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Processing and Testing of High Toughness Silicon Nitride Ceramics

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PROCESSING AND TESTING OF HIGH TOUGHNESS SILICON NITRIDE CERAMICS

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Abstract

High toughness silicon nitride ceramics were processed with the addition of small quantities of β-Si_3N_4 whiskers in a commercially available α-Si_3N_4 powder. These whiskers grew preferentially during sintering resulting in large, elongated β-grains, which acted to toughen the matrix by crack deflection and grain pullout. The fracture toughness of these samples seeded with β-Si_3N_4 whiskers ranged from 8.7 to 9.5 MPa$\sqrt{m}$ depending on the sintering additives.

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INTRODUCTION

Silicon nitride ceramics are candidate materials for high temperature structural applications such as advanced automobile and aircraft engines, heat exchangers, etc. However, like all ceramics, they are brittle and flaw intolerant. These limitations have lead to a great deal of interest in toughening silicon nitride ceramics. *In-situ* toughened silicon nitride ceramics, also called self-reinforced silicon nitrides, have received much attention in recent years as they are easier to process than whisker or fiber reinforced silicon nitrides. The mechanical properties of these *in-situ* toughened silicon nitride ceramics are attractive. They are among the toughest of monolithic ceramic materials, and some silicon nitrides retain good mechanical properties to temperatures as high as 1350 °C depending on the composition and amount of the grain boundary phase.

The disadvantage of *in-situ* toughening is that prolonged heat treatments at high temperature are required to promoted β-Si_3N_4 grain growth. These heat treatments are not only expensive, but also lead to decomposition of Si_3N_4 to its constitutive elements, Si and N, resulting in lower density and poor mechanical properties. In this paper, we present a simple, inexpensive technique which facilitates the processing of *in-situ* toughened silicon nitrides in almost any silicon nitride ceramic which is processed by sintering, hot-pressing or HIP'ing with small amounts of the grain boundary phase. Small quantities of β-Si_3N_4 whiskers were used to seed the growth of the large β-Si_3N_4 grains rather than using prolonged heat treatments to obtain grain growth. The fracture toughness of these silicon nitride ceramics will be presented and contrasted with traditional *in-situ* toughened ceramics. These results will be discussed in terms of microstructural evolution during liquid phase sintering.

MATERIAL PROCESSING AND TESTING PROCEDURE

Material Processing

Silicon nitride ceramics of two different compositions with and without β-Si_3N_4 whiskers were prepared. One composition contained 6 wt% Y_2O_3 and 2 wt% SiO_2 as sintering aids, and the other 8.6 wt% Sc_2O_3. They are designated as 6Y and 8Sc, respectively. A commercially available silicon nitride powder[**] was milled in ethanol with the appropriate sintering aids and

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[**]Kemanord Engineering Ceramics, Ljungaverk, Sweden.

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1 wt% stearic acid in a 1 L sintered, reaction-bonded silicon nitride mill. The milling media were hot-pressed silicon nitride cylinders (1 cm long by 1 cm in diameter). The milling time was 300 h. The samples with whiskers are designated as 6Y-W and 8Sc-W. The samples without whiskers were prepared by drying the slurry in an apparatus employing a hot water bath and vacuum to remove the ethanol, followed by drying in an oven at 110 °C. This dried powder contained some soft agglomerates which were crushed using hot-pressed silicon nitride hardware and sieved through a 150-μm screen. The samples with the whiskers were prepared by mixing commercially available β-Si_3N_4 whiskers[***] with the slurry by ultrasonic agitation after milling. This mixture was dried as before. Again, the dried powder was gently crushed but not sieved to prevent segregation of the whiskers and powder. Both types of samples were pressed using standard powder pressing techniques. The powders were uniaxially pressed at 25 MPa to fabricate preform bars (57 by 7.5 by 5 mm). These bars were vacuum sealed in latex tubing and isostatically cold-pressed at 414 MPa. The pressed bars were sintered in groups of 15 in a tungsten resistance furnace for 4 h at 2140 °C and 2.5 MPa nitrogen overpressure. Test bars were machined by grinding along the longitudinal axis of sintered bars with a 400-grit diamond grinding wheel.

Testing Procedure

   Fracture toughness of these ceramics was measured by the single-edge-precrack-beam (SEPB) method.[1] The prospective tensile surface of a flexural beam was indented with a Vicker's indenter under an indentation load of 294 N. The indented sample was loaded in a double anvil type geometry; and at some critical load the indentation crack would pop-in to form a sharp, single edge precrack. A detailed description of this technique is given elsewhere.[2] The precracked samples were loaded in a four-point bend geometry. The fracture toughness values were calculated as:

$$K_{IC} = \frac{3PY(l_o - l_i)\sqrt{\pi a}}{2WD^2} \tag{1}$$

where P is the fracture load, l_o and l_i are the outer and inner spans, respectively (l_o = 18 mm and l_i = 10 mm), D is the sample depth, and W is the sample width, and Y is the geometric factor given by:[3]

[***]UBE-SNWB, UBE Industries Ltd., Ube City, Japan.

$$Y = 1.122 - 1.121\left(\frac{a}{D}\right) + 3.74\left(\frac{a}{D}\right)^2 - 3.873\left(\frac{a}{D}\right)^3 + 19.05\left(\frac{a}{D}\right)^4 - 22.55\left(\frac{a}{D}\right)^5$$

(2)

where a is the crack length. Nine specimens of each composition were tested.

RESULTS

Particle size analysis of the starting Si_3N_4 powder revealed that 90 percent of the powder was under 0.9 μm and 50 percent was under 0.45 μm. The β-Si_3N_4 whiskers ranged from 5 to 60 μm in length and 0.2 to 3 μm in diameter as shown in Fig. 1. For a complete description of the β-Si_3N_4 whiskers the reader is directed to Homeny et al.[4] The whiskers are considerably larger than the starting powder size. Good dispersion of the whiskers in the starting powder was essential. Poor dispersion resulted in clumping of the whiskers which in turn lead to lower density, lower strength and lower fracture toughness. Damage to the whiskers during green processing must be kept to a minimum. Milling or crushing of the whiskers into more equiaxed particles resulted in properties similar to those of the samples without whiskers. The shrinkage during sintering was uniform in width, length and height for samples with and without whiskers. The densities of all four compositions were the same, 3.25 g/cm^3. The presence of inert particles, especially rod-shaped particles similar to the whiskers used in this investigation, hinder densification by applying "drag stresses" to the surrounding material during sintering. By dispersing small quantities of β-Si_3N_4 whiskers, we were able to keep these back stresses low and achieve high densities even in samples with whiskers.

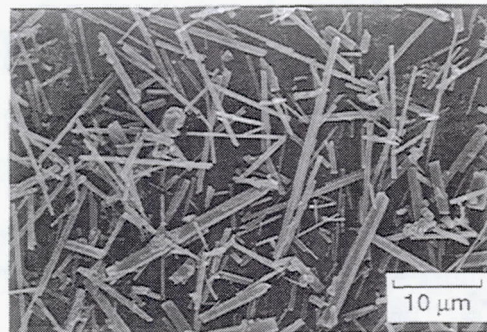**Figure 1** SEM micrograph of β-Si_3N_4 whiskers used to seed the starting powder.

The fracture toughnesses of the silicon nitride ceramics with and without whisker additions obtained by SEPB are given in Fig. 2. The fracture toughness of the $6Y$-Si_3N_4 with whiskers (6Y-W), 8.7 MPa$\sqrt{m}$, was almost double that of the $6Y$-Si_3N_4 without whiskers (6Y), 4.5 MPa$\sqrt{m}$. Similarly, the fracture toughness of the 8Sc-W was higher than that of 8Sc although the increase was not as dramatic as that between the 6Y and 6Y-W silicon nitride.
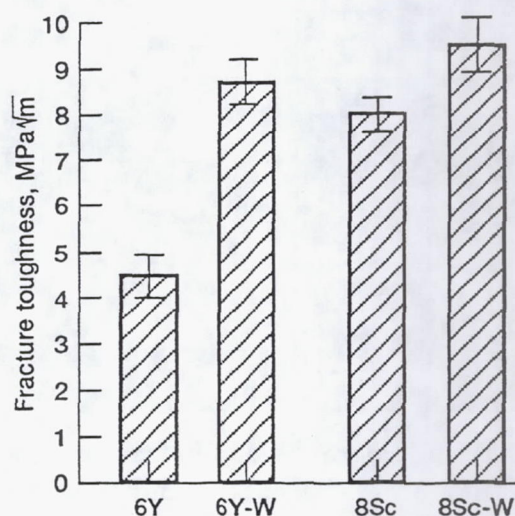

Figure 2 Average fracture toughness of the silicon nitride ceramics tested by SEPB. The error bar represents one standard deviation.

Scanning electron microscope (SEM) analysis of the fracture surfaces (shown in Figs. 3(a) to (d)) revealed two obvious differences between samples with and without whiskers. The samples with whisker additions had a few elongated Si_3N_4 grains which were much larger than the surrounding grains. Samples without whisker additions had a much more uniform grain size distribution. The second difference was that samples with whiskers had a much more tortuous fracture surface with extensive pullout of the large, elongated β-grains.

Crack trajectories of indentation cracks at the indent surface were examined to determine the toughening mechanisms. Figures 4(a) and (d) show that crack deflection and bridging are the toughening mechanisms in both the samples with and without whiskers added. However, more effective crack deflection is achieved by the large, elongated grains in the samples with whiskers as a result of their ability to deflect the crack further away from the original crack plane than that of the smaller grains.
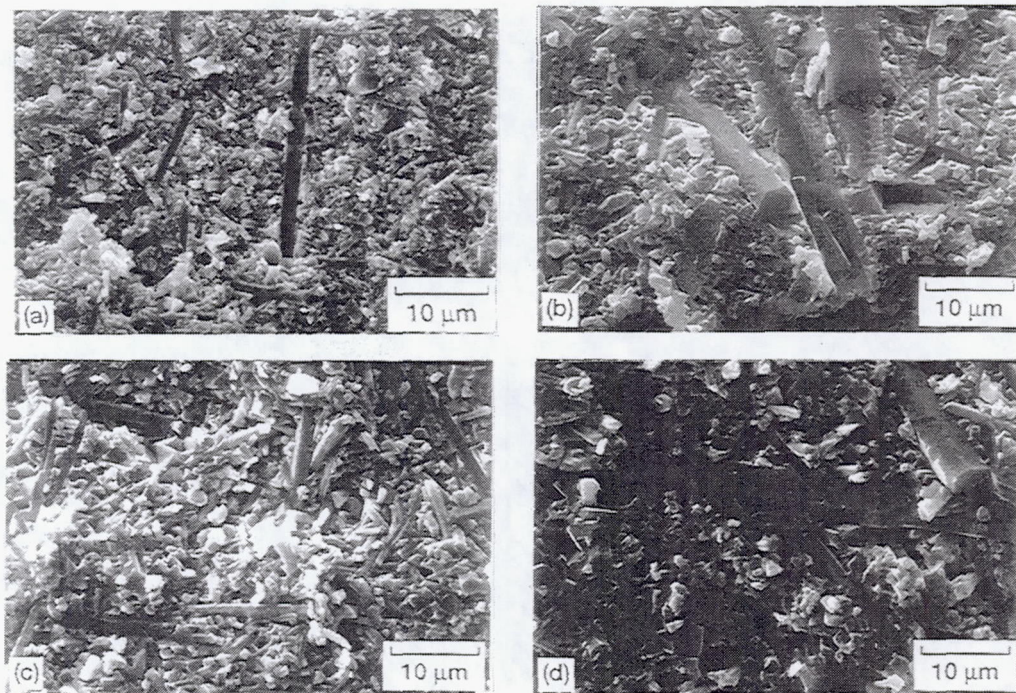
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Figure 3 SEM micrographs of the fractured surfaces of
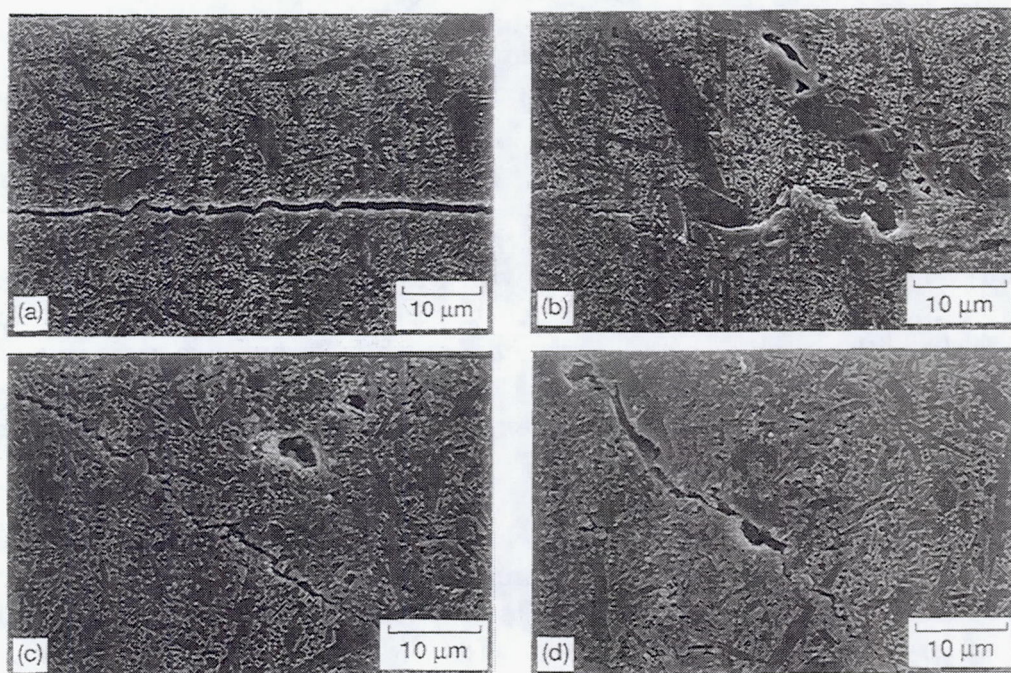a. 6Y, b. 6Y-W, c. 8Sc, and d. 8Sc-W.

Figure 4 SEM micrographs of indentation cracks showing crack
trajectories of a. 6Y, b. 6Y-W, c. 8Sc, and d. 8Sc-W.

DISCUSSION

The fact that large, elongated β-Si$_3$N$_4$ grains were seen only in the samples with whisker additions but not in the samples without whisker additions indicated that the large, elongated grains grew from the β-Si$_3$N$_4$ whiskers. It is now well established that grain growth in silicon nitride occurs by an Ostwald ripening mechanism. Smaller silicon nitride grains dissolve in the liquid silicate phase and reprecipitate onto larger grains leading to grain growth. Initially, the α-Si$_3$N$_4$ grains or particles dissolve and precipitate onto the β-Si$_3$N$_4$ particles which are invariably present in the starting composition. Later, when all the Si$_3$N$_4$ has transformed to the β-phase, Ostwald ripening occurs. In the materials with whiskers added, initially the α-phase and later, the smaller β-grains dissolve and reprecipitate onto the β-whiskers preferentially to give exaggerated grain growth of the whiskers.

Examination of these large, elongated grains from random two-dimensional cross-sections of as-sintered samples and from fracture surfaces revealed that the lengths of the large grains were typically 30 to 60 μm and the diameters 10 to 12 μm. Comparison of the large grain sizes to the whiskers (see Fig. 1) suggests that the whiskers grew much faster in diameter than they did in length. This is in agreement with the finding of Lai and Tien.[5]

It is not clear why the presence of a few large grains increased the fracture toughness of the 6Y-W composition over that of the 6Y composition so dramatically; whereas, only a modest increase in toughness was realized for the 8Sc-W composition over that of the 8Sc composition. Although, the grain sizes of the 6Y and 8Sc were similar, the crack deflection characteristics were very different as shown in Fig. 4. The 8Sc silicon nitride experienced extensive crack deflection; while, 6Y experienced modest crack deflection. Crack deflection was enhanced tremendously by the large, elongated β-Si$_3$N$_4$ grains in 6Y-W. The large β-grains in 8Sc-W increased crack deflection, but extensive crack deflection was already occurring in 8Sc. Thus the increase between 8Sc and 8Sc-W was not dramatic.

An explanation for the difference in fracture toughness of the 6Y and 8Sc materials in spite of their similar grain size may be due to differences in their grain boundary phases. X-ray diffraction analysis of 6Y and 8Sc revealed that the grain boundary phase in 8Sc had devitrified to Sc$_2$Si$_2$O$_7$. In contrast, no crystalline silicate phase was detectable in 6Y. Perhaps crystallization of the grain boundary phase in 8Sc created some residual stresses which enhanced crack deflection in the 8Sc silicon nitride ceramic.

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It has been known for some time that only a few elongated grains are necessary for toughening by crack deflection. Faber and Evans[6] have shown that fracture toughness does not increase significantly with increasing volume fraction of rod-shaped particles above 20 vol%. Li and Yamanis[7] have shown that a few large, elongated Si_3N_4 grains increase toughness by increasing crack deflection. Yet *in-situ* toughening of silicon nitride ceramics has been achieved primarily through coarsening of all the grains. Prolonged heat treatments at temperatures exceeding 1850 °C in N_2 overpressure environments or prolonged heat treatment under HIP'ing conditions with glass-encapsulated samples are primarily the techniques used to achieve grain growth in silicon nitride ceramics. The data given in this paper suggests that seeding the starting powder with a small amounts of well dispersed β-Si_3N_4 whiskers and sintering with conventional techniques yields the desirable microstructure (a few large, highly elongated grains surrounded by smaller grains) and high toughness without the prolonged heat treatments.

We have only used this seeding technique with cold pressed compacts that were sintered in a N_2 overpressure furnace. However, it should also work with any silicon nitride which relies on the presence of a liquid phase for densification and grain growth. Silicon nitride ceramics made by colloidal techniques, injections molding, cold compaction, etc. can be easily modified to used seeded compositions. These can then be hot pressed, HIP'ed with glass-encapsulation or other encapsulation methods or sintered in N_2 overpressure atmospheres at temperatures where liquid phase sintering occurs.

CONCLUSIONS

High toughness silicon nitride ceramics can be processed by seeding the starting powder with small quantities of β-Si_3N_4 whiskers. The β-whiskers grow faster than the surrounding grains to give a microstructure consisting of a few large, highly elongated grains surrounded by much smaller elongated grains. The large grains enhanced crack deflection, grain pullout and crack bridging leading to higher toughness. Future work will determine if the strength and creep properties of these materials are compromised via the seeding approach.

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