Journal of the European Ceramic Society 20 (2000) 2673–2677

Microstructural development of silicon nitride with aligned β-Si_3N_4 whiskers

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Received 13 January 2000; received in revised form 11 April 2000; accepted 29 April 2000

Abstract

Silicon nitride was sintered with 3 wt.% silicon nitride whiskers that were aligned using tape casting. Sintering was carried out at temperatures between 1550 and 1850°C for 1 h. The α to β phase transformation was complete at 1750°C. XRD results also showed that the amount of β-phase grains in the matrix increased faster than growth rate of the whisker grains at the early stage of sintering. The intensities of the peaks diffracted from the whisker grains increased faster than those diffracted from the matrix β-phase grains after the α to β phase transformation was complete. Both XRD results and the etched microstructures indicated that the whisker grains grew preferentially in the length direction.

Keywords: Aspect ratio; Grain growth; Microstructure-final; Si_3N_4; Whiskers

1. Introduction

Silicon nitride has been considered as a candidate material for structural applications. It exhibits excellent properties including the strength, the fracture toughness, and the high temperature strength among ceramics. Those good properties are closely related to the microstructure that consists of large and fine elongated grains bonded with the glassy grain boundary phase. It has been reported that the large elongated grains not only were contributed to high fracture toughness but also led to the low flexural strength.[1] Such a trade-off between the strength and the fracture toughness according to the grain size was also observed from silicon carbide ceramics that consisted of plate-like grains.[2] Recently, it has been demonstrated that both the strength and the fracture toughness of silicon nitride can be increased at the same time by aligning the large elongated grains.[3]

Microstructural development of silicon nitride has been a subject of many studies.[4–6] Petzow and Hoffmann reported that β-silicon nitride grain growing in oxynitride glass showed a maximum aspect ratio at the completion of α to β phase transformation.[4] They concluded that growth of the grain in the length direction was independent of its width and that the smaller grains exhibited higher aspect ratio. However, the grain growth behavior became more complicated for polycrystalline silicon nitride due to the steric hindrance between β-silicon nitride grains. According to Krämer et al., growth of β-silicon nitride grain was controlled by an interface reaction when it was not hindered by impingement of other β-silicon nitride grains.[5] That also suggests a preferential growth in the length direction before the impingement.

Most of the previous reports on the microstructure of silicon nitride have been performed by analyzing the micrographs taken from the etched surface. However, the micrographs often represent only a small portion of the sample, and it is worth trying a method that can cover a larger portion of it. In this study, microstructural development of silicon nitride was carried out using samples with the aligned silicon nitride whisker seeds. X-ray diffraction (XRD) patterns were employed as major data for analyzing the microstructural development of the samples, and they were compared with SEM micrographs of the plasma-etched samples.

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0955-2219/00/$ - see front matter
PII: S0955-2219(00)00147-3

2. Experimental

90 wt.% α-Si_3N_4 powder (E10, Ube Industries, Tokyo, Japan), 6 wt.% Y_2O_3, 1 wt.% Al_2O_3 and 3 wt.% β-Si_3N_4 whiskers (SN-WB, Ube Industries) were used for this study. According to the manufacturer's information, width and length of the whiskers are 0.1–1.5 μm and 10–50 μm, respectively. However, the whiskers were possibly broken into smaller ones during further processing. Silicon nitride tape with the aligned silicon nitride whiskers was prepared according to the same procedure as previously reported.[6] The tape, after drying was about 150 μm thick, and was cut into sheets with 35 × 35 mm dimensions. Fifty to fifty-three sheets were stacked at 80°C under 50 MPa for 0.5 h to make a sample, and then were placed in an alumina tray for the binder burn-out process. Binder burn-out was carried out in a box furnace in an ambient atmosphere at 550°C for 10 h. Heating rate was 1.5 K/h and cooling was accomplished by simply turning off the power.

After the binder burn-out process, the sample was cold isostatically pressed (CIP'ed) under 250 MPa for 180 s. The CIP'ed green body was sintered at 1550°C for 0.5 h. The bisque fired body was cut into 4 parts. One quarter was left for the microstructural and phase analysis, and the other three quarters were sintered at 1650, 1750 and 1850°C, respectively, for 1 h.

After the sintering, XRD analyses were carried out on the casting surface and surface normal to the casting direction using CuK_α radiation under the condition of 35 kV–25 mA. The area exposed to XRD analysis was larger than 5 × 5 mm. In order to examine the whisker alignment within green body, sample with 5 wt.% whiskers was prepared in the same way as the sample with 3 wt.% whiskers.[6] For comparison, a green body without the whisker addition was also prepared in the same way as the others. Those two surfaces of sintered sample, i.e. the casting surface and surface normal to the casting direction, were machine-polished down to 1 μm diamond slurry, and were plasma etched using equal vol.% of oxygen and CF_4 gas.

3. Results and discussion

Fig. 1 shows XRD patterns from green bodies of samples without the whisker addition and with 5 wt.% whiskers. T, P and N represent the surfaces schematically shown in the diagram. The samples mainly consist of α-silicon nitride. The two patterns from sample without the whisker addition do not show any significant difference meaning that there is no significant microstructural anisotropy. According to the manufacturer's information, the α-silicon nitride powder contains less than 5 wt.% of β-phase. The patterns of sample without the whisker have very weak (210) peak

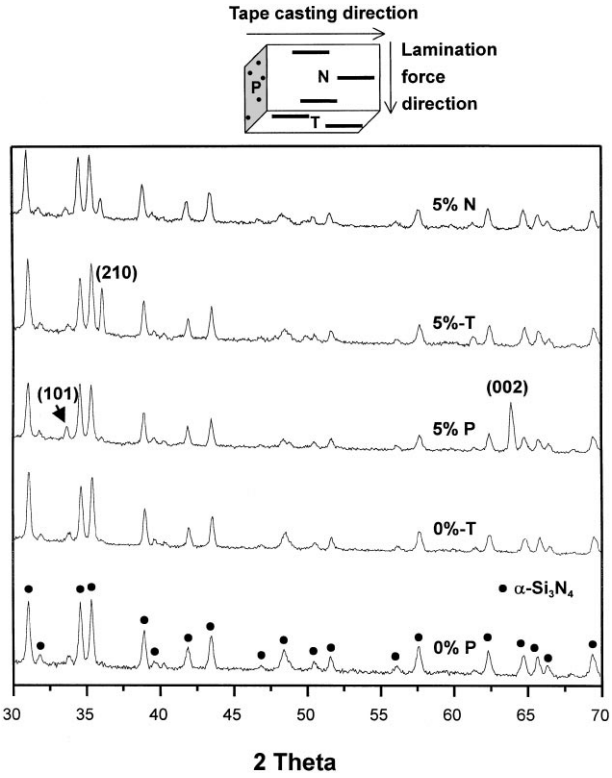

Fig. 1. XRD patterns of green samples without the whisker addition and with 5 wt.% whiskers; the peaks match the standard pattern of α-Si_3N_4 (JCPDS # 09-0250) except the ones marked by the indices; the diagram schematically shows the diffraction surfaces.

of β-silicon nitride. The XRD patterns of sample with 5 wt.% whiskers show a significant difference depending on the diffraction surface. While the pattern diffracted from surface P has a strong (002) peak of β-silicon nitride, those from surfaces T and N have a strong (210) peak of β-silicon nitride. Also, it is interesting to note that the former pattern has a very weak (210) peak of β-silicon nitride and the latter patterns do not have any detectable peak corresponding to the (002) peak. The XRD patterns of sample with 5 wt.% whiskers shown in Fig. 1 support that the whiskers are highly aligned in the casting direction. Moreover, intensity of (210) peak of β-silicon nitride diffracted from surface P of sample with 5 wt.% whiskers is as weak as that of the (210) peak of sample without the whisker addition. It implies that few whiskers were oriented normal to the casting direction. The pattern of surface T of sample with 5 wt.% whiskers has (101) peak of β-silicon nitride as weak as that of sample without the whisker addition. It implies that few whiskers on surface T are oriented to diffract (101) peak of β-silicon nitride.

Fig. 2 shows variations of XRD patterns diffracted from surfaces P and N of samples with 3 wt.% whiskers according to sintering temperatures. The patterns indicate that the α to β phase transformation is complete at 1750°C. During sintering, the microstructures of samples consist of large elongated grains of β-phase growing

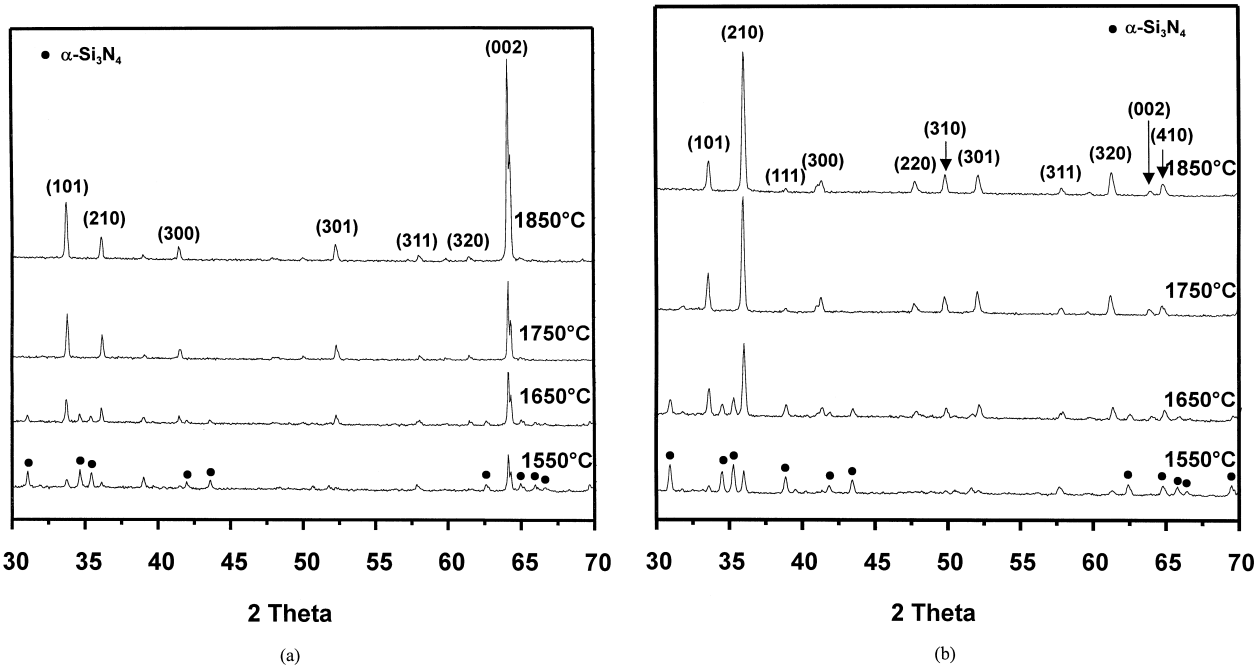

Fig. 2. XRD patterns of sintered samples with 3 wt.% whisker seeds; (a) patterns from surface P and (b) from surface T; peaks marked by closed circle is α-phase and those by the indices β-phase.

from the whiskers (“whisker grains”) and the matrix. The matrix contains fine rod-like β- phase grains that are transformed from the equiaxial α-phase grains. The XRD patterns of Fig. 2(a) have very strong (002) peaks of β-silicon nitride while those of Fig. 2(b) have very weak (002) peaks that are detectable only at the temperature higher than 1650°C. According to a standard XRD pattern of β-silicon nitride (JCPD #33-1160) that assumes a random orientation of the grains, intensity of (002) peak is about 16% that of (210) peak and (101) peak is no weaker than that of (210) peak. Comparison of the patterns of Fig. 2 with that standard pattern suggests that both strong (002) peak of Fig. 2(a) and (210) peak of Fig. 2(b) are diffracted from the aligned whisker grains. As previously shown in Fig. 1, the patterns diffracted from surfaces P and T of green body with 5 wt.% whiskers have as weak (210) peak and (101) peak of β-silicon nitride as those from the corresponding surfaces of samples without the whisker, respectively. Therefore, (210) peak of surface P and (101) peak of surface T can be considered to represent the β-phase grains of the matrix. Then, variations of the intensity ratios of the peaks, (002)/(210) for surface P and (210)/(101) for surface T, provide interesting information on the microstructural development of the current sample according to sintering temperature. Fig. 3 shows variations of those peak ratios. The two peak intensity ratios vary similarly. Both of them decrease and then increase as the temperature increases. They show minima at 1750 and 1650°C, respectively. It means that the amount of β-phase in the matrix increases faster than the growth rate of the whisker grains at the early stage of sintering. During sintering, α-phase grain is less stable than β-phase grain. The former dissolves into the liquid and precipitates onto a more stable grain as β-phase, and the phase transformation proceeds. Fig. 3 shows that those elements dissolved in the liquid are deposited not only onto the whisker grains but also onto the matrix grains in spite of their large size difference. Between 1750 and 1850°C, the two intensity ratios increase. This implies that the whisker grains grow at the expense of the matrix grains after the phase transformation is complete.

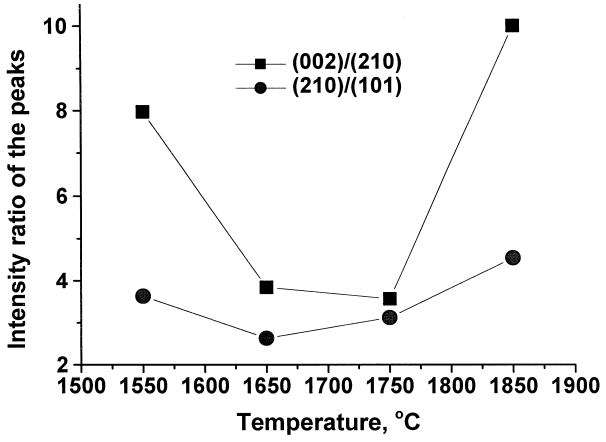

Fig. 3. Variation of the ratios of the two peak intensities shown in Fig. 2(a) and (b); the intensity ratio of (002) peak and (210) peak is taken from Fig. 2(a) and that of (210) peak and (101) peak from Fig. 2(b).

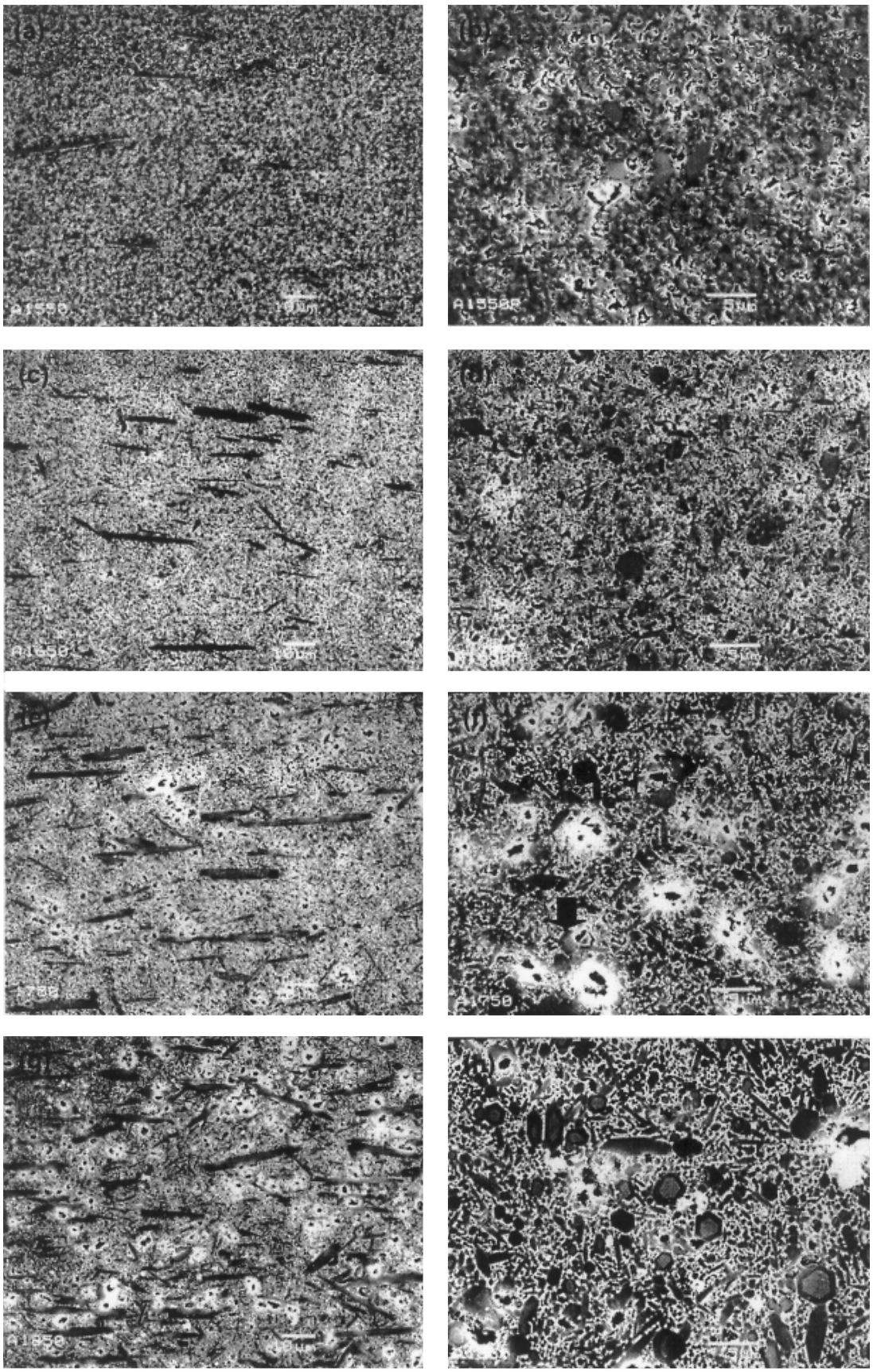

Fig. 4. SEM micrographs of sintered samples; (a), (b) sintered at 1550°C, (c),(d) at 1650°C, (e), (f) at 1750°C, and (g), (h) at 1850°C; (a), (c), (e), (g) surface T and (b), (d), (f), (h) surface P.

The (002) peak of Fig. 2(a) and the (210) peak of Fig. 2(b) represent the basal plane and the prismatic plane of the whisker grain, respectively. Meanwhile, both the (210) peak of the former figure and the (101) peak of the latter figure represent the β-phase grains of the matrix that assume random orientations. Since the intensities of those two peaks representing the β-phase grains of the matrix are proportional to each other and the proportionality is independent of the whisker grains, they can be used as internal references. Variation of the ratio, {(210)/(101)}/{(002)/(210)} of Fig. 3, provides a qualitative information on how aspect ratio of the whisker grains changes according to the temperature. It should be pointed out that the ratio can not be a quantitative measure of the aspect ratio since, among other things, the (210) peak is only one of many peaks representing the whisker grains lying parallel to the casting direction. The ratio shows a maximum at 1750°C. In other words, the aspect ratio shows a maximum at the completion of the α to β phase transformation. It means that the whisker grains grow preferentially in the length direction before the phase transformation is complete, and then, they become thicker for further heat treatment. It is consistent with Krämer's report that is based on the microstructural observation.[5]

Fig. 4 shows the microstructures of samples after sintering. As the temperature increases, both sizes of the whisker grains increases and those grains are observed more often. However, closer examination of samples sintered at low temperature reveals that they have as many whisker grains as the ones sintered at high temperature. Plasma etching does not clearly delineate the whisker grains within the matrix except large ones of sample sintered at 1550°C. Actually, it hardly etches the matrix grains that are mostly in α-phase. Average length and width of the whiskers after the casting are 10.5 and 0.6 μm, respectively. Even though the whiskers grow at 1550°C, they do not seem to grow very much judging from the XRD patterns shown in Fig. 3. As the temperature increases to 1650°C, the microstructure becomes clearer. The whisker grains grow mostly in the length direction as shown in Fig. 4 (c) and (d). Fig. 4(d) shows that the matrix mainly consists of fine acicular grains characteristic of β-silicon nitride. The matrix grains are randomly oriented. Fig. 4(e) shows the microstructure of a sample sintered at 1750°C. Lighter area within the large elongated grain represents the starting whisker and dark area surrounding it the growth region. It can be seen clearly from Fig. 4(e) that the whisker grains grow preferentially in the length direction. Fig. 4(f) shows that the whisker grains also grow slightly in the width direction as indicated by the arrow. Growth of the whisker grains in the width direction can be recognized from the microstructural observation only at the temperature higher than 1650°C. Fig. 4(f) shows that the matrix grains also grow as the temperature increased. Fig. 4(g) also shows the preferential growth in the length direction of the whisker grains. The matrix grains grow big enough to be recognized in Fig. 4(g), and they are randomly oriented. A significant growth in the width direction is readily recognized from Fig. 4(h). The growth in the width direction results in the decrease of aspect ratio at 1850°C as suggested in Fig. 3.

4. Conclusion

Microstructural development of silicon nitride with the silicon nitride whisker seeds is examined using XRD analysis and SEM micrographs. XRD analysis reveals the followings. The α to β phase transformation is complete at 1750°C. At early stage of sintering, the whisker grains grow slower than the rate at which the matrix transforms from α phase to β phase. The whisker grains grow at the expense of the matrix grains on further heat treatment. Aspect ratio of the whisker grains has a maximum at 1750°C. Microstructural change of the etched samples is consistent with the above analysis based on XRD results.

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