot pressing at 1,700 °C for 6 h, the seeds doubled their size compared to initial size.

It can also be inferred from the above data that, in spite of the continuous transformation, no equivalent grain growth was observed with seed contents.

It is interesting to note that, while the mean grain length increases sharply with seed content, there is a very small increase in grain diameter. This behaviour has significant implications in defining the key microstructural feature

Table 2 Values for the rate constant and activation energy for three different seed contents

Temperature (°C)	Phase transformation rate constant (min^{-1}) $\times 10^2$			
	0 wt%	1 wt%	3 wt%	5 wt%
1,500	1.56	1.89	2.13	2.34
1,550	2.78	2.93	3.07	3.21
1,600	5.66	6.09	6.34	6.74
E_a (KJ/mol)	397	378	355	348

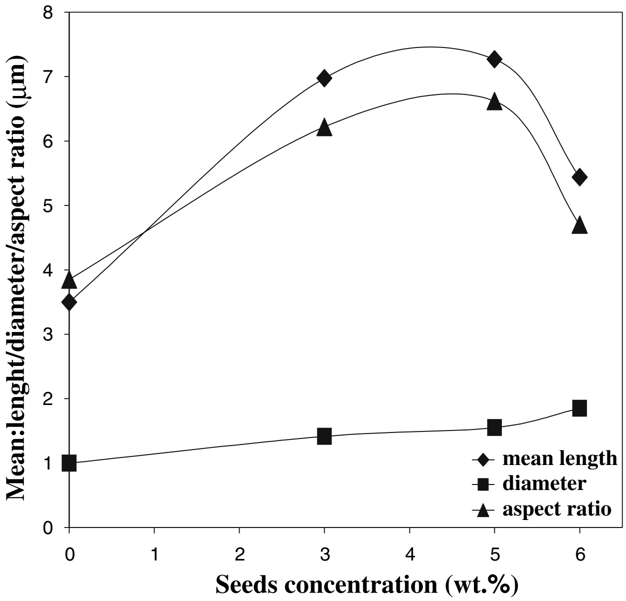

Fig. 4 Mean length, diameter and aspect ratio of the elongated grains vs. seeds concentration after 6 h of hot pressing

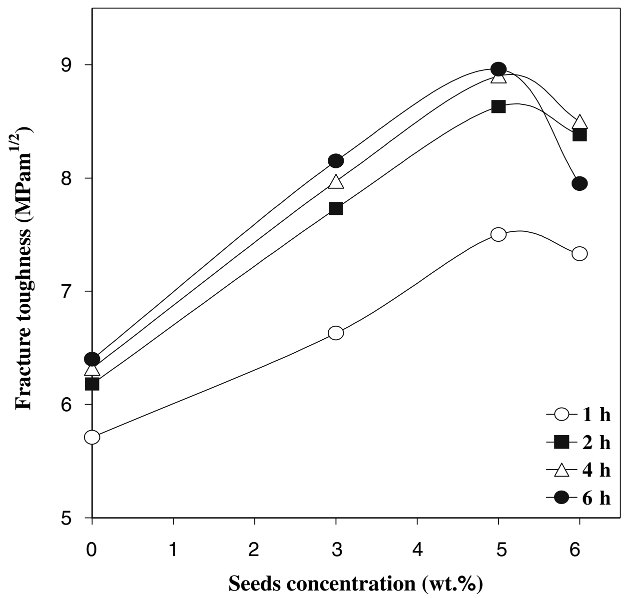

Fig. 5 Effect of β-seeds concentration on fracture toughness for samples hot-pressed at 1,700 °C for different times

which controls toughening in this system. According to one model put forward to explain the effect of microstructure on fracture toughness [12], the most important factor is the grain aspect ratio and it predicts a linear relationship between the fracture toughness and grain aspect ratio:

$$K = K_{\mathrm{m}}(1 - V) + \left\{ \frac{4E\tau Vu}{(1 - v^2)K_{\mathrm{m}}} \right\} \frac{l}{d} \tag{3}$$

where K_{m} is the fracture toughness of the silicon nitride matrix with eqiaxed grains, V the volume fraction of the elongated grains, E the Young's modulus of Si_3N_4, τ the interfacial sliding friction stress, u the pull-out length, v the Poisson's ratio, l the elongated grain length and d is the grain diameter. l/d is defined as the aspect ratio of the grain. Equation 3 displays an upper limit for fracture toughness for it assumes all elongated grains to be positioned parallel to applied stress. Assuming that only one third of the grains is at an angle favourable for de-bonding and pull out (<~30° from the direction of applied stress) and substituting values for E = 320 GPa, τ = 40 MPa, u = 0.6 μm, K_{m} = 5 MPa m$^{1/2}$, V = 1.66 vol% (this assumes that only 1/3 of elongated grains generated by seeds participates in pull-out) in Eq. 3 gives values for fracture toughness of K = 6.6 MPa m$^{1/2}$. However, it should be stressed that this calculation is based on the assumption that only grains generated by seeds participated in toughening and that only grains with aspect ratio of over 2 were assumed to contribute to toughening through. However, beside seeds, there will be a number of other grains with smaller aspect ratio which may participate in pull out and thus in toughening. When it is assumed that a total of 10 vol% grains participate in toughening, the predicted fracture toughness of the system becomes K = 8.76 MPa m$^{1/2}$ much is closer to the measured value for fracture toughness of 9 MPa m$^{1/2}$ (see Fig. 5).

According to the results presented in Fig. 5 and Eq. 3, the fracture toughness is linearly related to both the volume fraction of elongated grains (equivalent to seed concentration) and the elongated grain aspect ratio. For the present system, the optimum seeds concentration is 5 wt% for all hot-pressing times. These maximum values are approximately 30% higher then those measured in equivalent non-seeded samples. Also note that the maximum in fracture toughness coincides with maximum aspect ratio (Fig. 4) which confirms the validity of Eq. 3.

As expected, the addition of seeds to Si_3N_4 matrix lead to an increase in volume fraction of elongated grains and thus to an increase in fracture toughness. At some optimum volume fraction of seeds, the growth of elongated grains will be inhibited mainly by the grain impingement phenomenon thus preventing their growth as observed in Fig. 6d. It is worth noting that, in spite of relatively low seeds concentration, the maximum fracture toughness is relatively high suggesting the existence of a highly effective mechanisms of toughening such as crack deflection and grain bridging known to operate in this system [8]. The measured values for fracture toughness in the present system are higher compared to reported values [9].

As expected, the smaller length of the seeds in coarser-grained UBE E03 powder produced lower values for fracture toughness as compared with those obtained for

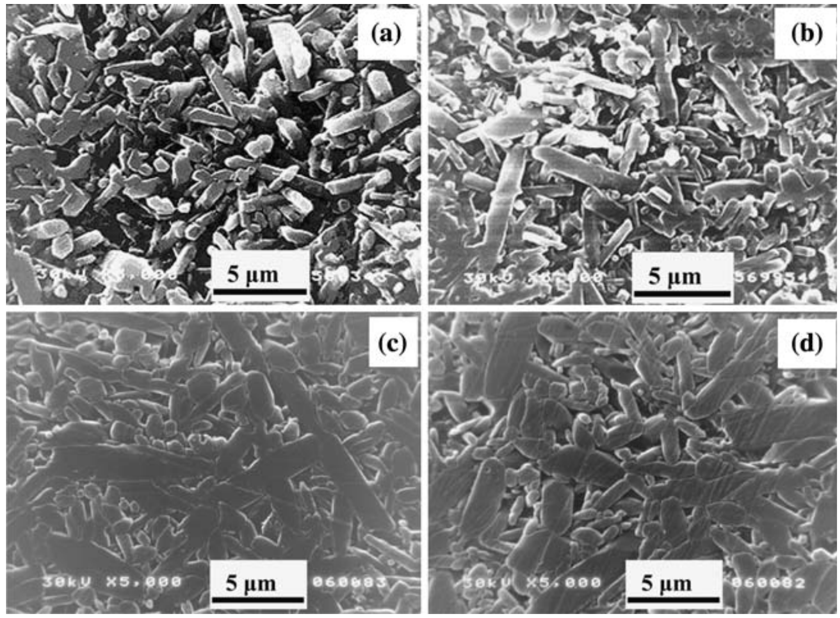

Fig. 6 SEM images of microstructure after 6 h of hot pressing at 1,700 °C for three different β-seeds concentrations: (**a**) 0 wt%, K_{IC} = 6.4 MPa m$^{1/2}$, (**b**) 3 wt%, K_{IC} = 8.1 MPa m$^{1/2}$, (**c**) 5 wt%, K_{IC} = 9.0 MPa m$^{1/2}$ and (d) 6 wt% seeds, K_{IC} = 8.0 MPa m$^{1/2}$

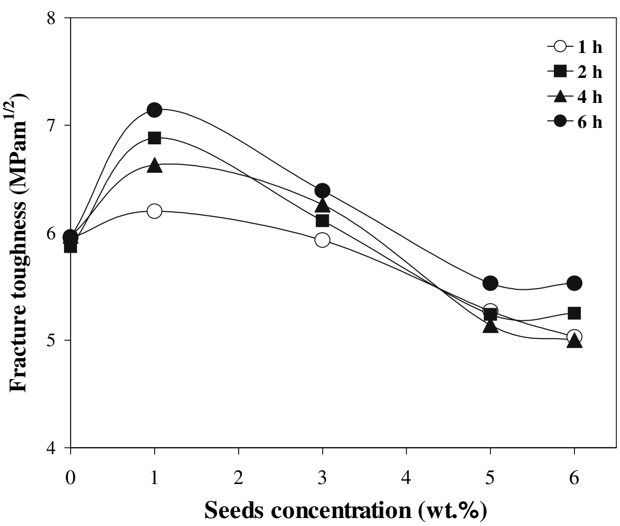

Fig. 7 Fracture toughness dependence on seeds concentration in samples with coarser starting powder UBE SN-E03 sintered at 1,700 °C

ultra fine powder LC 12-SX (Fig. 7). The maximum fracture toughness was achieved at 1 wt% seeds, for the same hot pressing times. Microstructure of these samples is given in Fig. 8. Based on Fig. 8 and the results in Table 3 it is clear that the elongated grains are indeed smaller (Table 3) than in the ultra fine powder LC 12-SX (Fig. 6). Comparison of microstructure in Figs. 6c and 8a, reveals that the fine-grained powders developed mostly elongated grains whereas coarse-grained powder developed rather equiaxed grains. The aspect ratio of the elongated grains in coarse-grained powder does not exceed 5.03, whereas in ultra fine powder it is over 6 (Figs. 4 and 6).

Silicon nitride seeds in silicon nitride–titanium nitride matrix

In order to investigate the effect of TiN particles on fracture toughness and microstructure of Si_3N_4, a series of fracture toughness tests were done with samples containing 36 wt% TiN particles. The 36 wt% TiN addition was selected on the basis that this amount of TiN ensures sufficiently high electrical conductivity of the system to allow EDM machining [5, 6]. Another objective for introducing TiN was to determine its effect on grain growth and

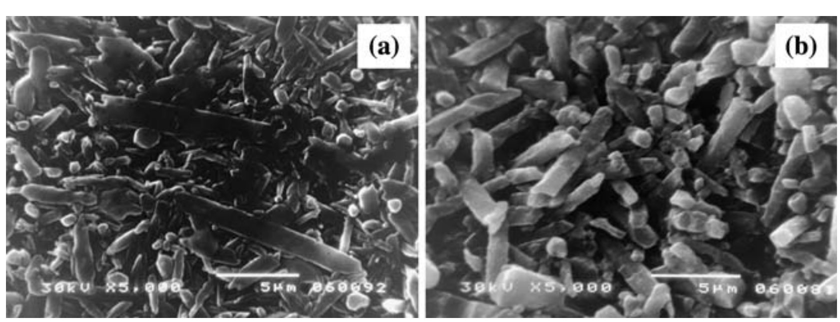

Fig. 8 SEM images of samples with coarse-grained UBE E03 powder sintered at 1,700 °C for 6 h with (**a**) 1% seeds and (**b**) 5% seeds

Table 3 Seeds size in coarse-grained matrix

Time (h)	Seeds concentration (wt.%)	Grain length (μm)	Grain width (μm)	Aspect ratio
1	1	4.9	1.10	4.48
6	1	5.57	1.21	4.58
6	5	5.95	1.25	5.03

microstructure uniformity. In this set of experiments, up to 5 wt% seeds were added. Figure 9 shows the microstructure of the samples without and with 5 wt% seeds (1,700 °C for 6 h). Inhibiting effect of TiN on elongated grain growth is observed in all samples containing TiN. In samples containing no TiN particles the grain length was in access of 20 μm, whereas in samples containing 36% TiN the grain length did not exceed 10–15 μm. The major reason for a significant reduction in grain size appears to be the impinging effect whereby TiN particles serve to block the growth of β-Si_3N_4 grains. Although the addition of TiN particles did increase the fracture toughness of the composite compared to equiaxed grained monolithic Si_3N_4, the highest value achieved was 6.4 MPa $m^{1/2}$ which was far below the value for monolithic Si_3N_4 with elongated grain structure (9 MPa $m^{1/2}$) (Fig. 10).

The results produced in this work indicate that the maximum fracture toughness is attained in samples with 5 wt% seeds which had the highest aspect ratio of elongated grains. Again as with fine grained matrix, the grain width did not play a significant role in controlling the toughness of the system. Under the present experimental conditions, it was found that, although higher amount of seeds generated larger number of elongated grains, it also produced smaller size β-grains due to the large number of nucleation sites and impingement of elongated grains. Smaller size grains are also generated using a courser matrix powder and/or adding grain growth inhibitor like TiN.

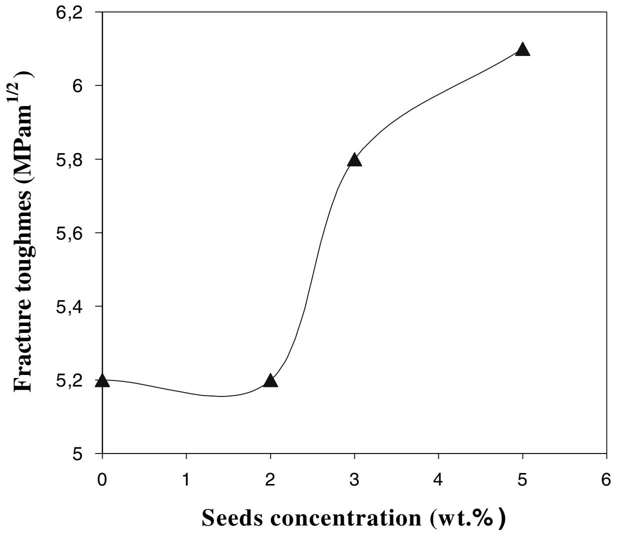

Fig. 10 Fracture toughness vs. seeds content in Si_3N_4–36 wt% TiN matrix

Conclusions

The presence of seeds plays an important role in the development of larger aspect ratio grains and thus in imparting high resistance to fracture in Si_3N_4 ceramics. It has been shown that the grain aspect ratio is the key microstructural feature that contributes to toughening rather than the grain width. The addition of β-Si_3N_4 seeds to silicon nitride matrix enhances the growth of elongated grains in the final microstructure and contributes to the development of silicon nitride with higher resistance to fracture. Fracture toughness value increases with increasing seeds content in ultra fine powder matrix up to optimum amount of 5 wt% of seeds, at which point it reaches a toughness of 9 MPa $m^{1/2}$. With coarse-grained powder, the optimum seed concentration was found to be 1 wt% and the maximum fracture toughness 7.1 MPa $m^{1/2}$. Maximum fracture toughness coincides with maximum aspect ratio of elongated grains. With samples containing no seeds the maximum fracture toughness was 5.7 MPa $m^{1/2}$ and with samples containing 36 wt% TiN the maximum fracture toughness was 6.4 MPa $m^{1/2}$. Regardless of the reason for the inhibition of the growth of elongated grains, the measured values for fracture toughness tend to decrease with a decrease of grain aspect ratio.

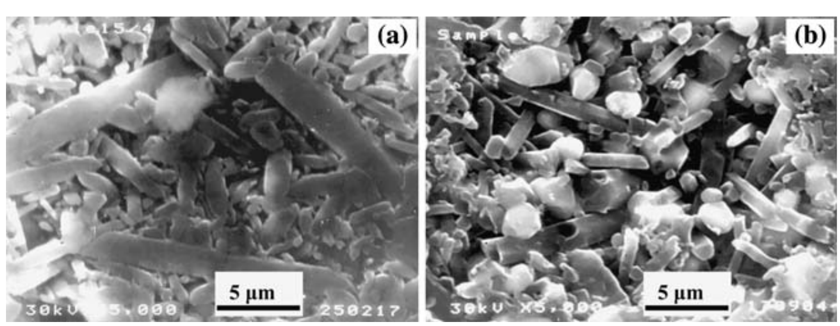

Fig. 9 SEM images of (**a**) Si_3N_4 with 5% seeds and without TiN and (**b**) Si_3N_4 with 36% TiN particles

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