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Effects of α/β ratio in starting powder on microstructure and mechanical properties of silicon nitride ceramics

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Abstract

The effects of α/β ratio in the starting powder on microstructure development and mechanical properties of sintered silicon nitride ceramics were investigated. With increasing β-phase content, the microstructure became finer, the finest-grained microstructure was developed from the powder with pure β-phase, whereas a duplex microstructure was developed from high α-phase content powder. The results show that the microstructure of silicon nitride ceramics can be tailored by changing the α/β ratio in the starting powder. The mechanical properties have an optimum region where the α/β ratio equals 1. Both flexural strength and fracture toughness can be improved by controlling size, number, aspect ratio and size distribution of the rod-like β-Si_3N_4 grains

Keywords: B. Microstructure; C. Mechanical properties; α/β Ratio; Si_3N_4 ceramics

1. Introduction

Silicon nitride has attracted most attention among the advanced structural ceramic materials in the research and industrial community due to its overall excellent mechanical properties including high strength, high hardness, high fracture toughness and strength retention at elevated temperatures. As it is well known, the powder characteristics have significant influence on the liquid-phase sintering behavior of Si_3N_4 ceramics [1,2]. Powders with high α content have usually been used as the starting material since the sintered Si_3N_4 body consists of a composite-like microstructure due to the α-β phase transformation [3]. It has been reported that the large, elongated grains with high-aspect-ratio deflect the propagation of cracks, thus increasing the fracture toughness of the material [4,5]. However, large grains can also act as crack origin and this will lower the flexural strength of the sintered material. So, it is important to control the amount and aspect ratio of the large β grains in order to improve the mechanical properties of silicon nitride materials [6–9].

In the present work, the effects of α/β ratio in the starting powder on the microstructure development and mechanical properties of silicon nitride ceramics were investigated.

2. Experimental procedure

Commercially available α-Si_3N_4 ($>95\%$ α-Si_3N_4, 2.0 wt.% O, $d_{50}=0.45$ μm) and β-Si_3N_4 ($\sim 100\%$ β-Si_3N_4, 1.8 wt.% O, $d_{50}=0.42$ μm) powders were used as the starting material. Five batches were mixed by using the above-mentioned two powders and additives containing Y_2O_3, Al_2O_3 and CaO. The relative contents of β powder in those batches were 0, 25, 50, 75 and 100 wt.%. All powder batches were ball milled in ethanol for 72 h by using Si_3N_4 balls as grinding media, the milled slurry was then dried, sieved and uniaxially pressed into bars following by isostatic pressing at 200 MPa. The green compacts were immersed in a powder bed within a graphite crucible and pressureless-sintered at 1800 °C for 2 h.

Bulk density of sintered specimens was determined by the Archimedes method. Three-point bending strength was measured on 3×4×36 mm bars, a span of 30 mm was used with a crosshead speed of 0.5 mm/min. Fracture toughness value (K_{1C}) was measured by using a diamond

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indenter under a load of 100 N. Microstructure of the sintered materials was observed by SEM on fracture surfaces of specimens which were etched in NaOH melt for 25–35 s.

3. Results and discussion

The bulk density values for specimens of all compositions sintered at 1800 °C are >98% of the theoretical density. Fig. 1 shows the etched fracture surfaces of the sintered materials with the relative content of the β powder: (a) 0, (b) 25%, (c) 50% and (d) 100%, respectively. As shown, with the increase of β powder content, the microstructure changes from duplex to a more uniform microstructure. The microstructure of the materials from powder with a high α content consists of large elongated grains, while the material fabricated from powder with 100% β-phase consists of mainly fine rod-like grains. The diameter of the grains decreases as the β phase content increases.

At the time of liquid phase sintering of Si_3N_4, grain growth occurs during the solution-precipitation process, in which the grains with higher solubility are dissolved in the liquid phase and subsequently precipitated on β-nuclei with a lower solubility [6]. The solubility of a smaller grain in the liquid phase is higher than that of a larger one of the same phase, and the solubility of α-phase grains is higher than that of β grains with a similar particle size. Therefore, the amount and size of large β-nuclei in the batch powder are the key factors for the microstructural design of Si_3N_4 ceramics [10]. With increase in the β content, the amount of β nuclei is also increased. The driving force for grain growth is related to the difference of solubility between nuclei and matrix grain in liquid phase, and a high α grain content in the matrix will increase the driving force for grain growth.

In our investigation, the silicon nitride powder with a small amount of β-phase typically form a coarse microstructure with large elongated grains. The formation of this grain morphology is due to the small amount of β-nuclei, high driving force for grain growth, and large interparticle spacing that allows grains to grow freely without space limitation. As the amount of β phase in the starting powder increases, the microstructure will go through a refinement because the driving force for grain

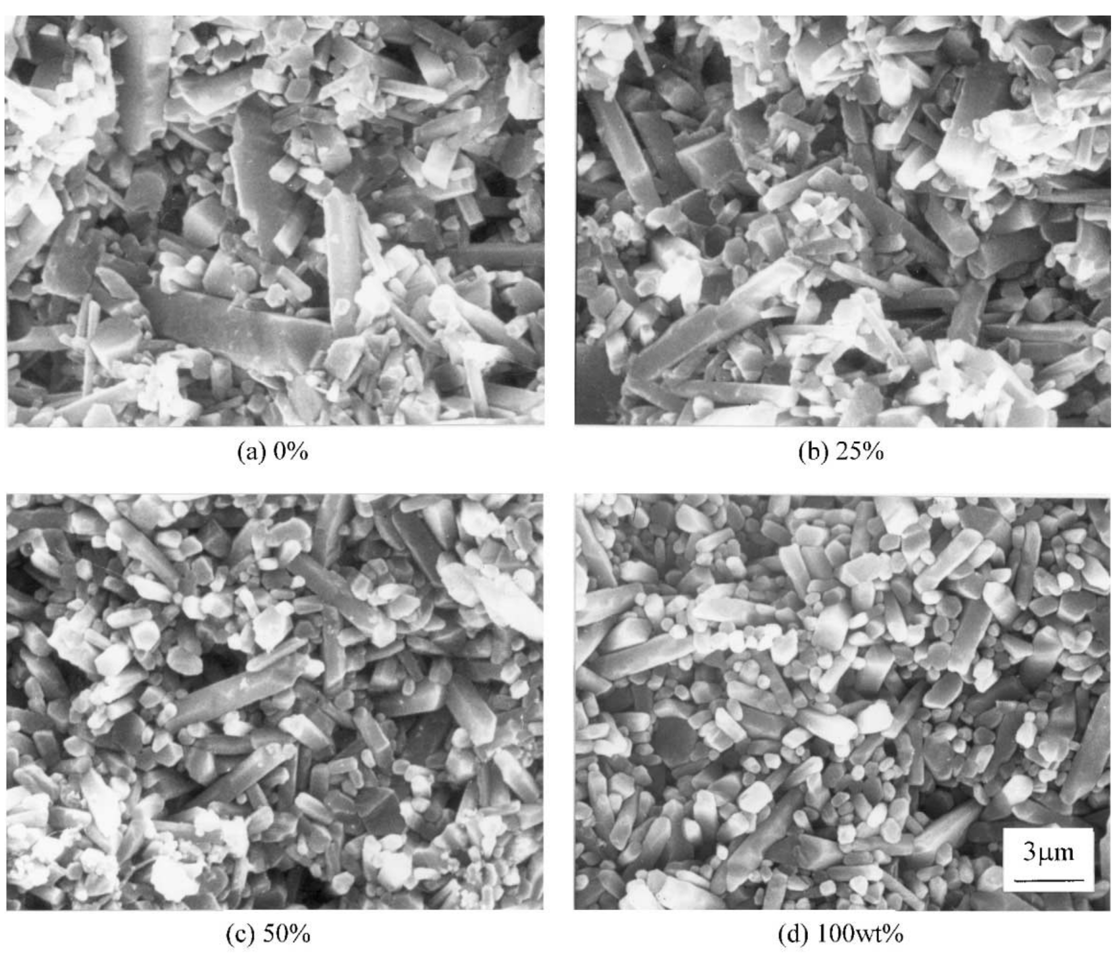

Fig. 1. SEM photographs of the sintered materials prepared from starting powder with different β powder volume contents.

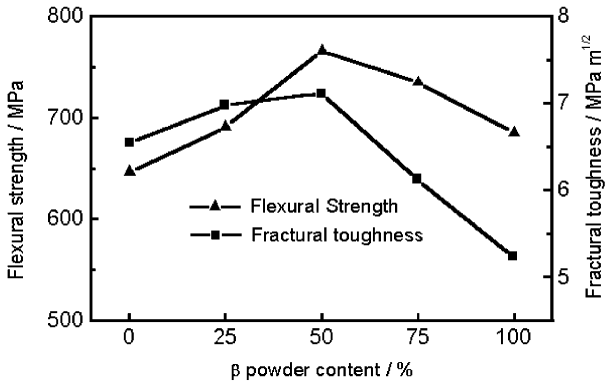

Fig. 2. Effects of β powder content in starting powder on mechanical properties.

growth is lower and the grain growth is inhibited by other β-Si_3N_4 grains.

Thus, an optimum phase ratio in the starting powder allows the development of such a microstructure in which large elongated grains with a uniform size distribution and a good dispersion will be formed.

Fig. 2 shows the variation of flexural strength and fracture toughness as a function of β powder content in the starting powder. Both flexural strength and fracture toughness reach a maximum with the increase of β-phase in the starting powder.

The relationship between microstructure and its resistance to the propagation of crack is well known. It has been reported that the toughening effect increases with increase of the diameter of elongated grains [11] and the volume content of elongated grains [12]. The fracture toughness is found to be increased proportionally to the square root of the diameter of large elongated grain. This phenomenon agrees with the predicted behavior from grains bridging and pull-out mechanisms. However, it is expected that the fracture toughness will eventually be limited by other factors. In our investigation, the amount and size of the large elongated grains are different in each batch. With the increase of β-Si_3N_4 from 0 to 50%, the increase of K_{1C} values is the result of an increase in elongated grain fractions with increasing β content in the starting powder, which promotes energy absorption by crack deflection, as well as by grain debonding, pull-out, and bridging mechanisms. However, with further increase of β-phase in the starting powder, the K_{1C} values are decreased while the diameter of elongated grains is decreased.

Flexural strength is generally given by the Griffith's equation: $\sigma_f = K_{1C} / (Y \cdot C^{1/2})$ where K_{1C}, Y, and C are fracture toughness, numerical constant and flaw size, respectively. When the amount of β-phase changes from 0 to 50%, the flexural strength is increased rapidly due to the increase of fracture toughness and decrease of flaw size. However, when the amount of β-phase increases further, the fracture toughness decreases, and flaw size has no significant change, so the flexural strength is decreased.

In conclusion, the development of a duplex microstructure and the control of the size of large elongated grains make the achievement of both high fracture toughness and high strength in Si_3N_4 ceramics possible.

4. Conclusions

The effects of α/β ratio in starting powder on microstructural development and mechanical properties of silicon nitride ceramics sintered were investigated by using α-Si_3N_4 and β-Si_3N_4 with similar particle size. Two conclusions can be drawn as follows:

1. Microstructure of sintered body can be tailored by changing α/β ratio of starting powders.
2. Both flexural strength and fracture toughness can be improved by controlling the size, number and distribution of rod-like β-Si_3N_4 grains.

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