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Microstructure Designing of Silicon Nitride

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Abstract

A new concept of materials design that allows simultaneous control of the morphologies and distribution of the structural elements at plural scale levels to create a new family of advanced ceramics was proposed. The validity of the concept was experimentally demonstrated using silicon nitride ceramics as model materials. Controlling anisotropic grain growth by seeding of small amounts of morphologically regulated, β-silicon nitride single crystals (micro-scale level control), combined with alignment of the seed particles by tape casting followed by stacking of laminates (macro-scale level control) allows compatibility of high strength and high fracture toughness in this material, with a high degree of reliability for the mechanical strength. © 1997 Elsevier Science Limited.

1 Introduction

As the properties of a material are closely related to the type and structure of its constitutive elements, the realization of a material with certain property can be achieved through the control of the composition, structure, and microstructure of this material. Ceramic materials consist of many kinds of microstructural elements whose different morphologies in terms of size, shape, configuration, distribution, orientation and arrangement determine the material microstructure. These microstructural elements can be classified by size into four scale levels: (1) atomic-molecular scale; (2) nano-scale; (3) micro-scale, and (4) macro-scale (Fig. 1). Accordingly, microstructure control should be interpreted as control of microstructural elements at single or multiple scale levels in terms of these morphological factors. A notable feature of microstructural control at mono-scale level, as currently applied to conventional ceramics, is that while it would grant a marked improvement of a specific property, a simultaneous improvement of other properties is difficult to achieve. Since microstructural elements extend over more than one scale level, the harmonic enhancement of many properties cannot be realized using mono-scale level microstructure control. It is necessary to exert simultaneous microstructural control at plural scale levels.

2 Microstructure Designing Concept

By introducing the new microstructure designing concept of 'hyper-organized microstructure control,' that is simultaneous control of morphologies and distribution of microstructural elements at plural scale levels, diverse properties will be made compatible inside a material. Properties and functions realized through hyperorganized microstructure control will be explained using a simplified model as presented in Fig. 2. Strengthening, for example, requires a fine grained, homogeneous microstructure whereas toughening can require a coarse grained anisotropic microstructure.[1,2] Current microstructure control methods, operating at a single particular scale level have been unable to make these two properties compatible in one material. However, control technology for intragranular dispersion of nano-particles to produce nano composites [Fig. 2, Model (b)] has been recently developed,[3,4] and research on control technology for the orientation of anisotropic grains [see Fig. 2, Model (a)] is now in progress. The development of these technologies of simultaneous microstructure control exemplifies the possibility of obtaining highly strengthened and toughened materials through hyper-organized microstructure control technology [Fig. 2, Model (d)]. Moreover, such technology will also make other properties compatible. Magnetism, for example will be manifested through structural control at the atomic–molecular level as seen in Model (c). Conventional techniques based on the dispersion of magnetic particles with the same or a larger size than the

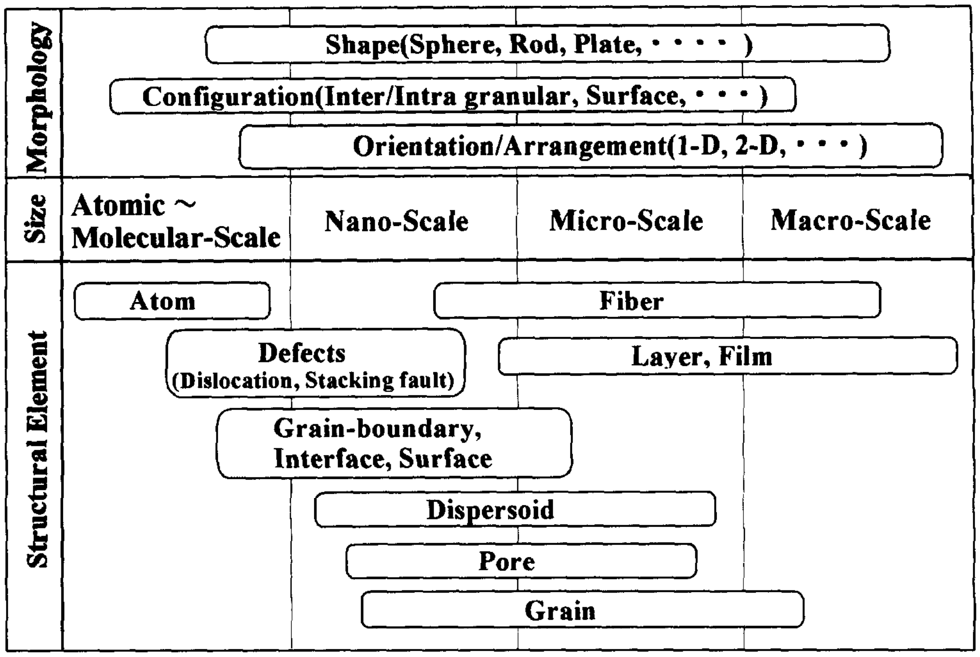


Fig. 1. Classification of the material structures.

matrix grains degrade significantly the strength of the materials because of the introduction of large defects. However, by using microstructure control technology for distribution of nano particles [Model (b)], a structure as represented by Model (d) will be created. Such technology will not only impart magnetic properties to the material without decreasing its strength but, in some cases, a synergistic effect may be expected, with the strength of the material enhanced as a consequence of the presence of the nano sized magnetic particles.

3 Strengthening and Toughening Strategy for Monolithic Silicon Nitride: A Case Study

During the past decade, technologies for microstructure design and control have been extensively developed to achieve either high strength or high toughness in silicon nitride, but these properties have seldom been made compatible.[5–7] As it is conventionally accepted, a homogeneous and fine grained microstructure yields materials with high strength but with low values of fracture toughness,[8] while materials with a coarse anisotropic microstructure may exhibit high toughness but their flexural strengths are negatively affected due to the introduction of large defects.[9] In an attempt to overcome this limitation in microstructure design, the concept of hyperorganized microstructure control has been applied to silicon nitride-based ceramics to explore the possibility of achieving compatibility of these two mechanical properties in materials.

3.1 Microstructural control

As discussed above, nature and distribution of the structural elements, and the microstructure of the grains, determine the mechanical properties of a given material. In the case of silicon nitride, the characteristics of certain structural elements such as crystal structure and grain boundary phases are largely fixed by the chemical composition of the material. In the present work, we have concentrated our efforts on the control of structural elements related to grain morphology, such as grain size, shape, and orientation. Control of grain size and shape was attempted through seeding techniques, whereas control of grain orientation was carried out through the utilization of the tape casting manufacturing process. In both cases, powders of α-Si_3N_4 with 5 wt% of Y_2O_3, 2 wt% Al_2O_3 and a dispersing agent were planetary milled to form a slurry to which β-Si_3N_4 seed particles were added. The β-Si_3N_4 seed particles were grown by heating a powder mixture of α-Si_3N_4, 5 mol% Y_2O_3 and 10 mol% S_iO_2 in a silicon nitride crucible at 1850°C for 2 h under a nitrogen pressure of 0.5 MPa. The product, a partially sintered porous powder, could be easily screened through a 100-mesh sieve. The screened powders were treated with acid rinse to remove the residual glassy phase. Details of the preparation procedure and the characteristics of synthesized particles are reported elsewhere.[10]

Figure 3 shows a schematic representation of the process developed to control morphology and distribution of elongated grains in self-reinforced silicon nitride. When the size of β-Si_3N_4 particles is

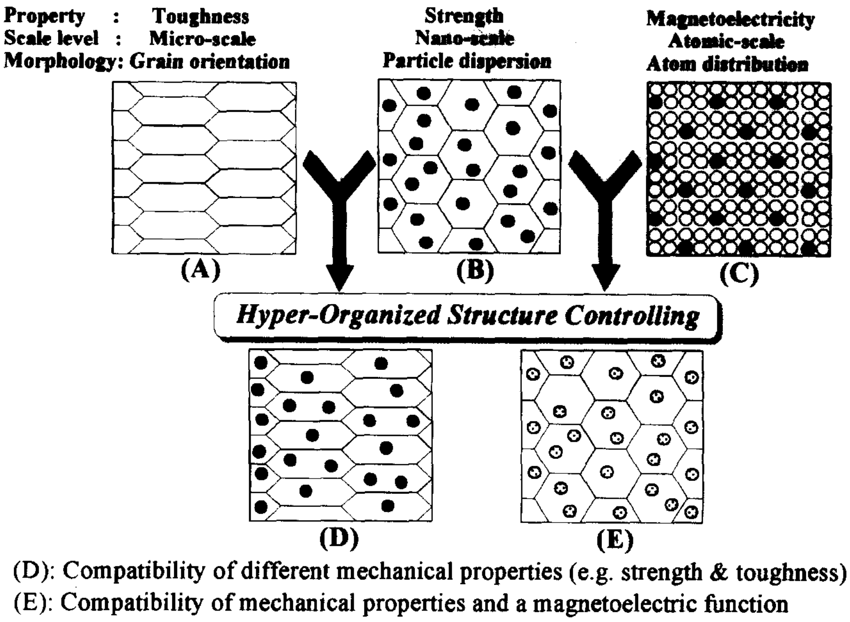


Fig. 2. Conceptual diagram of hyperorganized microstructure control.

larger than that of the raw powders, they act as seeds for the development of large elongated, β-Si_3N_4 grains, and the final microstructure is determined by the number and size of such β-Si_3N_4 particles. From the point of view of nucleation and growth, individual seed particles should consist of single crystals with crystalline facets that allow the effective growth of β-Si_3N_4.[11] Furthermore, these seed particles should have a large diameter and a relatively short length in order to develop a self-reinforced microstructure without hindering the densification process.[12] Therefore, in order to improve the fracture toughness without inducing strength degradation, controlling the development of elongated grains within the silicon nitride matrix becomes crucial. According to this guideline, we have developed an original process to control the microstructure of self-reinforced silicon nitride. The key point of this process is that size and distribution of elongated grains are controlled by seeding of small amounts of morphologically regulated, β-Si_3N_4 single crystals, shown in the scanning electron micrograph and in detail in the high resolution micrograph of Fig. 4. These β-Si_3N_4 single-crystal particles have a mean diameter of 0·96 and a mean length of 3·84 μm, that is an aspect ratio of 4. The effect of the amount of seed particles on the relative density of specimens sintered at 1850°C under 0·9 MPa nitrogen pressure for various times is shown in Fig. 5. For short sintering times, specimens with 5 vol% seed particles had slightly lower densities than those with 0 and 2 vol% seed particles, but all specimens could be sintered to a relative density of 99% after sintering

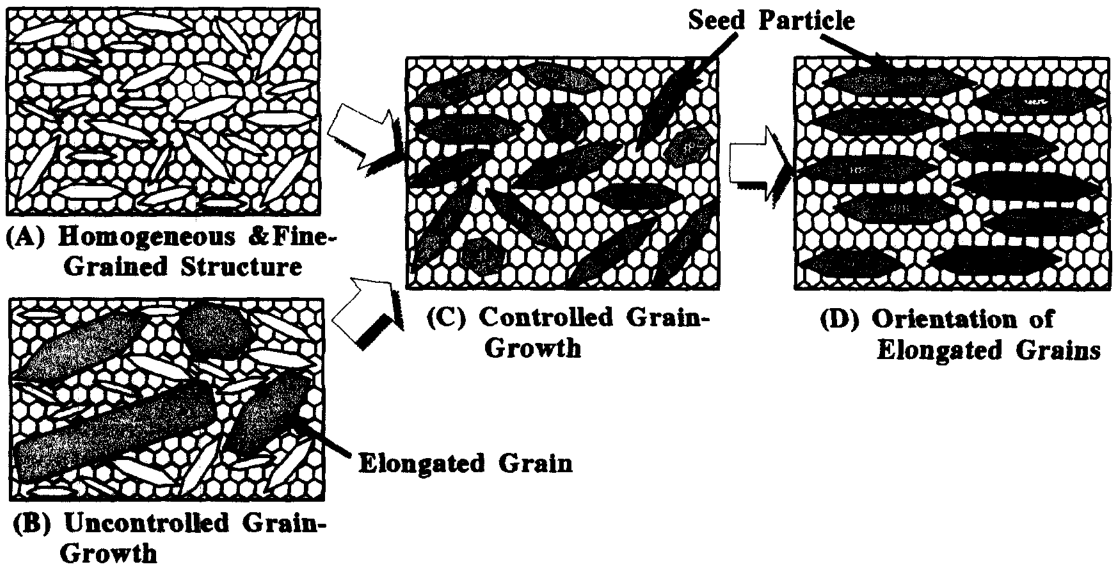
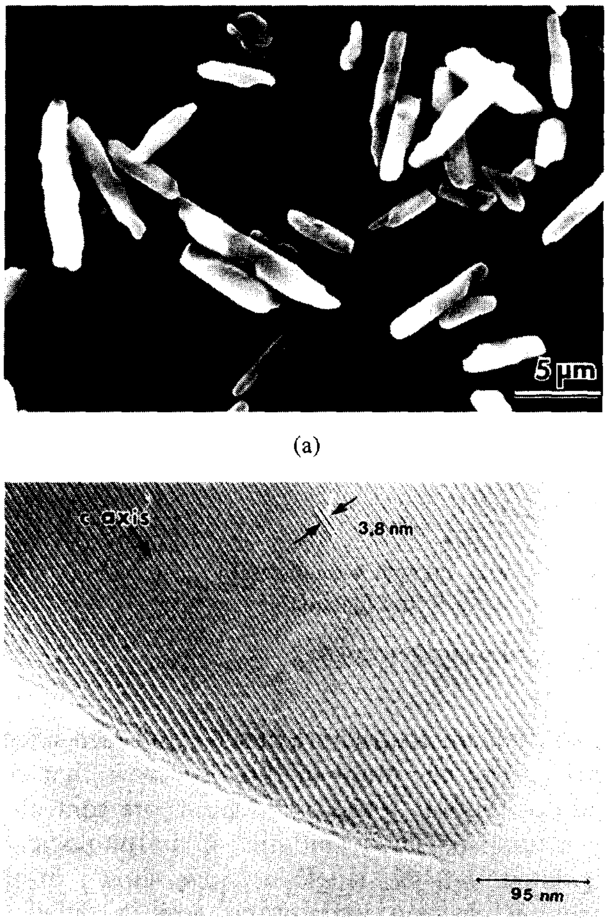


Fig. 3. Schematic representation of microstructure control.



(a)

(b)

Fig. 4. (a) Scanning electron micrograph of synthesized rod-like β-Si_3N_4. (b) Transmission electron micrograph of the synthesized rodlike β-Si_3N_4.

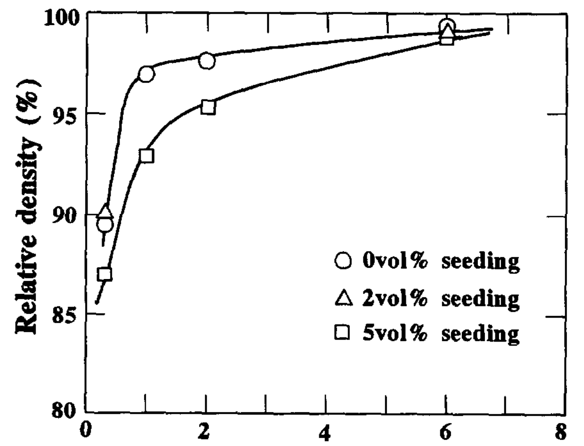


Fig. 5. Effect of the amount of particles on the relative density of specimens.

for 6 h, and a silicon nitride with a well-tailored bimodal structure composed of small matrix grains and of large rod-like grains 1–2 μm diameter and 5–10 μm long was successfully obtained. The approximate surface area of the grains can be calculated as product of the diameter and the length, assuming a rectangular shape (Fig. 6). Curves of

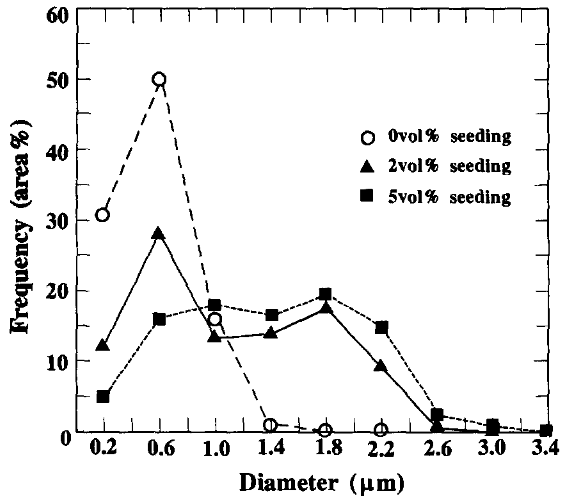


Fig. 6. Grain size distribution of silicon nitride with 0, 2, and 5 vol% seed particles sintered at 1850°C for 6 h.

surface area fraction versus diameter[11] for specimens with seeding show a dual modality in the distribution, reaching maximum values of around 0·5 and 2 μm. An important feature of the curves for specimens with seeding is that the peak diameters for larger grain groups are independent of the amount of seed particles and larger than that of seed particles. It is also important to notice that peak diameters for smaller grain groups are also independent of the amount of seed particles. These results suggest that large elongated grains grow from seed particles and smaller grains from β-Si_3N_4 present in the starting Si_3N_4 powder. As expected, the fraction of large grains increases with an increase in the amount of seed particles.

Figure 7 shows a SEM photograph of silicon nitride with 2 vol% seed particles. The large rod-like grains, morphologically corresponding to the grains developed from seed particles, exhibit a core/rim structure (indicated by arrows). This photograph constitutes direct evidence of grain growth from seed particles. When the proper size and amount of the seed crystal were selected, a high strength and high fracture toughness material was obtained (Fig. 8). Specimens without seeds have a high flexural strength of 1 GPa and a relatively low fracture toughness of 6·3 MPa $m^{1/2}$. By adding seed particles, the fracture toughness was increased to 8·5 MPa $m^{1/2}$.

3.2 Orientation controlling

Since the elongated grains in the final structure of silicon nitride were randomly oriented, further improvement of the mechanical properties could be expected by alignment of these large elongated β-Si_3N_4 grains perpendicular to the direction of crack propagation, as schematically shown in Fig. 3(d). This microstructure, where elongated

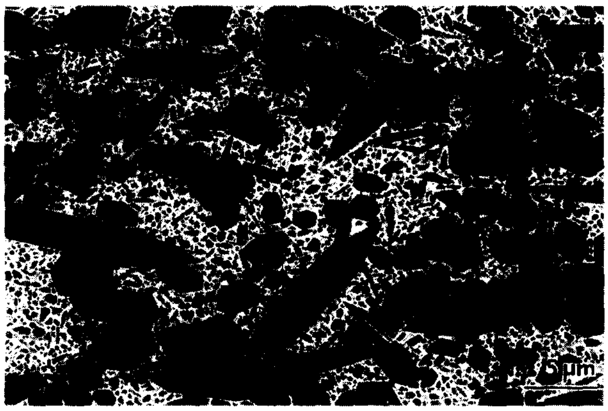


Fig. 7. Scanning electron micrograph of Si_3N_4 with 2% vol seed particles.

grains are unidirectionally oriented (macro-scale level control), could be obtained through sintering of stacked tapes from raw powders seeded with rod-like, β-Si_3N_4 particles prepared according to the process described above. Green sheets 100 mm width were produced by laboratory-scale doctor-blade equipment, with the thickness of the sheets adjusted in a range from 130 to 150 μm by controlling the blade height and casting rate.[13] The green sheets were subsequently punched into rectangular shape (50 x 50 mm) and stacked at 130°C under a pressure of 70 MPa aligned in the casting direction. The stacked sheets were then calcined at 600°C under a flow of N_2–5% H_2 gas mixture, followed by calcination at 400°C under dry air flow. Sintering was performed at 1850°C for 6 h under a nitrogen pressure of 1 MPa with heating and cooling rates of 10°C min^{-1}. Microstructure of the sintered specimens was observed by scanning electron microscopic examination of polished and plasma-etched surfaces. Test pieces for mechanical property measurements were sliced parallel and perpendicular to the casting direction. Four-point bending strength measurements were carried out at room temperature and fracture toughness was determined by the single-edge-precracked-beam (SEPB) method, also at room temperature.

Figure 9 shows SEM photographs of a seeded and tape-cast specimen parallel (a), and perpendicular (b) to the casting plane. Large elongated grains appearing in the polished surface perpendicular to the casting plane [Fig. 9(b)] are aligned parallel to the casting plane, and those appearing in the polished surface parallel to the casting plane [Fig. 9(a)] exhibited a rather random orientation, although always lying within the casting plane.

In contrast with microstructures with randomly distributed elongated grains in the matrix, anisotropy in the microstructure correspondingly imparts to silicon nitride an anisotropic mechanical behavior. Figures 10 and 11 present the results from mechanical tests of sintered specimens with diverse amounts of seed. As mentioned above, these tests were carried out on specimens sliced in the direction orthogonal (O), and parallel (P) to the casting direction. In both figures a broken line representing the respective values for a specimen with the grains randomly orientated (cold pressed

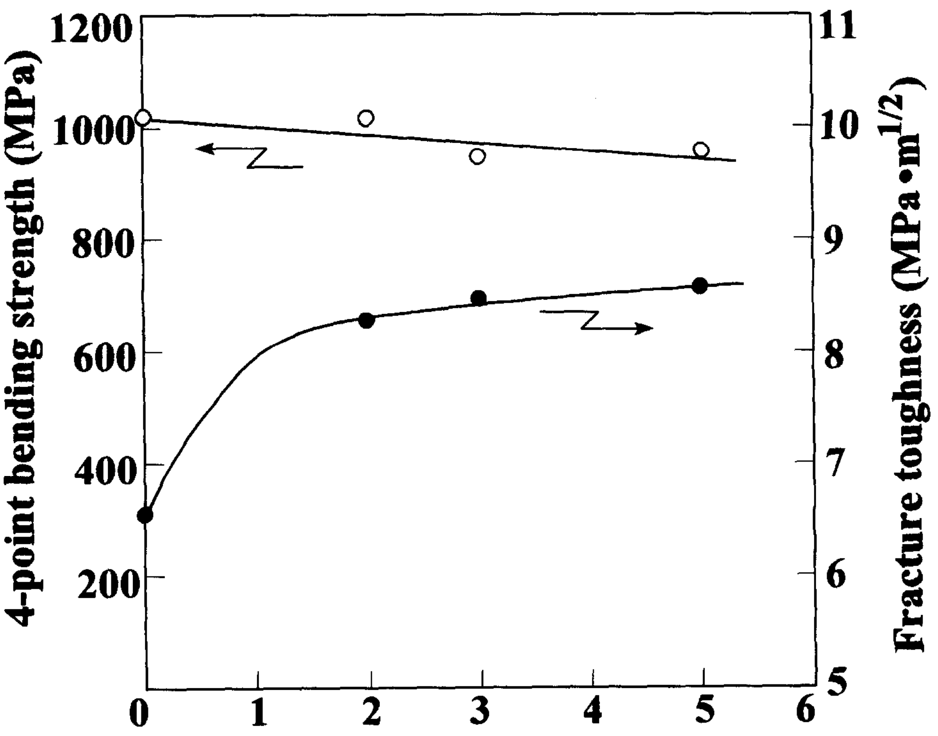


Fig. 8. Mechanical properties of silicon nitride sintered at 1850°C for 6 h as a function of amount of seed particles.

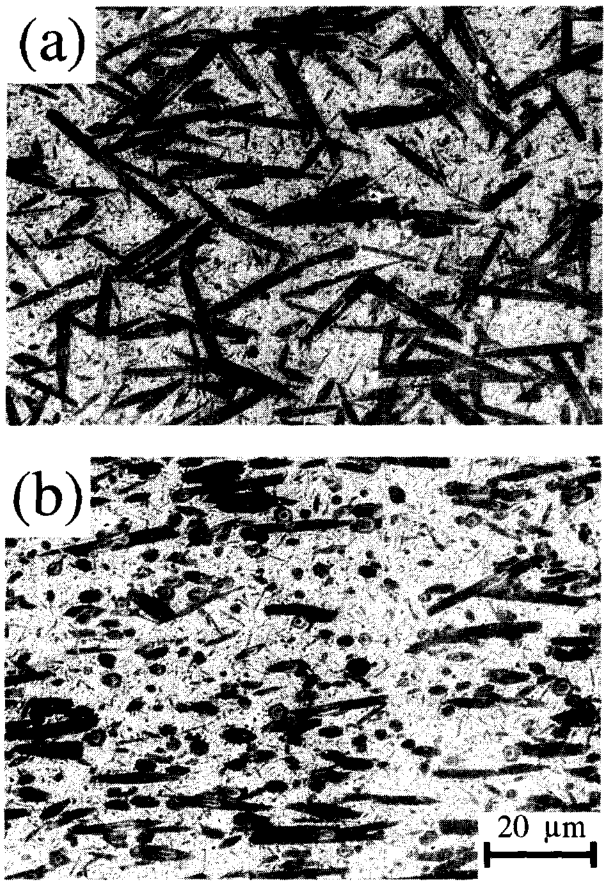


Fig. 9. Scanning electron micrograph of polished and plasma etched surface of a seeded and tape-cast specimen, (a) parallel and (b) orthogonal to the casting plane.

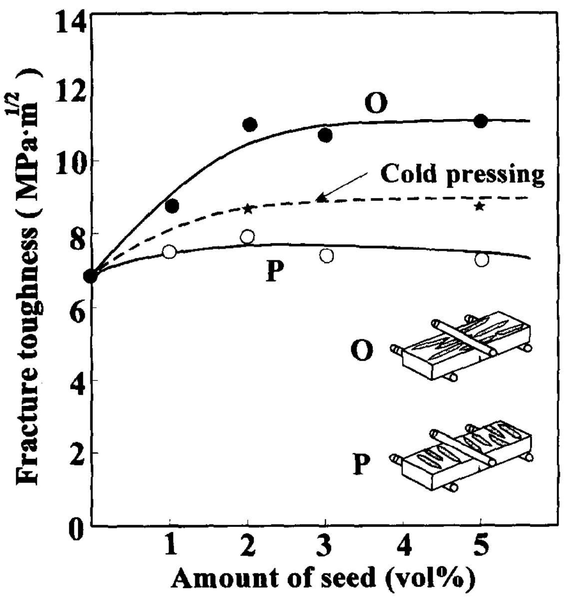


Fig. 10. Effect of seed amount on fracture toughness (SEPB method) of tape-cast silicon nitride.

specimen), is shown for comparison. From this figure it is clear that bending strength as well as fracture toughness are affected by the orientation of the elongated grains. Specimens cut in the direction orthogonal to the casting direction have better mechanical properties than the ones cut in

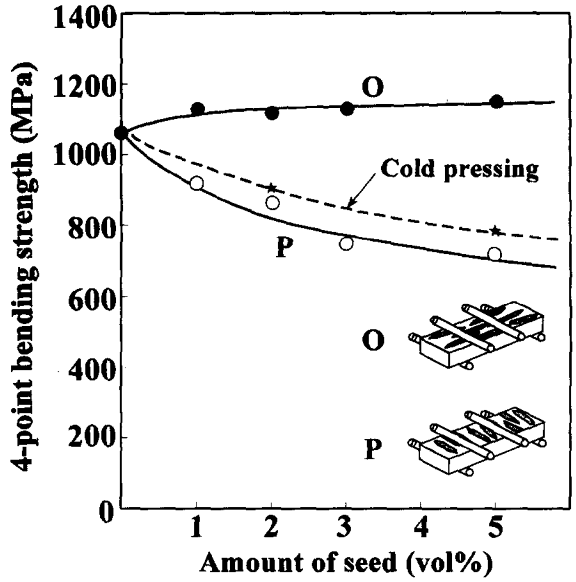


Fig. 11. Effect of seed amount on bending strength of tape-cast silicon nitride.

the parallel direction and than the cold pressed specimens. The toughening effect of elongated grains is enhanced when they are aligned parallel to the casting direction as the inherent flaw orthogonal to the casting direction is limited to the maximum diameter of these grains. On the other hand, an increment in the orientation degree of the elongated grains with respect to the crack plane increases their effectiveness against crack propagation. Finally, the alignment of elongated grains results in a more homogeneous flaw size distribution in the material which translates into a high reliability of the mechanical strength indicated by a Weibull modulus of 46 (Fig. 12).

Anisotropy in the microstructure not only resulted in dramatic improvement of mechanical properties, but also allows exploitation of other intrinsic

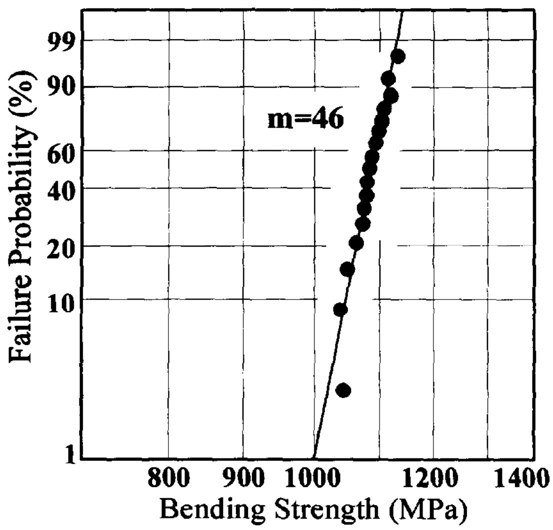


Fig. 12. Weibull plots of the bending strength for the seeded specimens formed by tape casting.

properties. In the specific case of silicon nitride, an increase can be expected in thermal conductivity in the direction parallel to the elongated grains. Preliminary experimental results indicate a close relationship between microstructure and thermal conductivity for silicon nitride.[14]

4 Concluding Remarks

In situ control of the microstructure of silicon nitride at micro- and macro-scopic level was accomplished experimentally based on a novel concept of microstructural control. Control of anisotropic grain growth by seeding (micro-scale level), combined with alignment of the seed particles by tape casting (macro-scale level), yield a highly anisotropic microstructure allowing not only the harmonic enhancement of mechanical properties such as high strength and high toughness, but at the same time attaining a high degree of reliability of the mechanical strength.

The concept of microstructural control discussed in the present paper can be extended to other ceramic materials. It is expected that expanding the range of application of these techniques of microstructure control will make it possible the incorporation and enhancement of other properties, such as high thermal conductivity, into such materials. Topics for future work in this field include optimization of the size and aspect ratio of seed particles, a strict control of the orientation degree of elongated grains, and control of the chemistry of grain boundaries in order to achieve higher toughness values and better high temperature properties.

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