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Spark Plasma Sintering of Nanosized Amorphous Silicon Nitride Powder with a Small Amount of Sintering Additive

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Dense and fine-grained β-Si_3N_4 ceramics were successfully obtained with a small amount of sintering additives, 1.5 mass% Y_2O_3 and 0.5 mass% Al_2O_3, using nanosized amorphous Si_3N_4 powder by spark plasma sintering at temperatures of 1500°–1800°C and a pressure of 30 MPa under N_2. The β-Si_3N_4 ceramics were composed of equiaxed grains with an average size of 300 nm. A higher sintering temperature was required for the densification of submicrometer-sized α-Si_3N_4 powder with the small amount of the additives. The use of nanosized amorphous Si_3N_4 powder accelerated the densification and the transformation to the β-phase.

I. Introduction

Silicon nitride (Si_3N_4) ceramics are one of the most promising materials for structural applications at high temperature. However, Si_3N_4 is very difficult to densify by solid-phase sintering because of its strong covalent nature and low self-diffusion coefficients of Si and N. In general, the conventional densification of Si_3N_4 ceramics is achieved by liquid-phase sintering with metal oxides additives such as MgO, Al_2O_3, and Y_2O_3. In contrast, the grain-boundary phase derived from the sintering additives degraded the high-temperature mechanical properties, and the corrosion and oxidation resistance of Si_3N_4 ceramics.[1] Therefore, in order to improve these properties, it is necessary to minimize the amount of sintering additives used for dense Si_3N_4 ceramics. The densification of Si_3N_4 using conventional sintering techniques such as gas-pressure sintering and hot pressing typically required the total amount of sintering additives of 5–10 mass%.[2,3]

Spark plasma sintering (SPS) technique can heat specimens rapidly because the pulsed direct current used in this technique is possible to pass through the graphite die and punch rods.[4] Thus, the entire sintering process can be completed in a short time, leading to suppression of grain growth during sintering at high temperature. Accordingly, densification of low-sinterable materials was accelerated and a fine-grained microstructure was formed by SPS.[5–10] The SPS technique is sometimes called as pulse electric current sintering (PECS),[11–13] field-assisted sintering technique,[14] and plasma-assisted sintering,[15] because the generation of spark discharge and/or plasma during SPS process has not been verified. By using the SPS process, low-sinterable oxides, nitrides, and carbides, which are difficult to densify by conventional sintering techniques, have been fabricated as fully dense materials. With regard to Si_3N_4 ceramics, there were reports on the fabrication by SPS.[10,12,15] The total amount of the sintering additives of >5 mass% was used for the densification of Si_3N_4 powders by the SPS technique, which was the same amount of additive as that by conventional sintering techniques.

We reported that fine-grained β-Si_3N_4 ceramics were prepared with a general amount of sintering additive of 6 mass% Y_2O_3 and 2 mass% Al_2O_3 using submicrometer-sized α-Si_3N_4 and nanosized amorphous Si_3N_4 powders by SPS.[5] Furthermore, at the amount of the sintering additives, the densification of the nanosized amorphous Si_3N_4 powder was easier to proceed than that of the submicrometer-sized α-Si_3N_4.[5] The use of nanosized amorphous Si_3N_4 is expected to fabricate nanostructured Si_3N_4 ceramics that reduce the amount of sintering additives for the densification.

In the present study, nanosized amorphous Si_3N_4 powder was sintered with a relatively small amount of Y_2O_3 and Al_2O_3 additives by SPS, and densification, phase transformation, and microstructure of the Si_3N_4 sintered bodies were studied. Also, these results were compared with those of the products prepared using submicrometer-sized α-Si_3N_4 powder.

II. Experimental Procedure

Nanosized amorphous Si_3N_4 powder was prepared by a vapor-phase reaction from $SiCl_4$ and NH_3 gases. The amorphous Si_3N_4 powder consisted of spherical particles with an average size of 80 nm (number mean diameter via SEM analysis). The total oxygen content of the nanosized amorphous Si_3N_4 powder was 4.8 mass%. As a reference, submicrometer-sized α-Si_3N_4 powder (β-phase: <5%, total oxygen content: 1.2 mass%, SN-E10 grade, Ube Industries Ltd., Ube, Japan) with an average particle size of 170 nm (number mean diameter) was also used as a starting material. 1.5 mass% Y_2O_3 (average particle size: 300 nm, UU-HP grade, Shin-Etsu Chemical Co. Ltd., Tokyo, Japan) and 0.5 mass% Al_2O_3 (α-phase, average particle size: 500 nm, AKP-20 grade, Sumitomo Chemical Co. Ltd., Tokyo, Japan) powders were added to Si_3N_4 powders as sintering additives. These powders were mixed with a small amount of ethanol, dried, and then sieved with a pore-opening size of 300 μm. The powder mixture was filled in a graphite die of 15 mm in inner diameter and sintered at a temperature of 1500°–1700°C for a holding time of 30 min and at 1800°C for 1 min under a uniaxial pressure of 30 MPa in N_2 atmosphere by SPS (SPS-515S, SPS Syntex Inc., Kanagawa, Japan). The mixed powder was heated at rates of 150 and 300°C/min. The overshoot of the temperature of about 15°C occurred at the rapid heating rate of 300°C/min, although little overshoot of the temperature was monitored at 150°C/min. The heating temperature on the surface of the die was measured with a radiation thermometer. The relative densities of the sintered samples were determined by the Archimedes method. The phase composition and phase transformation of the samples were evaluated using X-ray diffractometry (XRD; MiniFlex, Rigaku Corp., Tokyo, Japan) with Cu$K\alpha$ radiation for sintered samples. The content ratio of the α- and β-Si_3N_4 phases in the samples was estimated from the peak intensities using the

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equation proposed by Gazzara and Messier.[16] The sintered specimens were polished with a 3-μm diamond slurry, and then etched by plasma in CF_4 and O_2 gases. The etched surfaces were observed by scanning electron microscopy (SEM; S-5200, JEOL Ltd., Tokyo, Japan). The average grain size (number mean diameter) of the Si_3N_4 bodies was determined from the linear intercept length of 100 grains in the SEM pictures.

III. Results and Discussion

In the products prepared from nanosized amorphous Si_3N_4 powder at 1500°–1700°C for a holding time of 30 min at a heating rate of 150°C/min, Si_2N_2O was slightly detected as a secondary phase by XRD analysis. The formation of Si_2N_2O may be due to a reaction of Si_3N_4 with the surface oxide in amorphous Si_3N_4 particles during the long sintering process at high temperatures, i.e., 1700°C for 30 min.[2] In a previous study of the sintering of nanosized amorphous Si_3N_4 powder with a typical amount of Y_2O_3 and Al_2O_3 additives,[5] Si_2N_2O was not observed in the products.

Figure 1 shows the effect of sintering temperature on the relative density and α-phase ratio of specimens sintered at 1500°–1700°C for 30 min and at 1800°C for 1 min at 150°C/min using nanosized amorphous Si_3N_4 and submicrometer-sized α-Si_3N_4 powders. In the submicrometer-sized α-Si_3N_4 powder, with sintering at 1500°C, the relative density of the specimen was about 60%. When the temperature increased to 1700°C, the density increased to 93%. At 1800°C for 1 min, the specimen with a high density of >98% was obtained. The transformation from α- to β-phase occurred with the increasing density of the specimens. With sintering at 1800°C, only the β-phase formed. In nanosized amorphous Si_3N_4 powder, on the other hand, only β-phase was observed even at 1500°C and the amorphous phase directly transformed into the crystalline β-phase. The density of the specimens reached 95% even at 1500°C, although the densification of the submicrometer-sized α-Si_3N_4 powder required a high temperature of 1800°C. This suggested that the densification of nanosized amorphous Si_3N_4 powder was achieved at a lower temperature than that of the submicrometer-sized α-Si_3N_4 powder with a relatively small amount of sintering additive. The high sinterability of nanosized amorphous Si_3N_4 powder might be caused by a smaller particle size and a larger amount of total oxygen content of the nanosized amorphous Si_3N_4 powder. The transformation from α- to β-phase for Si_3N_4 ceramics is mainly dependent on the densification.[3] Consequently, because nanosized amorphous Si_3N_4 powder was fully densified at a lower temperature than the submicrometer-sized α-Si_3N_4 powder, the transformation to β-phase might be completed at a lower temperature.

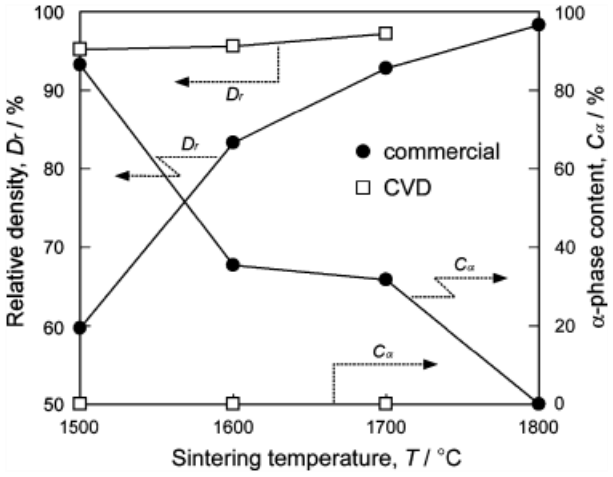

Fig. 1. The effect of sintering temperature on the relative density and α-phase ratio of Si_3N_4 ceramics prepared at 1500°–1700°C for a holding time of 30 min and at 1800°C for 1 min at a heating rate of 150°C/min.

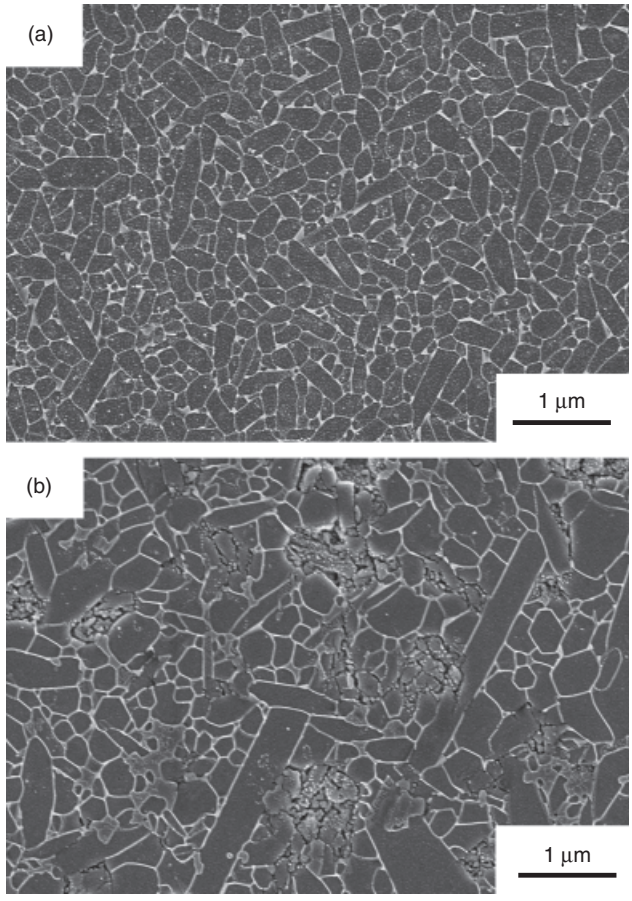

Fig. 2. Scanning electron micrographs of the etched surfaces of Si_3N_4 ceramics prepared at 1700°C for 30 min at 150°C/min using nanosized amorphous Si_3N_4 (a) and submicrometer-sized α-Si_3N_4 powders (b).

Figure 2 shows SEM micrographs of the etched surfaces of the Si_3N_4 ceramics prepared at 1700°C for 30 min at 150°C/min using nanosized amorphous Si_3N_4 and submicrometer-sized α-Si_3N_4 powders. The Si_3N_4 ceramics obtained from nanosized amorphous Si_3N_4 powder were composed of finer equiaxed and elongated grains, compared with those from submicrometer-sized α-Si_3N_4 powder. The growth of elongated Si_3N_4 grains was quite noticeable in Si_3N_4 ceramics prepared using submicrometer-sized α-Si_3N_4 powder. In addition, a residual pore was clearly observed in the Si_3N_4 ceramics obtained from the submicrometer-sized α-Si_3N_4 powder. This supported that the densification of submicrometer-sized α-Si_3N_4 powder was not achieved at 1700°C as shown in Fig. 1. The use of nanosized amorphous Si_3N_4 powder enables to achieve densification at a lower temperature, because nanosized amorphous Si_3N_4 had a higher sinterability compared with the submicrometer-sized α-Si_3N_4. Therefore, the grain growth was inhibited during sintering, resulting in the production of fine-grained Si_3N_4 ceramics.

Using rapid sintering at a heating rate of 300°C/min and at 1800°C for 1 min, dense β-Si_3N_4 ceramics with a relative density of 96% were successfully fabricated without the formation of Si_2N_2O in the product. A SEM micrograph of the β-Si_3N_4 ceramics is shown in Fig. 3. The nearly equiaxed grains with an average size of 300 nm (number mean diameter via SEM images) were observed in the fully dense β-Si_3N_4 ceramics. Suganuma *et al.*[12] and Schneider *et al.*[15] reported dense Si_3N_4 ceramics consisting of fine and equiaxed Si_3N_4 grains from the submicrometer-sized α-Si_3N_4 powder using SPS. Nishimura *et al.*[10] revealed how to form a homogeneous microstructure without elongated grains using nanosized β-Si_3N_4 powder by SPS. Szépvölgyi and Mohai[2] reported that hot pressing of nanosized amorphous Si_3N_4 powder produced Si_2N_2O as a secondary phase. For the densification of these Si_3N_4 powders, the total

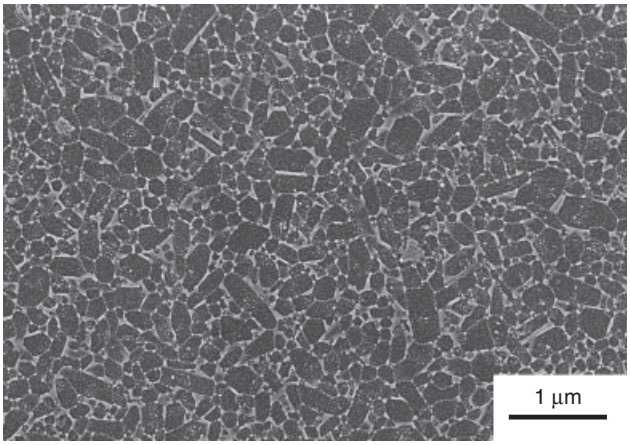

Fig. 3. Scanning electron micrograph of the etched surface of Si_3N_4 ceramics prepared at 1800°C for 1 min at 300°C/min using nanosized amorphous Si_3N_4 powder.

amount of sintering additives over 5 mass% was used. When the amount of additives decreases, the sintering temperature for the densification generally increases, leading to a significant grain growth. In this work, dense and fine-grained Si_3N_4 ceramics were able to be fabricated with a small amount of sintering additives, 2 mass%, and using nanosized amorphous Si_3N_4 powder.

IV. Conclusions

Nanosized amorphous Si_3N_4 powder was sintered with a relatively small amount of sintering additives, 1.5 mass% Y_2O_3 and 0.5 mass% Al_2O_3, by SPS. Densification, phase transformation, and microstructure of the Si_3N_4 sintered bodies were investigated. The densification and phase transformation to β-phase in the nanosized amorphous Si_3N_4 powder were completed at a lower temperature, i.e., 1500°C, than those in the submicrometer-sized α-Si_3N_4 powder. Si_2N_2O formed as a secondary phase in the long sintering at 1500°–1700°C for 30 min at 150°C/min using nanosized amorphous Si_3N_4 powder. When rapid sintering at a heating rate of 300°C/min and at 1800°C for 1 min was used, fully-dense β-Si_3N_4 ceramics consisting of equiaxed grains with an average size of 300 nm were prepared without forming Si_2N_2O.

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