

Nanostructure Ceramics of Silicon Nitride Produced by Spark Plasma Sintering

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Abstract

The nanostructure control of Si₃N₄ ceramics can be achieved by using fine starting powder and retardation of grain growth. The spark plasma sintering technique is useful to retard the grain growth by rapid heating. In the present work, the change of microstructure was investigated with emphasis on the particle size of starting powder, the amount of sintering additive and the heating schedule. The rapid heating by spark plasma sintering gave the fine microstructure consisting of equiaxed grains with the same size as starting particles. The spark plasma sintering of Si₃N₄ fine powder was effective to control the microstructure on nano-meter level.

Keywords : silicon nitride, nanostructure, spark plasma sintering, sintering additive, heating schedule.

1. Introduction

Si₃N₄ is difficult to densify without sintering additives, because of its high covalent bonding and low diffusivity. By using sintering additives such as Y₂O₃ and Al₂O₃, liquid phase sintering takes place, giving dense Si₃N₄ ceramics. The grain morphology and grain boundary phase in the resulting Si₃N₄ ceramics dominate the mechanical properties and heat resistance. In general, mechanical strength increases with decreasing grain size. Although the high toughness of Si₃N₄ ceramics is achieved by the growth of β-Si₃N₄ elongated grains with high aspect ratio, the fine-grained microstructure is preferable for wear-resistance application. When the sintered product is cooled, the liquid phase forms a glassy phase at grain boundary. The glassy phase lowers the strength at high temperature. In order to increase heat resistance, it is necessary to reduce the amount of sintering additives. Densification is strongly affected by the characteristics of starting powder [1,2]. Especially, the sinterability improves with a decrease in particle size of starting powder. Using highly sinterable starting powder, dense ceramics can be produced at a low temperature and in a short time, resulting in the retardation of grain growth during sintering process. Moreover, the amount of sintering additive can be reduced, leading to decrease of the amount of glassy phase at grain boundary.

Spark plasma sintering (SPS) technique is characterized by rapid heating rate and very short holding time to obtain fully dense ceramics. Therefore, it is possible to control the microstructure of Si₃N₄ ceramics on nano-meter level.

The purpose of this work is to investigate the effect of the characteristics of Si₃N₄ starting powders, the amount of sintering additives and the heating schedule on the densification behavior of

Si₃N₄ powder and the microstructure of Si₃N₄ ceramics by SPS. By using nano-sized Si₃N₄ particles, we can expect the fabrication of fine-grained Si₃N₄ ceramics with small amounts of sintering additives.

2. Experimental and Results

2.1 Heating schedule

α-Si₃N₄ commercial powder was used as starting powder. The average size of the Si₃N₄ particles was 500nm. 6wt% Y₂O₃ and 2wt% Al₂O₃ powders were added as sintering aids. The mixed powder was compacted into graphite die and sintered by SPS at a temperature of 1500 to 1800°C under a pressure of 30MPa in N₂ atmosphere. The heating rate was 100 to 370°C/min and the cooling rate was 600°C/min. Shrinkage behavior of the powder compact during SPS process, and density, crystalline phase and microstructure of the sintered bodies were investigated.

The shrinkage of the powder compact started at about 1300°C, which was not dependent on heating rate. The relative density of the final products sintered at 1700°C for holding time of 2min at 100 to 370°C/min was over 98%. The α-phase content of all products was about 50%. The average grain size determined from SEM images of the microstructure decreased with increasing heating rate. The rapid heating gave the fine microstructure consisting of equiaxed grains with the same size as starting particles.

The powder compact was sintered at 1700°C for holding time of 1min. The grain size of the final product was small as 260nm, but the full densification was not achieved, in which the relative density was 91%. The density increased to 99% when the holding time was changed from 1 to 2min,

whereas the grain size was increased from 260nm to 350nm.

Heating schedule was changed as follows. The powder compact was heated at 1700°C for holding time of 1min and then cooled to 1500°C slowly at the rate of 200°C/min. The resultant sample had almost full density. Furthermore, the grain size of the sintered body was 300nm. It was possible to inhibit the grain growth compared with the sintering for holding time of 2min.

2.2 Particle size of Si₃N₄

Amorphous Si₃N₄ fine powder (CVD powder) was used as starting powder instead of α-Si₃N₄ commercial powder. The fine powder was prepared by a vapor phase reaction method. The average size of the particles was 100nm. Figure 1 shows the SEM image of Si₃N₄ ceramics obtained from the CVD powder using the same heating schedule as above. The microstructure of the product consisted of equiaxed grains. The average grain size was 200nm. It was possible to fabricate fine-grained dense Si₃N₄ ceramics from the CVD powder.

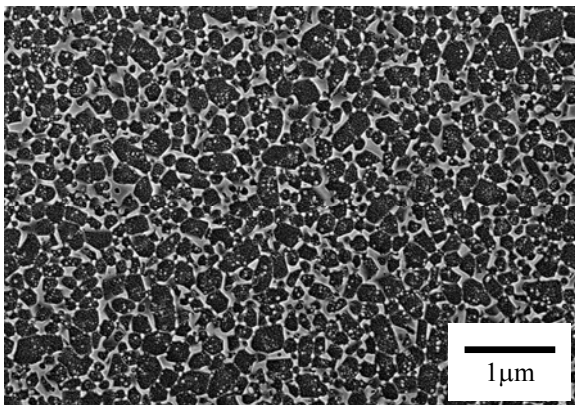


Fig. 1. SEM micrograph of Si₃N₄ ceramics obtained from amorphous Si₃N₄ fine powder.

2.3 Amount of sintering additives

The commercial powder and the CVD powder were sintered with small amount of sintering additives, 1.5wt% Y₂O₃ and 0.5wt% Al₂O₃, at heating rate of 100°C/min by SPS. Figure 2 shows the relative density and α-phase content of the final products obtained at various heating temperature of 1500 to 1800°C. In the case of the commercial powder, when the heating temperature was 1500°C, the density of the product was about 60%. As the temperature was raised to 1700°C, the density reached 93%.

At 1800°C for holding time of 1min, the sample with high density up to 98% was obtained. When the density increased, the α- to β-phase transformation took place. Only β-phase formed at 1800°C. On the other hand, in the case of the CVD powder, the amorphous phase directly changed into crystalline β-phase. The densification proceeded to 95% even at 1500°C. Therefore, it was found that the CVD powder had high sinterability than the commercial powder. On the product at 1700°C for 30min, the SEM observation showed that the Si₃N₄ ceramics obtained from the CVD powder was composed of fine equiaxed and elongated grains, compared to grains in the ceramics from the commercial powder.

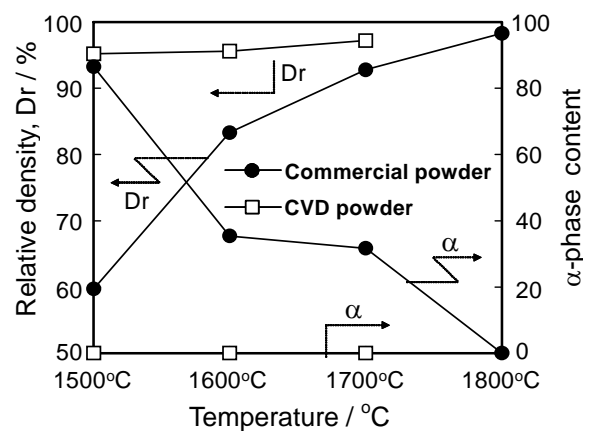


Fig. 2. Relative density and α-phase content as a function of heating temperature. Holding time: 30min at 1500, 1600 and 1700°C; 1min at 1800°C

3. Summary

Si₃N₄ ceramics with inhibited grain growth during SPS process were obtained by selecting optimum heating schedule such as heating rate, temperature and holding time. Using amorphous Si₃N₄ nano-sized powder as starting material, dense and fine-grained Si₃N₄ ceramics were fabricated with small amount of sintering additives by SPS.

4. Reference

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