Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 23 (2003) 1543–1547
www.elsevier.com/locate/jeurceramsoc

Effect of the residual phases in β-Si_3N_4 seed on the mechanical properties of self-reinforced Si_3N_4 ceramics

Jinhui Dai*, Jianbao Li, Yongjun Chen, Liu Yang

State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 10 June 2002; received in revised form 13 September 2002; accepted 28 September 2002

Abstract

In this work, the self-reinforced silicon nitride ceramics with crystal seed of β-Si_3N_4 particles were investigated. Firstly, the seeds were prepared by heating of α-Si_3N_4 powder with Yb_2O_3 and MgO, respectively. Then the self-reinforced silicon nitride ceramics were obtained by HP-sintering of α-Si_3N_4 powder, Yb_2O_3 and the as-prepared seeds which were not treated with acid and/or alkali solution. The results indicated that the introduction of seed with Yb_2O_3 could obviously increase the toughness and room temperature strength of the ceramics. Furthermore, its high temperature strength (1200 °C) could nearly keep higher value as the one of room temperature measured from unreinforced ceramic. However, the seed with MgO abruptly decrease the high temperature strength of the ceramics. The SEM and TEM characterization showed that the rod-like seed particle could favor the toughness and the presence of the Mg promote the formation of crystalline secondary phase.

Keywords: Grain boundaries; Hot pressing; Mechanical properties; Si_3N_4; Seeding

1. Introduction

Silicon nitride ceramics have been identified as one of the promising structural ceramics. Their high strength, high hardness, and good resistance to erosion place silicon nitride ceramics among the prime candidates in high-temperature industrial, automotive, and aerospace application such as cutting tools, wire drawing, dies, and blast nozzles. However, the low toughness is still a handicap that hampered wide potential application. So at present, the improving toughness of silicon nitride ceramics all the same is the one of important problems.

Since the toughness of Si_3N_4 ceramics was improved by Lange[1] with augmentation of aspect ratio of Si_3N_4 grains, a number of research activities have in the past focused on reinforcing Si_3N_4 ceramics by improving of the microstructural features of grains particle.[2–4] It was an effective method in the similar researches that silicon nitride was reinforced by addition of β-Si_3N_4 single crystal used as a seed.[5–10] However, synthesis of higher purity β-Si_3N_4 seed particles without additives must run at temperature over 2000 °C.[11] While β-Si_3N_4 seed particles could be generally achieved at relative lower temperature by sintering of α-Si_3N_4 and different additives.[12] In this case, glass phase more or less formed in these seeds. Acid and/or alkali rinse treatments were always used for the removing of the glass phase. Hirao[13] produced Si_3N_4 ceramics by adding elongated β-Si_3N_4 grains which were obtained by means of growth from a melt flux and subsequent treatments with acid rinse. But β-Si_3N_4 grains produced using these methods include impurities composed of Y and F or S, and these impurities decrease the strength at high temperatures. The baleful secondary phase strongly affects mechanical properties of silicon nitride. If the seed contained the secondary phase with low melting point, it would greatly decrease the flexure strength of materials at high temperature. Therefore it is worth seeking an easy method by which ideal β-Si_3N_4 particles (without low melting point secondary phase) can be achieved and understanding the effect of the secondary phase on the properties of materials. In this work, two kinds of β-Si_3N_4 seed were prepared. These seeds were not treated with acid and alkali rinse and then added to the original α-Si_3N_4 powders for preparing ceramic materials. The effect of the residual phase in the seed on the mechanical properties of materials was detailed discussed.

* Corresponding author. Fax: +86-10-6278-2753.
E-mail address: djh99@mails.tsinghua.edu.cn (D. Jinhui).

0955-2219/02/$ - see front matter
PII: S0955-2219(02)00348-5

2. Experimental process

2.1. Preparation of β-Si_3N_4 seeds

Commercial available α-Si_3N_4 powder (β-Si_3N_4 <3%, 0<1.55, AT&M Industries, Beijing, China) was used as the original powder in this study. Yb_2O_3 and MgO powders (99.9% purity) were used as the transformation additive and the amounts are 2, 4, 6, 8 wt.% and 0.5, 1, 1.5, 2 wt.% respectively. All original powders were mixed with ball milling in ethanol for 24 h, dried at 60 °C for 6 h then were placed in a graphite crucible and heated in a graphite furnace in nitrogen atmosphere for 90 mm. The heating temperatures were 1650 °C for the MgO-contained powders and 1700 °C for the Yb_2O_3-contained powders, respectively. The heated powder were milled and dispersed for characterization.

The as-prepared powder was identified with an X-ray diffractometer. From 20 to 80°, specimens were scanned at a rate of 4°/mm. In addition, from 30 to 40°, the XRD was performed again with a rate of 0.5°/mm for calculating phase ratio. The phase ratio, β-Si_3N_4 to total Si_3N_4 (α-Si_3N_4 + β-Si_3N_4), was determined by a technique derived by Gazzara and Messier.[14] The morphologies of the powder were characterized by scanning electron microscopy (SEM, Model: JSM-6301F).

2.2. Preparation of ceramics specimens

The ditto original powder of α-Si_3N_4 powder, 10 wt.% Yb_2O_3 and 10 wt.% of selective as-prepared β-Si_3N_4 seed were blend with ball milling in ethanol for 24 h and dried at 60 °C in air for 6 h. Then it was hot-pressure sintered into a disk in a graphite die (Φ50 mm) under 25 MPa at 1800 °C for 60 mm in nitrogen atmosphere. The as-prepared disks were cut and ground into the specimens of 3×4×35 mm^3 for the measurement of flexural strength and 4×6×30 mm^3 for the measurement of fracture toughness, respectively. By comparison, a specimen merely added with 10 wt.% Yb_2O_3 was prepared by the same process. The flexure strength was measured by three-point method with a 30 mm span at a loading speed of 0.5 mm/min at room temperature and 1200 °C, respectively. The fracture toughness was determined by single-edge-precracked-beam (SEPB) method at room temperature with 24 mm span at a loading speed of 0.05 mm/mm. The density of specimens was determined by Archimedes method. The theoretical density of the specimens was calculated according to the rule of mixtures. The specimens were characterized by TEM (JEM-200CX) and the intergranular phases were analyzed by using the selected-area electron diffraction (SAED). The TEM specimens were prepared by cutting and grinding the sintered specimen to a plate with a thickness of 20 μm, then dimpling and ion beam milling.

3. Results and discussion

3.1. The transformation of Si_3N_4 and morphologies of β-Si_3N_4

As shown in Fig. 1(a), the X-ray diffraction (XRD) pattern of the MgO-added heated powders showed that they still contained α-Si_3N_4 phase when the amount of MgO is less than 1.5%. While when the amount of MgO is up to 2%, the heated powders are nearly composed of single phase of β-Si_3N_4. There is no Mg-contained phase found in the XRD pattern. However, according to the experimental process, Mg-contained phase must exist in the heated powders. We believed that two reasons are responsible for this result. At first, the content of this phase is too low to be identified by XRD. Secondly, the phase is possibly in an amorphous state. But its form is unknown; maybe it is in the form of Mg–Si–O–N or Mg–Si–O. Fig. 1(b) showed the XRD pattern of the Yb_2O_3-added heated powder. From it, it can be observed that when the amount of Yb_2O_3 is 2%, α-Si_3N_4 still existed. And when the amount of Yb_2O_3 is up to 4%, the transformation of α-Si_3N_4 to β-Si_3N_4 is nearly completed. In addition, a crystal phase of $Yb_4Si_2N_2O_7$ formed except β-Si_3N_4 and the amorphous phase of Yb–Si–O and/or Yb–Si–O–N. And when the

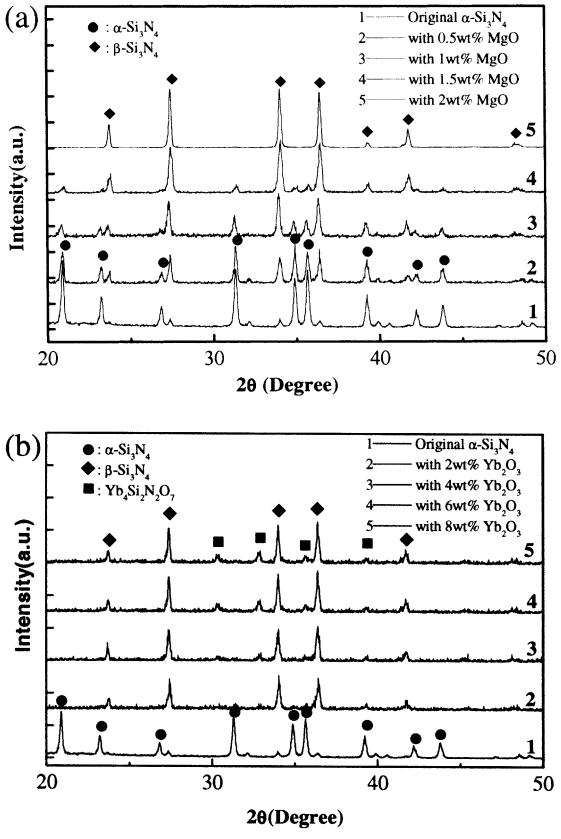

Fig. 1. Typical XRD patterns of (a) heated powders at 1650 °C with additive MgO (0, 0.5, 1, 1.5 2 wt.%), and (b) heated powders at 1700 °C with additive Yb_2O_3 (0, 2, 4, 6, 8 wt.%).

amount of Yb_2O_3 is up to 6 and 8%, the content of the $Yb_4Si_2N_2O_7$ phase increased.

It is well known that MgO is a good sintering additive. In earlier years, the densification of silicon nitride ceramics was foremost achieved by MgO. Actually, MgO is not only a good sintering additive but also a good transformation additive for Si_3N_4. Fig. 2(a) showed a relationship between β-Si_3N_4 ratio in the total Si_3N_4 and MgO amount. It obviously indicated the occurrence of transformation when 0.5 wt.% MgO was added. And the β-Si_3N_4 ratio increased with the increase of MgO content. When the content of MgO is 2 wt.% the β-Si_3N_4 ratio nearly achieved 100%. As an additive, rare earth oxide Yb_20_3 also accelerated the transformation of Si_3N_4. From Fig. 2(b), it can be observed that the β- Si_3N_4 ratio obviously increased when the content of Yb_2O_3 is over 2%. And it even achieved over 98% when 4% of Yb_2O_3 was added. Then it nearly kept this value even if the amount of Yb_2O_3 up to 8%. Sarin[15] has demonstrated that transformation of Si_3N_4 is a reconstructive process and requires a liquid phase or a vapor phase. The transformation of Si_3N_4 occurs by the solution-reprecipitation process when the liquid phase exists. So the temperature forming liquid phase is an important factor for the transformation. Since both Mg–Si–O–N and/or Mg–Si–O phase have relative lower eutectic point than that of Yb–Si–O and/or Yb–Si–O–N, the transformation of Si_3N_4 with MgO additive can be nearly completed when the heating temperature increased up to 1650 °C.

Morphologies of β-Si_3N_4 single particles obtained from 2 wt.% MgO and 4 wt.% Yb_2O_3 additive were observed by SEM and showed in Fig. 3. Both of them exhibit an integrated rod-like morphology with a diameter of 0.2–0.4 μm and a length of 1.2–1.5 μm [Fig. 3(a) and (b)]. With respect to nucleation and growth, research indicated that the individual seed particles having a larger diameter and relatively short length also have a better chance of developing the self-reinforced microstructure without hindering the densification process.[9] So the fabricated rod-like β-Si_3N_4 seeds will be especially designed for effectively developing the Si_3N_4 microstructure.

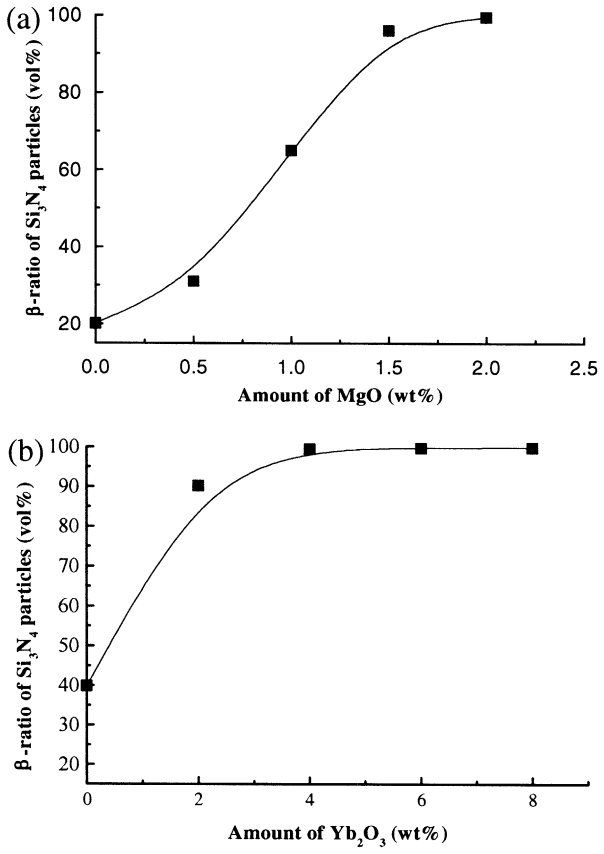

Fig. 2. The relationships between the β-ratio of Si_3N_4 of heated powders and amount of additive: (a) MgO additive, and (b) Yb_2O_3 additive.

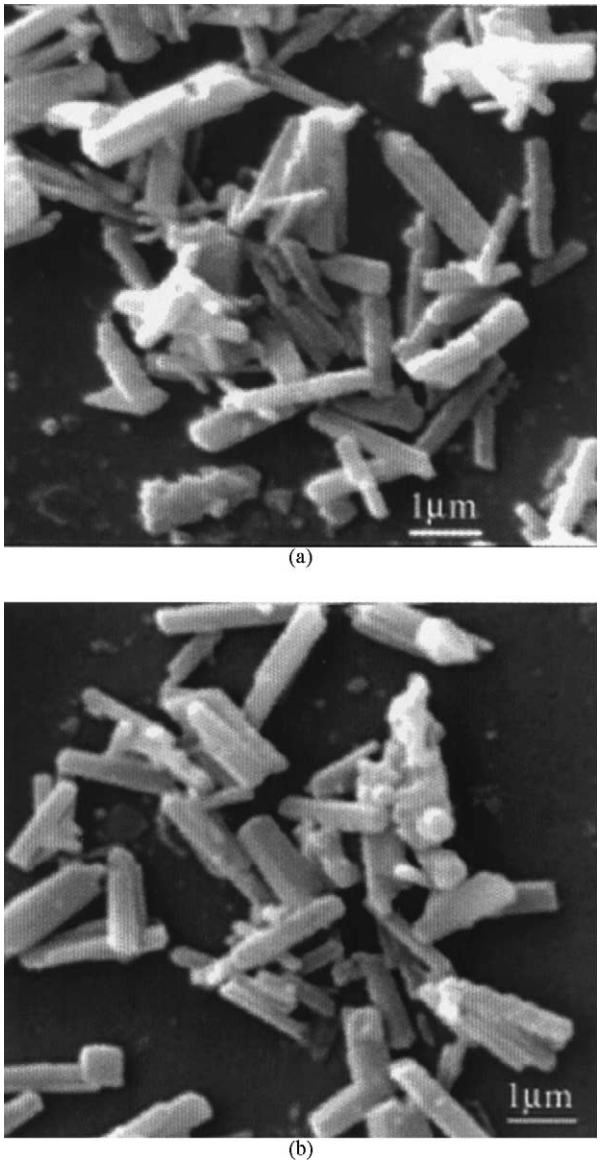

Fig. 3. SME morphologies of heated powders;(a) with additive MgO of 2 wt.% at 1650 °C, and (b) with additive Yb_2O_3 of 4 wt.% at 1700 °C.

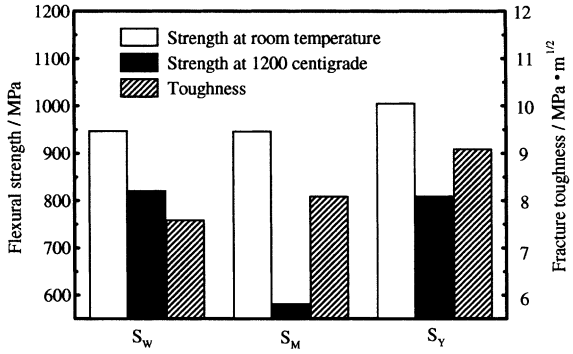

Fig. 4. Mechanical properties of the three specimens.

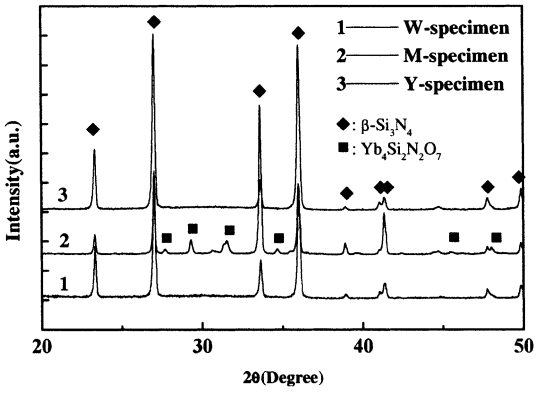

Fig. 5. Typical XRD patterns of HP-sintered Si_3N_4 specimens.

3.2. The intergranular phase and properties of self-reinforced silicon nitride

Two kinds of self-reinforced ceramic specimens were prepared by adding β-Si_3N_4 seeds obtained from 2% MgO and 4% Yb_2O_3, respectively. For comparison, another specimen adding no seed was also prepared by the same method. These specimens were called S_M (adding MgO seed), S_Y (Yb_2O_3 seed) and S_Y (without seed), respectively. The relative densities of the three specimens are 99.5% and more. Fig. 4 showed the mechanical properties of them. From it, it can be observed that all of the specimens have relative high flexural strength at room temperature, and the S_Y has the highest flexural strength of 1006 MPa among them. The fracture toughness was also improved. The fracture toughness of S_W is 7.6 Mpa $m^{1/2}$, while those of S_M and S_Y increased to 8.1 and 9.1 Mpa $m^{1/2}$, respectively. Both of the β-Si_3N_4 seeds can obviously make for the toughening process of silicon nitride materials. However, it can also be observed that the high-temperature (1200 °C) flexure strength of S_M decreases more quickly than that of S_W, whereas the S_Y have a relative high reserved strength at 1200 °C.

It is well known that the properties of materials are dependent on the chemical composition and microstructure of materials. The chemical composition and

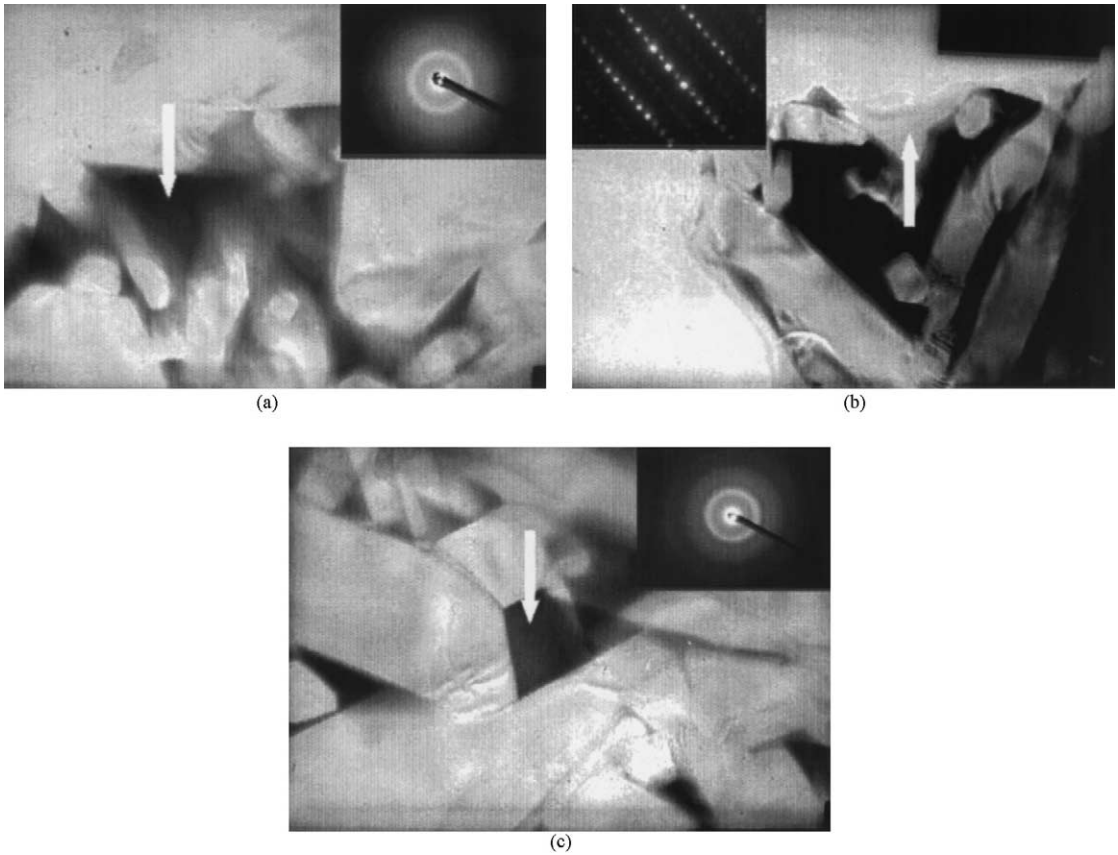

Fig. 6. TEM images of the specimens and SAED patterns of the intergranular phase: (a) S_W, (b) S_M and (c) S_Y.

content of intergranular phase have important effects on the properties of specimen. In present study, different types of intergranular phases were found in different specimens. The results of XRD analysis obviously indicated that the S_W and S_Y contained no secondary crystal phase, but the secondary crystal phase of $Yb_4Si_2N_2O_7$ was obviously seen in the SM (Fig. 5). Fig. 6 is TEM images of the three specimens. The inserted SAED patterns also confirmed such results. The ambiguous circles appeared in S_W and S_Y indicated that they contained no secondary crystal phase [Fig. 6(a) and (c)]. Fig. 6(b), however, showed that S_M contained secondary crystal phase, which is corresponding to the XRD results. Based on these evidences, high temperature strength of S_M should be higher than those of S_W and S_Y. because the secondary crystal phase of $Yb_4Si_2N_2O_7$ has 1870 °C high melt point.[16] However, the oppositional result was obtained. The main difference among S_M, S_W and S_Y is that in S_M, Mg-contained glass phase exists. We believed that the residual Mg-contained phase at grain boundary mainly plays two roles in the sintering process. At first, this phase with low melt temperature provides a chance for the crystallization of $Yb_4Si_2N_2O_7$ during the cooling process. Because when $Yb_4Si_2N_2O_7$ phase crystallized from the melt, the Mg-contained phase still exists in a liquid state that has a low viscosity, which can accelerate the diffusion process and bring on the crystallization of $Yb_4Si_2N_2O_7$. This role should result in an increase of the high-temperature strength. On the other hand, the Mg-contained phase has a lower softening temperature than that of Yb-contained phase; it will soften in an earlier time than the glass phase in S_Y and S_W during the heating process and result in decrease of the high-temperature strength. The latter role is a predominated factor that affects the high-temperature strength. Therefore, we can draw a conclusion that the residual Mg-contained glass phase caused the formation of different intergranular crystallized phase $Yb_4Si_2N_2O_7$ and lower high-temperature strength of specimens.

4. Conclusions

Two types of β-Si_3N_4 seed with MgO and Y_2O_3 were prepared. And self-reinforced ceramics were prepared by adding the β-Si_3N_4 seeds. The mechanical properties of them were investigated at room temperature and 1200 °C. The effect of intergranular phase on the high-temperature strength was analyzed. The main conclusions are:

1. Both of the β-Si_3N_4 seeds (Y-seed and M-seed) obviously improve the toughness of silicon nitride ceramic.
2. Presence of a bit of Mg-contained phase with relative lower softening temperature in the specimen results in the decrease of high-temperature strength of self-reinforced silicon nitride ceramics and brings on crystallization of $Yb_4Si_2N_2O_7$ phase.
3. The rod-like β-Si_3N_4 particles prepared with Yb_2O_3 additive, which were not treated by acid and/or alkali solution rinse, can be used as an effective seed to improve the toughness of silicon nitride ceramic. And this seed does not degrade the high temperature strength of ceramics.

Acknowledgements

The authors would like to thank the support from The National High Technology Research and Development Program of China (863 Program) (No: 2002AA332060).

References

1. Lange, F. F., Fracture toughness of Si_3N_4 as a function of the initial a-phase content. *J. Am. Ceram. Soc.*, 1979, **62**(7–8), 428–430.
2. Tani, E., Gas-pressure sintering of Si_3N_4 with concurrent addition of Al_2O_3 and 5wt% rare earth oxide: high fracture toughness Si_3N_4 with fiber-lick structure. *Am. Ceram. Soc. Bull.*, 1986, **65**, 1311–1315.
3. Kawashima, X., Grain size dependence of the fracture toughness of silicon nitride ceramics. *J. Ceram. Soc. Jpn.*, 1991, **99**, 320–323.
4. Kimin, L. and Wonho, L. *et al.*, Microstructural evolution and mechanical properties of gas-pressure-sintered Si_3N_4 with Yb_2O_3 as a sintering aid. *J. Mater Res.*, 1999, **14**(5), 1904–1909.
5. Emoto, H. and Mitomo, H., Control and characterization of abnormally grown grains in silicon nitride. *J. Eur. Ceram. Soc.*, 1997, **17**, 797–804.
6. Kanzaki, S., Manuel, E., Brito, M., Valecillos, C. and Hirao, K., Microstructure designing of silicon nitride. *J. Eur. Ceram. Soc.*, 1997, **17**, 1841–1847.
7. Hirosaki, N., Okamoto, Y., Munakata, F. and Akimune, Y., Effect of seeding on the thermal conductivity of self-reinforced silicon nitride. *J. Eur. Ceram. Soc.*, 1999, **19**, 2183–2187.
8. Peillon, F. C. and Thevenot, F., Microstructure designing of silicon nitride related to toughness. *J. Eur. Ceram. Soc.*, 2002, **22**, 271–278.
9. Lu, H. H. and Huang, J. L., Microstructure in silicon nitride containing β-phase seeding: part I. *J. Mater Res.*, 1999, **14**(7), 2966–2973.
10. Rhee, S. H. and Lee, J. D., Effect of β-seed addition on the microstructural evolution of silicon nitride ceramics. *J. Am. Ceram. Soc.*, 2001, **84**(12), 3040–3042.
11. Hirata, T., Akiyama, K. and Morimoto, T., Thesis of β-Si_3N_4 particles from α-Si_3N_4 particles. *J. Eur. Ceram. Soc.*, 2000, **20**, 1191–1195.
12. Hirao, K., Preparation of rod-like β-Si_3N_4 single crystal particles. *J. Ceram. Soc. Jpn.*, 1993, **101**(9), 1078–1080.
13. Hirao, K., Microstructure characterization of gas-pressure-sintered betα-Silicon nitride containing large β-silicon nitride seeds. *J. Am. Ceram. Soc.*, 1994, **77**, 1093–1097.
14. Gazzara, C. P. and Messier, D. R., Determination of phase content of Si_3N_4 by X-ray diffraction analysis. *Ceram. Bull.*, 1977, **56**(9), 777–780.
15. Sarin, V. K., On the alpha-to-beta phase transformation in silicon nitride. *Mater. Sci. Engin.*, 1988, **105/106**, 151–159.
16. Nishimura, T. and Mitomo, M., Phase relationships in the system Si_3N_4-SiO_2-Yb_7O_3. *J. Mater. Res.*, 1995, **10**(2), 240–242.