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Effect of β-Si_3N_4 seeds on densification and fracture toughness of silicon nitride

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Abstract

Composite materials based on Si_3N_4 were synthesized by introducing previously prepared β-Si_3N_4 seeds into a mixture of α-Si_3N_4 and 10 wt% of sintering additive. The densification process during pressureless sintering was studied in the presence of CeO_2 additive, which is less frequently used as sintering aid to Si_3N_4. The effect of seed concentration and sintering time on the densification and fracture toughness was followed. The results showed that the addition of seeds retarded densification. On the other hand, fracture toughness passes through maximum at the content of 3 wt% seeds.

Keywords: Pressureless sintering; Microstructure; Fracture toughness; Self reinforced Si_3N_4 with CeO_2 additive

1. Introduction

Due to its importance as structural material, the effect of composition and microstructure on mechanical properties of Si_3N_4 ceramic was widely studied by many authors. The intention to further increase the reliability of Si_3N_4 has shifted the emphasis towards seeding and prolonging sintering time in an attempt to grow further the elongated uniformly distributed grains in a matrix of equiaxed or slightly elongated grains[1–5]. By incorporating a controlled amount of elongated β-Si_3N_4 single crystal particles into the matrix, toughening mechanisms such as crack deflection and/or bridging via interfacial debonding, are activated [3,4]. It is now well accepted that seeding is a useful method of providing an effective way to improve the fracture resistance while retaining high strength, provided that the size, content and distribution of the elongated β-Si_3N_4 single-crystal particles are carefully controlled [5–7].

Sintering additives, which create a liquid-phase at high temperatures, allow mass transport via rearrangement and solution-reprecipitation processes leading finally to phase transformation and full densification of Si_3N_4. The role of liquid phase in the densification and in determining the properties of materials varies depending on its composition, type and concentration [1,2]. Although the presence of seeds was found useful in promoting the growth of elongated grains, their effect on sintering is not well documented and one of the objectives in this work was to examine the role of seeds in the development of microstructure during the pressureless sintering process. For this study, in-house produced seeds were used. Powder-bed technique was adopted instead of gas pressure synthesis technique developed by other authors [8,9]. Instead of yttria, less expensive ceria additive was used as sintering aid [10] bearing also in mind that our previous data [11] indicated that ceria was very good in assisting Si_3N_4 sintering. Special attention was paid to the preparation procedure of starting powder mixtures with seed particles in order to obtain homogeneous distribution of seeds throughout the samples.

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2. Experimental

2.1. Synthesis of β-Si_3N_4 seeds

Silicon nitride in α-form (H.C. Starck LC12-SX) with additive mixture consisting of 4.4 wt% Y_2O_3 (H.C. Starck P7/88) and 8.3 wt% SiO_2 (Merck), was homogenized in vibratory mill for 2 h using isopropyl alcohol as mixing medium. The powder mixture was dried, passed through 40-mesh sieve, and thereafter hydraulically compacted under 50 MPa of uniaxial pressure. It was, afterwards, isostatically compacted under a pressure of 250 MPa. From this mixture, particles of β-Si_3N_4 seeds were grown by heating in a graphite resistance furnace (Astro 606) at 1850 °C for 2 h under flowing nitrogen. Samples were placed in the powder bed (50% BN and 50% Si_3N_4) in a graphite crucible. Sintered samples were crushed (up to about 3–4 mm), and thereafter pulverized. The screened powder was then subjected to four different and successive acid rinse treatments [8]. Measurement of dimensions of seed particles was performed under optical microscope Leica MR D, in polarized light, using appropriate computer programme. The lengths and widths of seed particles were measured on total 60 grains.

2.2. Preparation of mixtures, sintering and toughness measurements

Starting powder mixture containing α-Si_3N_4 (H.C. Starck LC12-SX, α = 95%) with 10 wt%, CeO_2 (Merck) as a sintering additive (Table 1) was used in this study. The β-Si_3N_4 seeds were added to the starting powder in the amount 1, 3 and 5 wt%. For comparison, samples without seeds were also prepared (Table 1).

The powder mixtures of α-Si_3N_4 and ceria, without seeds, were first homogenized in vibratory mill for 2 h. In separate experiments, the rod-like β-Si_3N_4 seeds were ultrasonically dispersed and then added to the mixture of silicon nitride with additive. Further, homogenization was performed in attritor for additional 6 h. Si_3N_4 balls were used as milling media. The slurries of ceramic powder mixtures in isopropyl alcohol were dried and thereafter passed through 40-mesh sieve. Green pellets (ϕ = 10 mm, h = 10 mm) were obtained by hydraulic pre-pressing under the pressure of 50 MPa and by subsequent isostatical compaction under a pressure of 350 MPa. The densities of the green compacts varied in the range 60.0–58.2% TD for samples without and with 5 wt% seeds added to the mixture, respectively. Sintering of green pellets was performed in the graphite resistance furnace. Samples were placed in the powder bed in a graphite crucible and heated to sintering temperature of 1800 °C followed by isothermal heating for 1, 2, 4 and 6 h. The same sintering procedure was applied to samples without the seeds for comparison purposes.

Table 1
Starting composition of silicon nitride mixtures containing seeds with CeO_2 additive

Sample	Additive content CeO_2 (wt%)	Amount of β-Si_3N_4 (wt%)
Y	10.00	Non seeded
3	10.00	1.00
4	10.00	3.00
8	10.00	5.00

2.3. Characteization

Characterization of sintered samples involved X-ray diffraction (XRD, Siemens Instrument of the D-500 type) for phase identification. XRD was performed on the surface of the sintered samples. Bulk densities were measured by the Archimedes method. Theoretical density was calculated from the rule of mixtures. Polished surfaces were indented using a Vickers pyramid indenter. Fracture toughness was determined from 10 Vickers indents under a load of 30 kg using expression [12]. Sintered samples were polished and etched for microstructure and crack propagation studies, using scanning electron microscopy (SEM, JSM-5300, JEOL).

3. Results and discussion

Silicon nitride seeds in beta form are usually obtained by gas pressure sintering procedure at 1800 °C [8] as mentioned before. Composition of our starting powder mixture was adjusted in order to enable preparation of β-Si_3N_4 seeds under flowing nitrogen using powder bed method. After heat treatment, which was described in experimental part of the paper, the obtained products were analyzed. Large elongated rod-like grains shown in Fig. 1a and b were identified as β-Si_3N_4 single-crystal particles with mean diameter of 2.22 μm and mean length of 5.43 μm. The distribution of seeds in terms of their width and length are shown in Fig. 2. The lengths of seeds vary from 2.91 to 11.04 μm, while their width varies from 0.97 to 3.62 μm. It was found that 62% of seed particles are smaller than their mean width value of 2.22 μm, and that 60% of seed particles are shorter than average length value of 5.43 μm.

The effect of seed particle concentration on relative density of specimens sintered for various times is shown in Fig. 3. It should be pointed out that the green densities do not differ to a great extent for sample with different seeds concentration in the range studied. As can be inferred from Fig. 3 full density was achieved in samples denoted as Y (non-seeded), 3 (1 wt% seeds) and 4 (3 wt% seeds) in Table 1 after sintering at 1800 °C for 4 h. This is significantly shorter sintering time than used in other works [7]. The results also show that the particle rearrangement process proceeds smoothly with non-seeded samples, in which particles are equiaxed with the size of less than 0.5 μm which was the starting powder particle size as provided by the supplier. With increasing seeds concentra-

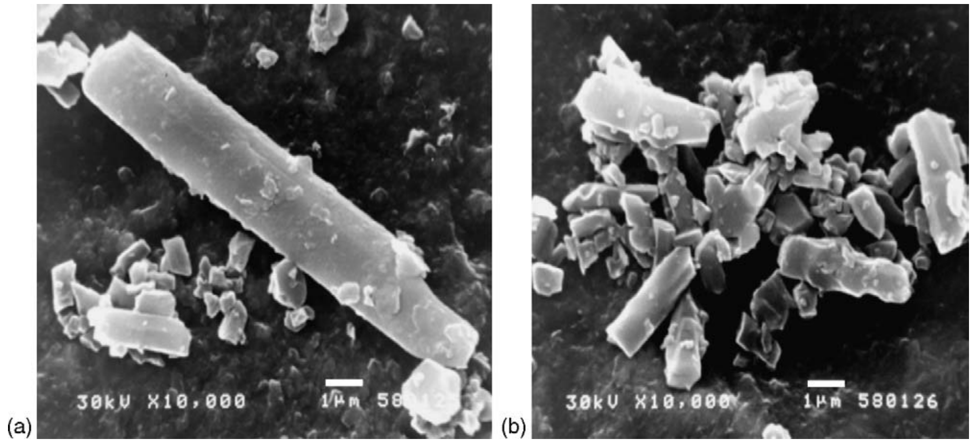

Fig. 1. An SEM microphotograph showing the as-synthesized seeds.

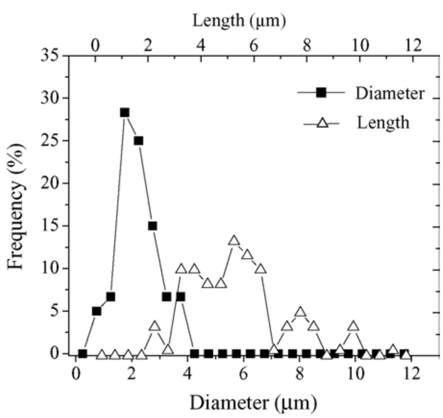

Fig. 2. Distribution of width and length of synthesized rod-like seeds.

tion (0–3 wt%) sintered density decreases for shorter sintering times (up to 4 h) while for longer sintering times (4–6 h) sintered density kept on being constant independent of seeds content within the studied range. Clearly, elongated seeds do not rearrange smoothly during consolidation process due to their geometry and are an obstacle to particles

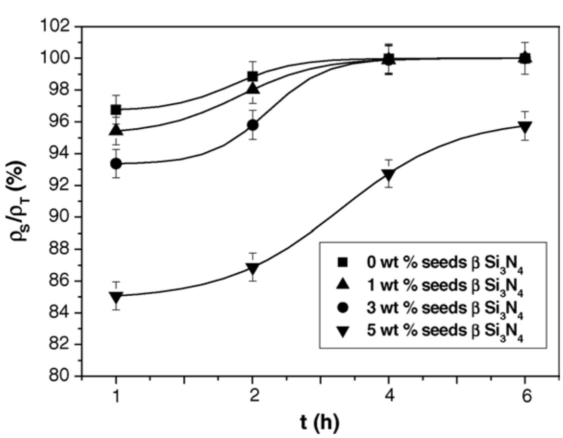

Fig. 3. Effect of sintering time (at 1800 °C) and the amount of seed particles on relative density of silicon nitride.

rearrangement process. That is why samples with increasing seeds concentration (1, 3 and 5 wt% seeds) show density decrease. Densities are lower than for unseeded samples. It can be seen from Fig. 3, that seeding with 5 wt% seed particles, caused considerable density decrease, for all soaking times, in line with reported results by Peillon and Thevenot [13].

XRD analysis of samples shows that the transformation a to β-Si_3N_4, proceeds at much higher rate and is complete after one hour of sintering, even for the samples without seed particles. This suggests that the presence of CeO_2 plays an important positive role in the transformation of α to β phase during sintering of Si_3N_4. All patterns exhibited the peaks of β-Si_3N_4 as the major crystalline phase (Fig. 4) and cerium N-apatite, Ce_5 $(SiO_4)_3N$ as a secondary phase was detected. Taking into account that at temperatures above 1400 °C [1] the SiO_2 from the surface of the Si_3N_4 particles in contact with CeO_2 additive forms the liquid, this phase could be expected. Namely, during cooling from sintering temperature, the liquid phase crystallizes giving secondary crystalline phase (Fig. 4), which was identified as the Ce-N-apatite, $Ce_5(SiO_4)_3N$. However, with prolonged sintering time, the $Ce_5(SiO_4)_3N$ diffraction line intensities increase indicating

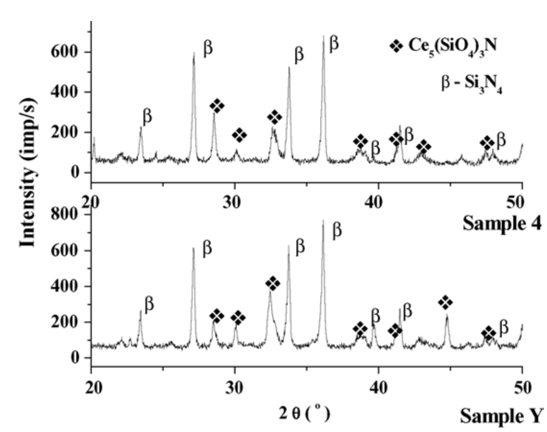

Fig. 4. XRD patterns of samples sintered with CeO_2.

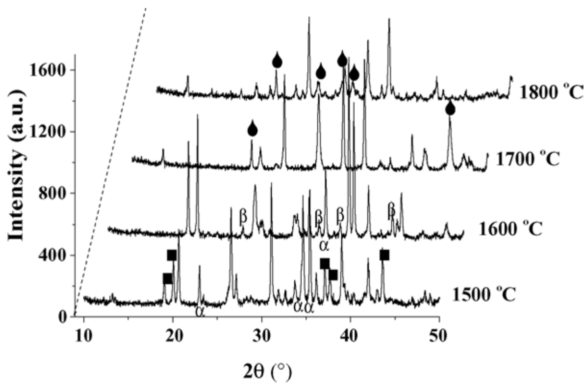

Fig. 5. XRD diffraction patterns of sample with 3 wt% β-Si_3N_4 seeds sintered at 1500–1800 °C, 2 h. (α) α-Si_3N_4, (β) β-Si_3N_4, (■) Si_2ON_2, (♦) $Ce_5(SiO_4)3N$.

that the amount of secondary crystalline phase increases. This result proved that chemical reaction between CeO_2 and Si_3N_4 was taking place during sintering [14], as can be seen from Fig. 5. These experiments were separately performed at lower temperatures in order to prove that Ce-N-apatite was formed, also in the studied system, via intermediate Si_2N_2O that reacted with ceria and silica to give Ce-N-apatite as a reaction product.

Fig. 6 shows the SEM photograph of the polished and chemically etched surface of silicon nitrides sintered at 1800 °C for 4 h with 3 wt% β-Si_3N_4 seed particles. Seeded samples, as expected, exhibit a bimodal microstructure composed of small matrix grains and large rod-like grains approximately 2 mm in diameter and over 10 mm long. The large rod-like grains in Fig. 6 which are fairly uniformly distributed throughout the sample morphologically correspond to the grains developed from the seed particles during sintering. In comparison with non seeded sample, matrix grains in seeded samples seem to be smaller, Fig. 6b. Besides, large rod-like grains in Fig. 6c, seem also to be smaller than in Fig. 6b, which indicates that the amount of seeds (apart from 5% β-Si_3N_4 particles in the starting powder, which is shown by our unpublished data [15]) may affect the bimodal microstructure features.

As the Fig. 7 shows, the addition of seeds to samples sintered for 4 and 6 h leads to an increase in fracture toughness with an increase in seeds concentration of up to 3 wt% and thereafter it decreases. However, an increase in fracture toughness with an increase in sintering time was observed for all samples. It is quite clear from the densification results in Fig. 3 and fracture toughness measurement in Fig. 6 that the addition of seeds had the dominant effect on fracture toughness and causes its increase despite the fact that density remained unchanged. The addition of seeds created conditions for activating grain

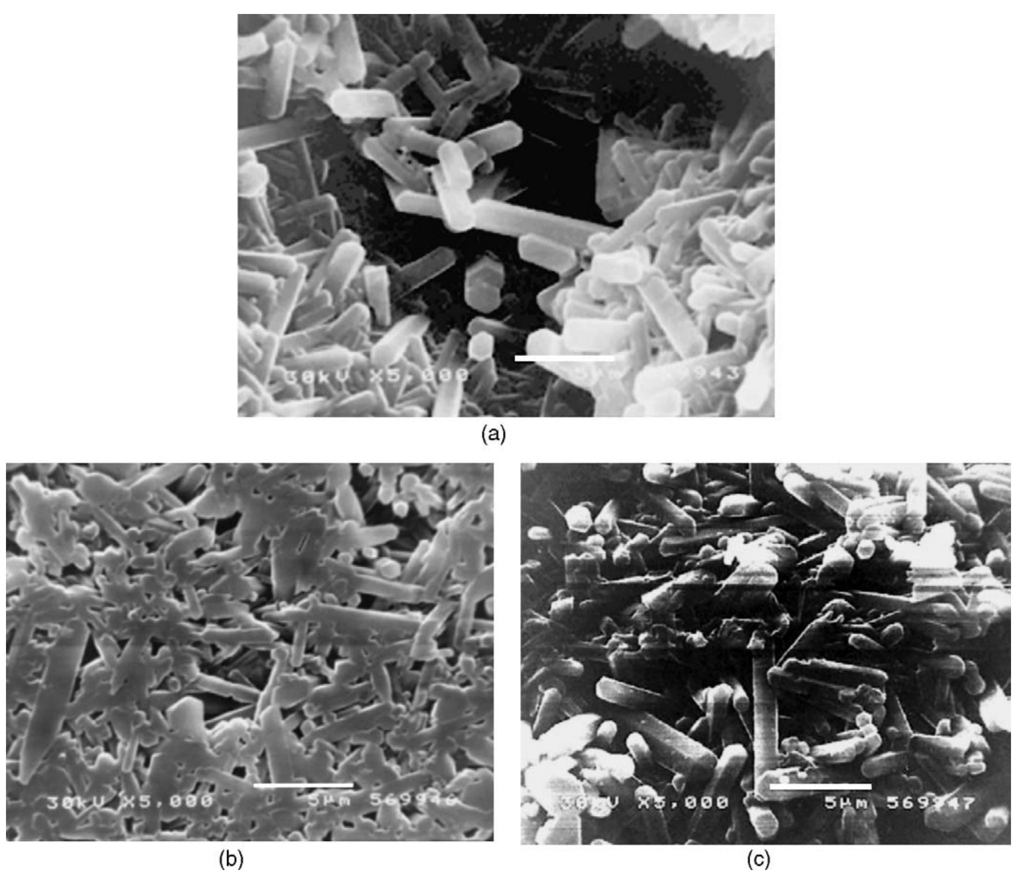

Fig. 6. Microstructure of silicon nitrides: (a) without seed particles, sample Y (Table 1); (b) with 3 wt% seed particles, sample 4 (Table 1), (c) with 5 wt% seed particles, sample 8 (Table 1), sintered at 1800 °C for 4 h.

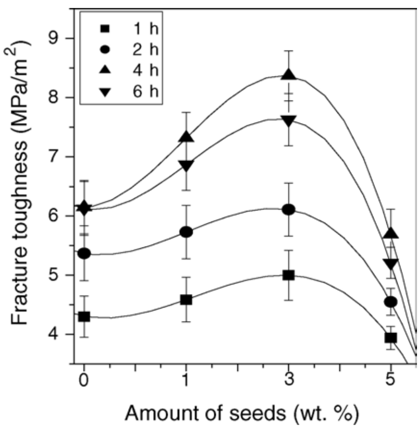

Fig. 7. Effect of sintering time and amount of seed particles on fracture toughness of silicon nitride sintered at 1800 °C with CeO_2.

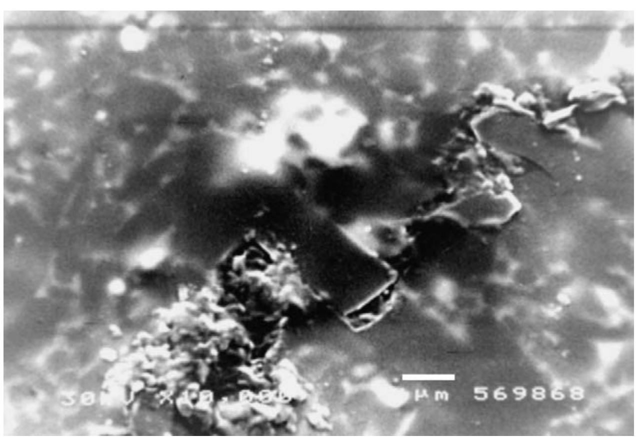

Fig. 8. SEM micrograph of sample with 3 wt% seeds showing the propagating crack.

bridging and pull out mechanisms capable of enhancing fracture toughness [3–8] (Figs. 7 and 8).

The decrease in fracture toughness in samples containing seeds above approximately 3 wt% suggests that the growth of elongated grains may be limited by their concentration. It seems that under the present experimental conditions, there is an optimum amount of seeds beyond which the growth of elongated grains is limited. This reasoning is in line with the kinetics of nucleation of the elongated grains. As the seed concentration (or their number) increases the number of nucleation sites also increases leading to grain growth inhibition.

4. Conclusions

Rod like β-Si_3N_4 seeds were obtained from a mixture of α-Si_3N_4, SiO_2, and Y_2O_3 using the pressureless sintering method developed in house.

The addition of ceria sintering aid at the level of 10 wt% is sufficient to cause the full densification for all samples containing 0–3 wt% of seeds. Only samples with 5 wt% of seeds exhibited densities well below 93.0% TD. As expected, the soaking time at 1800 °C had positive effect on densification in all samples regardless of seed concentration. Due to chemical reaction development between ceria, silica and silicon nitride, the process we are studying is the reactive liquid phase sintering process.

The presence of seeds in the initial mixture had positive effect on the growth of elongated rod-like grains and promoted the crack deflection and crack bridging leading to an increase in fracture toughness. In samples with 3 wt% of seeds, fracture toughness reaches maximum of 8.4 MPa m$^{1/2}$ after sintering for 4 h at 1800 °C. The addition of seeds above 3 wt% was found to decrease the fracture toughness due to mainly the inhibition of growth of elongated grains, which are responsible for toughening in this system. The addition of b-seeds above 5 wt% resulted in the decrease of both fracture toughness and the density.

Microscopic study of crack paths in the self-reinforced Si_3N_4 ceramics reveals that the crack deflection, pull-out and crack bridging are the most frequently observed toughening mechanisms in this system.

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