

Precise property control in silicon nitride ceramics by α/β phase ratio control

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Silicon nitride ceramics with various α/β phase ratio were fabricated by controlling sintering conditions of PECS process. Mechanical properties varied systematically with α/β ratio. Young's modulus and hardness increased with α -Si₃N₄ volume fraction, and fracture strength and toughness increased with β -Si₃N₄ content.

Key words: silicon nitride, α/β phase ratio, mechanical property, microstructure, PECS, SPS.

Introduction

Silicon nitride ceramics is one of most promising materials for high-temperature application. They show excellent thermal and mechanical properties up to high temperatures, which combined with good wear resistance, has led to them finding application as automotive parts, bearings, machine tools and a variety of other engineering components. Effect of α/β phase ratio of starting powder on resulting material has been investigated [1]. Generally α -Si₃N₄ powder is better to be used as a starting material, because resulting materials have bimodal grain morphology with elongated β -Si₃N₄ grains which increase fracture toughness by crack bridging/pull-out and/or crack deflection mechanisms [2, 3]. On the other hand, influences of α/β phase ratio of sintered materials to properties have not been evaluated. First reason is that elongated β -grains are more dominant to mechanical properties, especially fracture toughness. However, for some applications, a higher hardness and/or Young's modulus is required. Secondary, it is difficult to densify Si₃N₄ with inhibiting α/β phase transformation by conventional sintering methods. Then, Si₃N₄ ceramics have been researched for only fully phase-transformed materials, although it is very essential to understand the relationship between α/β phase ratio and properties.

Pulse Electric Current Sintering (PECS), which is commercially called as Spark Plasma Sintering (SPS) or Plasma Activated Sintering (PAS), has been developed for the fabrication of ceramics and metallic materials. This process allows rapid sintering due to the direct heating of powder and dies by pulsed direct current electrification [4]. Using this method, α/β phase ratio

of Si₃N₄ can be precisely controlled and dense Si₃N₄ ceramics with wide range of α/β ratio can be fabricated by modifying the sintering conditions [5]. Here we investigated about appropriate α/β phase ratio for two requests; one is high hardness and Young's modulus, and another is high fracture toughness and strength.

Experimental

Ube SN-E10 Si₃N₄ powder (>99.5% pure, >95% α -phase content, Ube Industries Co., Ltd., Ube, Japan) was used with oxide additives, 6 mol% of yttrium oxide (>99.9% pure, SU grade, Shin-etsu Chemical Industry Co., Ltd., Tokyo, Japan) and 2 mol% of aluminum oxide (>99.99% pure, Taimicron TM-DAR, Taimei Chemicals Co., Ltd., Nagano, Japan). These powders were mixed by wet ball-milling in polyethylene pot with ethanol and Si₃N₄ balls for 24 hours. Then, mixed powders were dried and milled by dry ball-milling in polyethylene with Si₃N₄ balls for 6 hours to eliminate the agglomerates. The powders were sintered using SPS equipment (Dr Sinter 2040, Sumitomo Coal Mining Co., Ltd., Tokyo, Japan) in a nitrogen atmosphere under an applied pressure of 30 MPa. The sintering temperatures used were 1650 and 1700°C, and the hold time was varied from between 1 and 10 minutes. XRD characterization was made using crushed specimens to avoid preferred orientation effects due to the elongated β -Si₃N₄ grains, and the $\alpha : \beta$ phase ratio was calculated from the peak heights of the $\alpha(200)$ and $\beta(200)$ reflections [6]. Microstructures were observed by scanning electron microscopy. Young's modulus was determined by resonance vibration, and hardness and fracture toughness were evaluated by Vickers indentation fracture using a 196 N load. The latter also used an indentation strength-in-bending method with a 30 mm span and a crosshead speed of 0.5 mm/min, the 196N Vickers indentation being used as the pre-crack. Fracture strength

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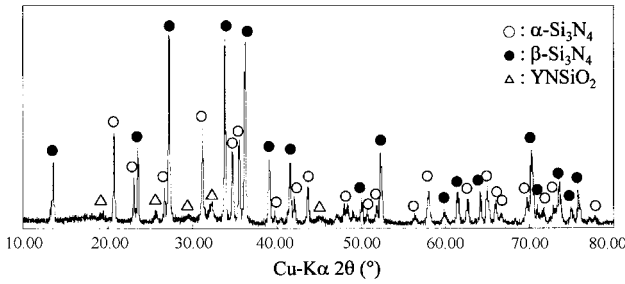


Fig. 1. XRD profile of Si_3N_4 ceramic with 53 wt% β -phase.

was again measured in three point bending mode with a 30 mm span and a crosshead speed of 0.5 mm/min.

Results and Discussions

α - and β - Si_3N_4 as matrixes and YNSiO_2 as grain boundary phase were identified by XRD profiles as seen in Fig. 1. As-sintered materials had a wide range of α/β phase ratio between 20 and 95 wt% of β phase. The α/β phase ratio varied according to controlled sintering conditions as shown in Fig. 2.

Figure 3 indicates variation of hardness and Young's modulus with increase β phase content. α - Si_3N_4 single crystal showed about 1.3 times higher hardness than β - Si_3N_4 single crystal [7]. Greskovich *et al.* [8] reported that dense Si_3N_4 ceramic (not single crystal) with 15% β -phase gave about 1.3 time higher hardness than 100% β specimen. When the hardness variation of present materials was approximated by straight line, the pure α - Si_3N_4 should be about 1.2 times higher than that of pure β - Si_3N_4 . As the reflection of the high hardness of α - Si_3N_4 , the tendency that the hardness increased with increasing α -ratio was recognized in present investigation according to rule of mixture. As expected from the hardness change, Young's modulus increased linearly

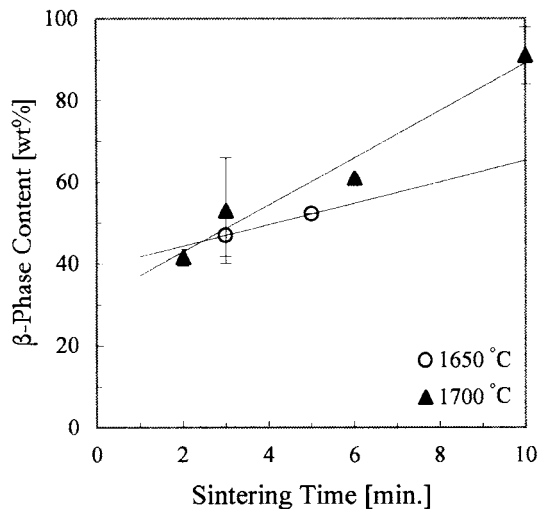


Fig. 2. The change of β -phase content according to sintering conditions.

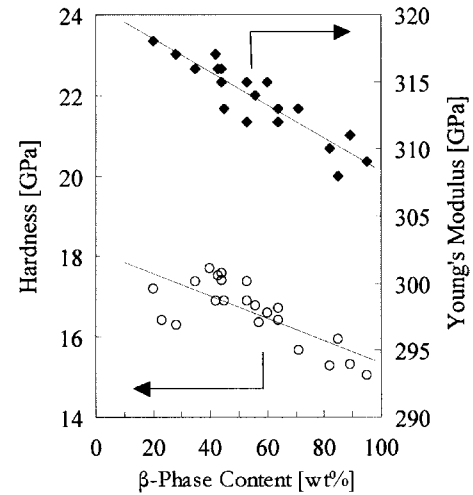


Fig. 3. Variation of hardness and Young's modulus.

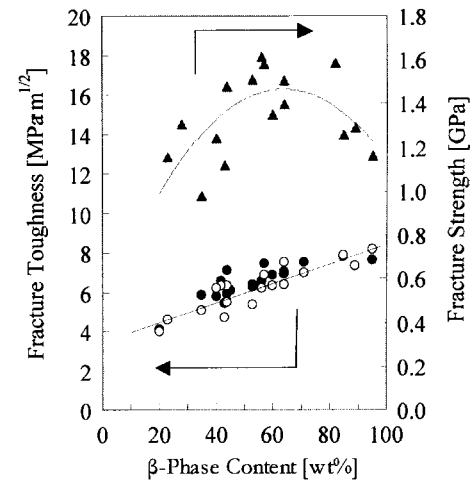


Fig. 4. Change of fracture toughness and strength.

from 310 to 318 GPa with decreasing β - Si_3N_4 volume fraction from 95 to 20 wt%. This tendency is similar to the result reported by Himsolt *et al.* [9] From these view point, Si_3N_4 ceramic containing high α phase, which is easily produced by PECS process, can satisfy the request for both high hardness and Young's modulus.

On the other hand, fracture toughness increased with increasing β -phase content. This is because elongated β -grains toughen the materials by crack bridging/pull-out mechanism [2, 3]. Fracture strength was very high, which was over 1 GPa for all range of α/β phase ratio. In the present work, the microstructure, and more specifically the critical flaw size, was so fine, because of the small initial particle size due to the very short sintering times, that the fracture strength was entirely high. Most unique thing in present work is that fracture strength showed nonlinear dependence on β -phase content. For high α -phase materials, the fracture strength increases approximately linearly with fracture toughness as expected. This behavior is observed up to

about 60 wt% of β -phase. In the high β -phase region, however, the relatively large exaggerated grain growth of β grains leads to an increase in the size of the fracture origin, and this is believed to be the reason for the decrease [10]. From these results, it can be seen that Si_3N_4 ceramics containing 60 to 80 wt% of β -phase can satisfy the simultaneous requirements of both high fracture toughness and high fracture strength.

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