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Effect of α-Si_3N_4 initial powder size on the microstructural evolution and phase transformation during sintering of Si_3N_4 ceramics

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Abstract

By using the Si_3N_4 ceramic specimens prepared with fine and coarse α-Si_3N_4 powders, respectively, the phase transformation from α- to β-Si_3N_4 and concurrent microstructural evolution during sintering were monitored. For the compact prepared with fine powder, the α/β transformation was completed much earlier than the coarse powder. The higher fraction of pre-existing β-grains in fine powder and its higher reactivity compared to those of coarse one are likely to cause a rapid phase transformation. The growth rate of β-Si_3N_4 grains at the expense of α-Si_3N_4 during phase transformation stage was quite significant while that after they impinge each other was very limited. As a result, the specimens prepared with coarse and fine initial α-Si_3N_4 powders resulted in coarse and fine grained β-Si_3N_4 ceramics, respectively. The specimen prepared with mixture of fine and coarse α-Si_3N_4 powders exhibited the microstructure containing a few elongated large grains and showed an increased value of fracture toughness.

Keywords: Grain growth; Microstructure; Si_3N_4; Structural applications; Toughness and toughening

1. Introduction

The control of grain size and its distribution is one of primary concerns in the processing of Si_3N_4 ceramics. Particularly, the design of duplex microstructure containing a few large elongated β-Si_3N_4 grains is quite important to ensure high fracture toughness.[1–16] Therefore, many investigations have already been carried out to examine the relations between the microstructure of Si_3N_4 ceramics and various processing parameters; sintering time,[2,8,9,11,12] sintering temperature,[1,2,6] and addition of sintering aids [5] as well as large seed particles.[7,9,10,11,13–16] The effect of Si_3N_4 starting powder has also been examined mainly in terms of α/β-ratio.[9,11,14–23]

Although the desired duplex microstructure has also been obtained by using the β-powders of a broad particle size distribution,[8,13] α-Si_3N_4 powders are more commonly used as starting powders.[1–3,5,6,12] In this case, however, the microstructure control during sintering becomes further complicated because the microstructural evolution is critically influenced by the α/β-transformation.[22–25] Krämer et al.[24,25] have examined the growth kinetics of β-Si_3N_4 grains highly dispersed in oxynitride glass, and suggested a theoretical model describing the growth of β-grains at the α/β-transformation stage. They have also shown that, with proceeding of α/β-transformation, the growth of β-grains is limited by a sterical hindrance caused by adjacent β-grains. On the other hand, Sajgalik et al.[22] have shown that the powder mixture containing the coarse α-Si_3N_4 particles exhibits slower transformation than a mixture consisting of the fine α-Si_3N_4 particles. However, the relationship between the microstructural evolution and the phase transformation is not yet determined in detail.

In the present investigation, the microstructural evolution and the phase transformation during sintering of α-Si_3N_4 powder compact were examined with the main focus on the effect of initial particle size. It was observed that the finer the initial powder, the higher the rate of phase transformation. As suggested,[24,25] the sterical hindrance by adjacent β-grains is an important limiting factor for the growth of β-grains. They can grow extensively at the expense of neighboring α-grains remained at

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the sintering temperature. The results were implemented for the fabrication of Si_3N_4 ceramics of duplex microstructure. When a small amount (10 wt%) of coarse α-powders were added into fine α-powders, the coarse α-particles persisting during sintering have provided a room for extensive growth of some β-grains.

2. Experimental procedure

High α-silicon nitride powders of fine and coarse size (SN-E10 and SN-E03, respectively, Ube Industries, Inc., Ube, Japan) were used as starting materials. The average particle sizes determined by the producer by using centrifugal sedimentation technique were 0.5 μm and 1.0 μm, respectively. The fraction of β-phase was approximately 5 wt% for the fine powder and 2 wt% for the coarse one. The powders were mixed with 6 wt% Y_2O_3 (Grade C, HCST Berlin GmbH, Goslar, Germany) and 2 wt% Al_2O_3 (AES-11C, Sumitomo Chemical Corp., Osaka, Japan), and ball-milled for 24 h with isopropanol. After drying, the powders were remilled dry for 4 h and then sieved using a 60-mesh sieve. Hereafter, the specimens prepared with fine and coarse powders will be referred to as F- and C-specimens, respectively. The powders were compacted into cylindrical specimens 10 mm in diameter and then cold isostatically pressed under a pressure of 150 MPa. The green densities were about 48% and 56% of theoretical for the F- and C-specimens, respectively.

In order to observe the microstructural evolution and the phase transformation from the early stage of sintering, heat-treatment was carried out for 0 min at temperatures ranging from 1100 to 1700°C, with an interval of 100°C. Heat-treatment for 0 min means that the specimens were immediately cooled after the desired temperature was reached. The specimens were also treated at 1760°C for different periods of time from 0 min to 3 h. The heating rate of 30°/min was used and all the treatments were carried out in a nitrogen atmosphere (pressure: 127 KPa).

The microstructures of the specimens after heat-treatment were examined either by fracturing or by polishing. For the specimens sintered at 1760°C for 3 h, the polished sections were chemically etched for 1 min with molten NaOH, and an image analyzer (IP Lab Spectrum, Signal Analytics Corp., Vienna, USA.) was used to determine the microstructural characteristics. The shortest diagonal and the longest diagonal of each grain, d and l, were determined and d was considered to represent its grain size. The characterization of large grains was made by determining the average size of the largest 10 grains, $\bar{d}_{LG}$.[6] A total of 6000 grains at least were observed for each specimen. The areal fraction was plotted as a function of grain size as suggested by Hirosaki et al.[26] For the microstructure with extensively grown large grains, the areal fraction of those large grains becomes quite important even though their numbers are very limited. On the other hand, the fracture toughness of the specimens was determined by using the indentation method proposed by Evans et al.[27] with the indentation force of 98 N. The fraction of β-Si_3N_4 phase content was determined by X-ray diffractometry with CuK_α radiation at 35 kV as proposed by Gazzara et al.[28]

3. Results and discussion

The observed variation of the relative density and the fraction of residual α-phase as a function of heat-treatment temperature and time are shown in Fig. 1(a) and (b), respectively. The green density of the F-specimen is lower than that of the C-specimen probably because the friction between the fine particles is more important than that of coarse particles. Up to 1300°C, practically no microstructural change has occurred except a very slight increase in density of the F-specimen. The density increased remarkably from 1500°C and the shrinkage rate of F-specimen was higher than that of C-specimen. After the sintering at 1700°C for 0 min, both specimens showed almost same density (79%), and they increased to 82% after sintering at 1760°C for 0 min. During

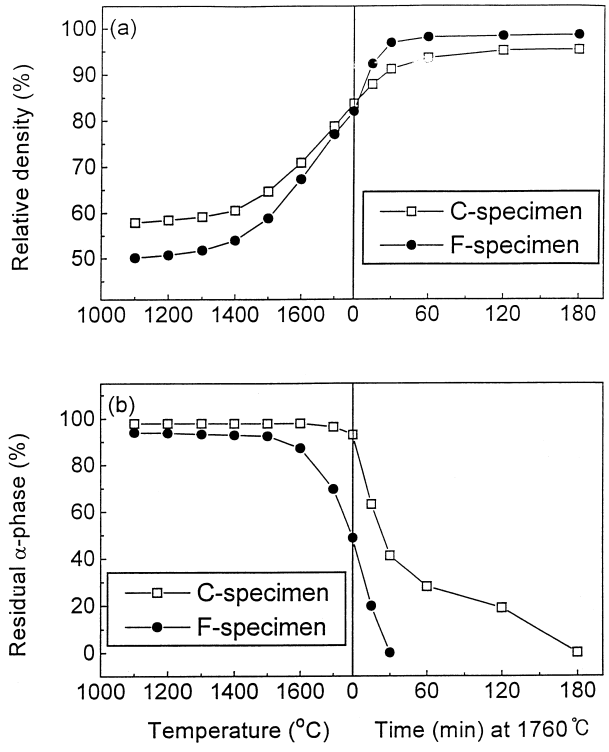


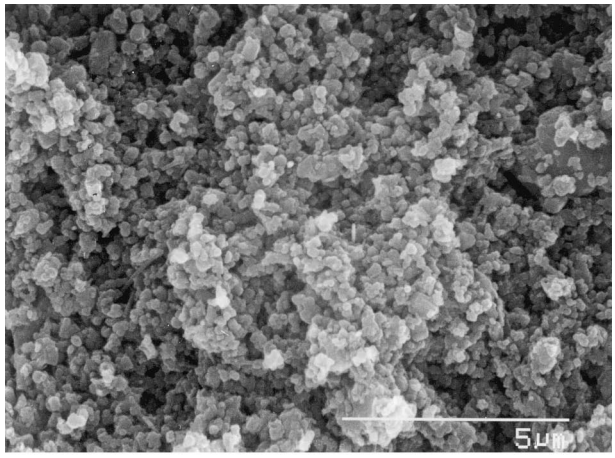
Fig. 1. The observed variation of (a) the relative density and (b) the fraction of α–phase as a function of heat-treatment temperature and time.

prolonged sintering at 1760°C, the densification of the F-specimen was more rapid than that of the C-specimen. The density of F-specimen increased and reached an endpoint value (98.7%) after 1 h. For the C-specimen, on the other hand, the density increased steadily and reached an endpoint density after 3 h. The final density of the C-specimen (97.5%) was slightly lower than that of the F-specimen.

As shown in Fig. 1(b), the size of α-powders had also a discernible effect on the transformation kinetics: the α/β-transformation in C-specimen is much slower than that of F-specimen. For the C-specimen, the transformed β-fraction was negligible up to 1600°C. It increased slightly with temperature and 7% of β-phase had been detected after the treatment at 1760°C for 0 min. With the increase of heat-treatment time at 1760°C, the amount of transformed β-particles increased rapidly and its fraction was determined to be 59% after 30 min. From this point, however, the transformation rate decreased again, so that it took 3 h to complete the transformation. For the F-specimen, on the other hand, the transformation was observed to occur from 1600°C and more than half of initial α-phase was already transformed to β after the treatment at 1760°C for 0 min. The α/β-transformation was completed after 30 min at this temperature.

Fig. 2(a) and (b) are the fracture surfaces of the specimens obtained after the heat-treatment at 1300°C for 0 min. As described previously, the treatment resulted in practically no change in density as well as in α/β ratio of the compacts so that the microstructures are almost the same as those of green compacts. In the F-specimen, however, the local densification is observed to occur most probably due to agglomerates presented in the initial powders. From Fig. 2(a), the average size of primary particles is seemed to be much smaller than 0.5 μm which is the value determined by sedimentation technique. In the case of C-specimen, on the other hand, it can be noted from Fig. 2(b) that the particles of cubic shape are more or less uniform in size and most of them still remained in a physically aggregated state.

As shown in Fig. 3(a) and (b), an appreciable change in microstructure occurred when the specimens were treated at 1600°C for 0 min. In both specimens, compared to Fig. 2, the particles approached significantly toward one another resulting in densification and pore elimination. In the F-specimen [Fig. 3(a)], the size of spherical α-grains has also increased notably. However, small amount of transformed β-Si_3N_4 particles (13%) in this specimen is not clearly distinguished from the microstructure. In the C-specimen, the grain growth was not observed to occur but the initial cubic shape of particles was changed to nearly spherical. Up to this heat-treatment condition, therefore, the microstructural change in Si_3N_4 specimens is quite similar to that which occurred in systems without any phase transformation.



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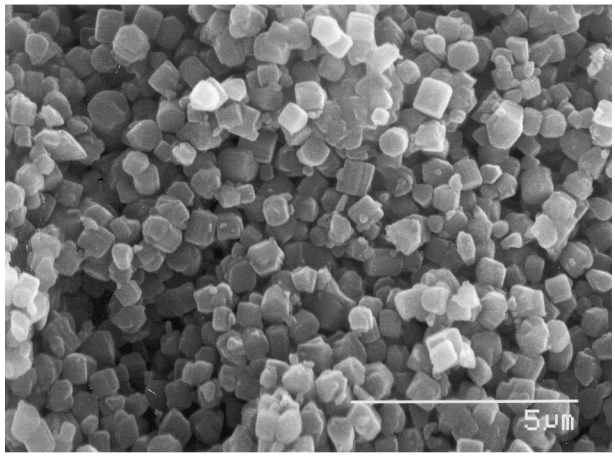
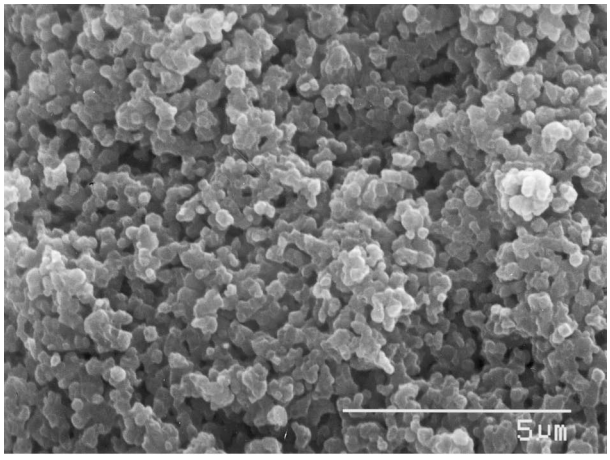


(b)

Fig. 2. Fracture surfaces of the specimens obtained after the heat-treatment at 1300°C for 0 h: (a) F-specimen and (b) C-specimen.

Densification and grain growth are the main features of microstructural change.

The α/β phase transformation and consequent microstructural change are clearly discerned when the specimens are treated at 1760°C. After the treatment for 0 min, the β-Si_3N_4 particles of elongated shape are easily distinguished in the F-specimen [Fig. 4(a)] for which the transformed β-amount is already 51%. For the C-specimen [Fig. 4(b)], however, the β-particles not yet appeared apparently but the coarsening of α-particles is noticed. After 5 min at this temperature (Fig. 5), most particles in the F-specimen shown in Fig. 5(a) are in β-form with an elongated shape. Note that the fraction of β-Si_3N_4 phase in this specimen is 81%. In the C-specimen, the presence of a few β-particles is also clearly noted from its elongated shape as indicated by arrows in Fig. 5(b). From the marked region, it can be noted that the growth of β-grain occurred mainly in length direction by consuming the adjacent α-particles. For that specific β-grain, the shortest diagonal was 0.2μm but its length was more than 5 μm.



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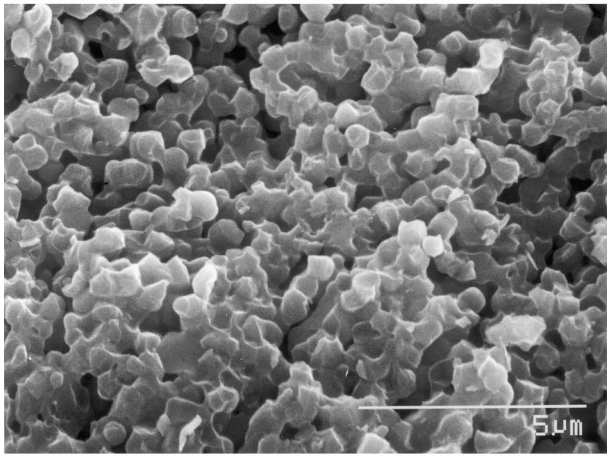
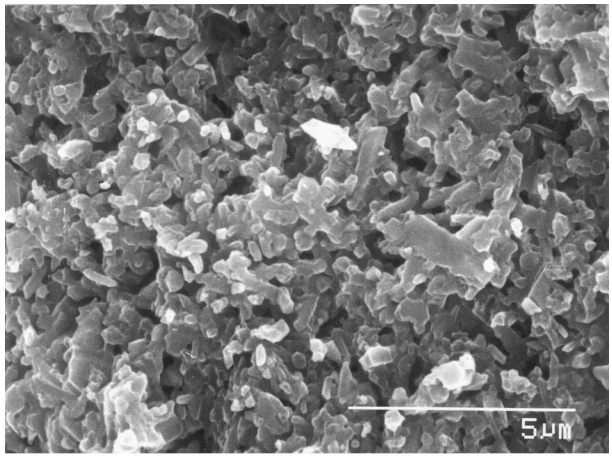


(b)

Fig. 3. Fracture surfaces of the specimens obtained after the heat-treatment at 1600°C for 0 h: (a) F-specimen and (b) C-specimen.



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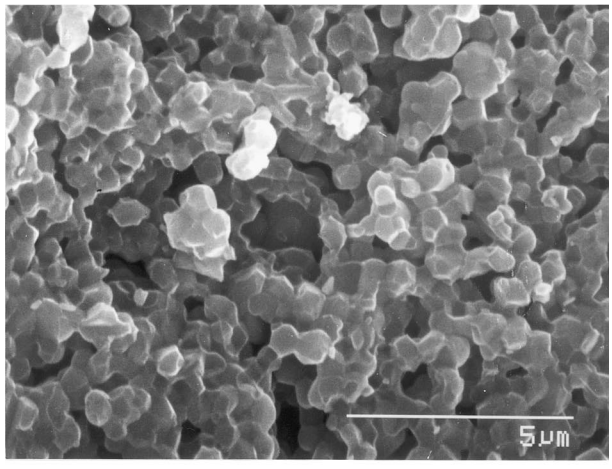


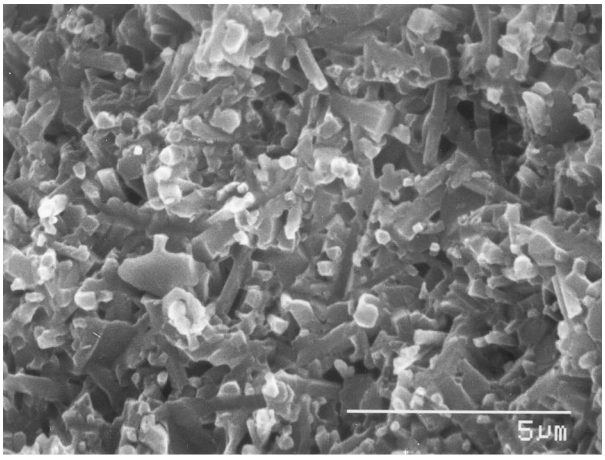
(b)

Fig. 4. Fracture surfaces of the specimens obtained after the heat-treatment at 1760°C for 0 h: (a) F-specimen and (b) C-specimen.

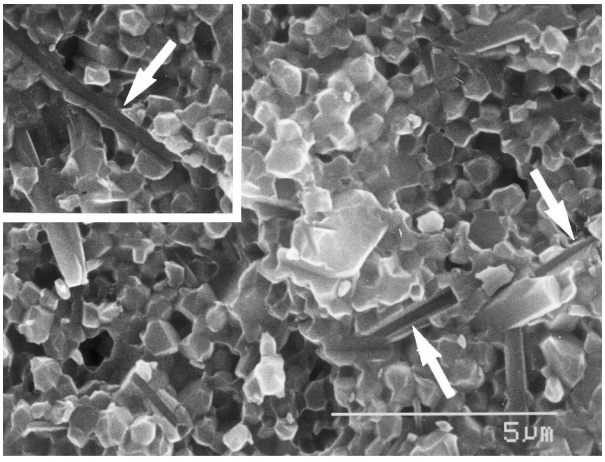
After 30 min at 1760°C, the α/β-phase transformation was completed in the F-specimen and its fracture surface is shown in Fig. 6(a). Compared to Fig. 5(a), the growth of β-particles was not notable, which means that the rate of grain growth after the completion of phase transformation is rather slow. On the other hand, for the C-specimen in which 41% of α-particles still remained [Fig. 6(b)], a significant growth of β-particles is noted. At this condition, the growth in shortest diagonal direction was more pronounced than that in length direction so that the aspect ratio of β-grains has decreased. It is believed that the growth of β-grains in length direction has been sterically hindered by impinging each other.

Fig. 7(a) and (b) show the polished microstructures of the specimen sintered for 3 h at 1760°C. The grain size of F-specimen was much finer than that of C-specimen. According to the microstructural parameters of the specimens given in Table 1, it can be noted that the average values of d, l and $\overline{d}_{LG}$ for the C-specimen are indeed all greater than those of the F-specimen. These experimental observations suggest that the final size of β-grains in Si_3N_4 ceramics is mainly determined at the α/β-transformation stage. The growth of β-grains when their adjacent grains are in α-phase is much more important compared to that after the completion of phase transformation.

In this respect, the effect of initial α-particle size on the final microstructure can be easily understood with the classical kinetics of crystal nucleation. The higher fraction of pre-existing β-grains in the fine powder (5 wt%) than that in the coarse one (2 wt%) may primarily cause the difference in nucleation rate, as suggested by Dressler et al.[15] Due to enhanced reactivity of the fine α-particles, the high rate of β-phase nucleation is also expected for the F-specimen and the large number of β-nuclei results in the small β-grains. However, it should be also noted that the other characteristics of initial powder such as oxygen content, powder morphology etc.[9,13,15 24,25] are also known to change the nucleation kinetics.

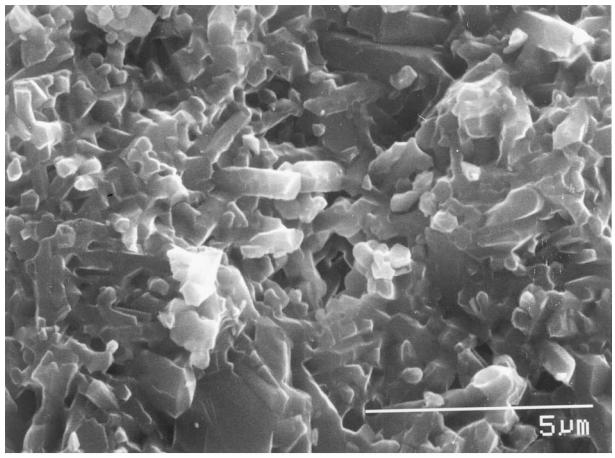


(a)



(b)

Fig. 5. Fracture surfaces of the specimens obtained after the heat-treatment at 1760°C for 5 min: (a) F-specimen and (b) C-specimen.



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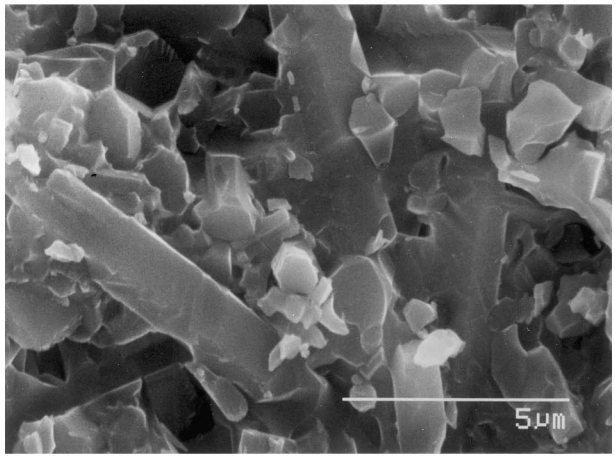


(b)

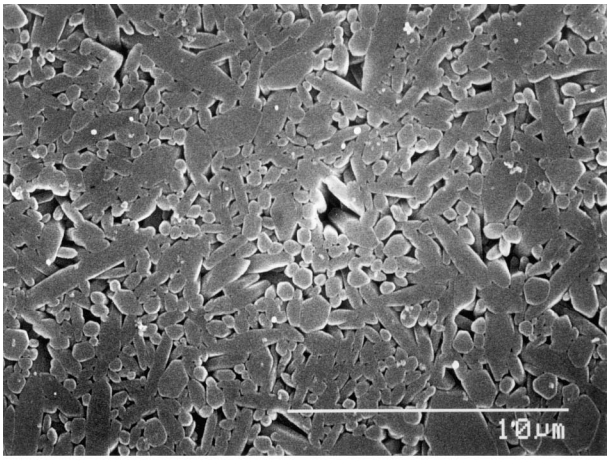
Fig. 6. Fracture surfaces of the specimens obtained after the heat-treatment at 1760°C for 30 min: (a) F-specimen and (b) C-specimen.

The results can be implemented to produce a desired duplex microstructure consisting of fine matrix and a few elongated β-grains. Since the growth of β-grain is greatly inhibited when they impinge each other, the presence of some α-particles until the later stage of sintering is expected to result in duplex microstructure. Note that the persisting α-particles would provide a room for further growth of β-grains. This has been tested experimentally by preparing the specimen with the mixture of fine and coarse powders: 10% of coarse α-powders in weight were mixed with fine α-powders. This specimen will be referred to as the M-specimen.

Fig. 8(a) and (b) are the microstructure of the M-specimen obtained after the heat-treatment at 1760°C for 0 and 30 min, respectively. For the specimen treated for 0 min, the amount of remained α-phase particles was determined to be 60%. It can be noted from Fig. 8(a) that the overall matrix microstructure resembles to that of F-specimen [Fig. 4(a)] except the presence of a few large particles. From their more or less rounded morphology, these large particles are believed to be the α-particles from added coarse powders. After the treatment for 30 min [Fig. 8(b)], the remained α-phase was determined to be less than 5%, and the β-grains which are almost same in size to those observed in Fig. 6(a) consist the microstructure. The important difference between two is that a few very large β-grains already grown up to 10 μm in length and 2 μm in thickness were observed in the M-specimen.

The microstructure of the M-specimen obtained after the sintering for 3 h at 1760°C is shown in Fig. 9. It shows a typical duplex microstructure with a few β-grains which have grown extensively to a size much larger than those observed in the C-specimen. However, the size of matrix grains is quite similar to that of the F-specimen. Note from Table 1 that the average size of the largest 10 grains of the M-specimen is much larger than those of two other specimens. Those large grains are

expected to be produced mainly by the material transfer from the remaining coarse α-powders to the neighboring β-grains. The grains once grown at this α/β-transformation stage and the preexisting large β-grains in the starting coarse powder may further act as the embryos for the exaggerated grain growth in the later stage of sintering.[29,30]



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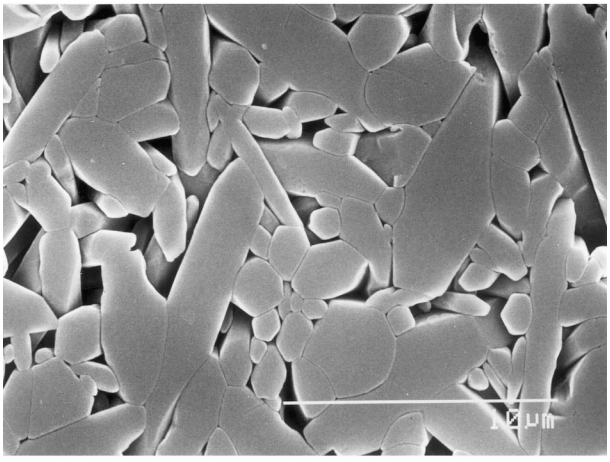


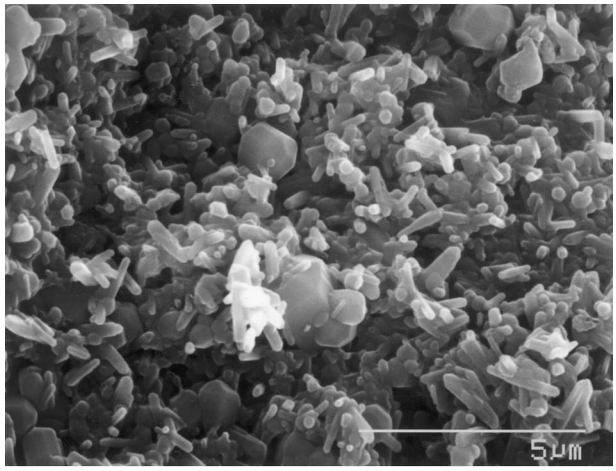
(b)

Fig. 7. Polished surfaces of the specimens obtained after the heat-treatment at 1760°C for 3 h: (a) F-specimen and (b) C-specimen.

Table 1
Microstructural parameters of the specimens sintered at 1760°C for 3 h

	$\bar{d}$ (μm)	$\bar{l}$ (μm)	$\bar{d}_{LG}$ (μm)
F-specimen	0.2	0.5	2.3
C-specimen	0.8	1.6	2.7
M-specimen	0.3	0.7	3.9

The characteristic of duplex microstructure of the M-specimen is again clearly revealed when the areal fraction is plotted as a function of grain size (Fig. 10). The areal fraction of grains larger than 5 μm in the M-specimen reached almost 20%. The fracture toughness determined was indeed higher for the M-specimen than those for other specimens. It was 7.8, 5.3 and 5.2 MPa $m^{1/2}$ for M-, C- and F-specimen, respectively. The production of Si_3N_4 ceramics of duplex microstructure by this simple powder mixing method has a great advantage because the heat-treatment temperature is much lower than usually used. In general, the specimens were treated at temperatures ranging from 1850 to 2000°C to induce an exaggerated grain growth of some β-grains.[1,2,4,6,8–11,13,15,16,26,29] Note that those elongated large grains are formed after the completion of the α/β-transformation, while the large grains in the M-specimen are formed mainly during the α/β-transformation stage.



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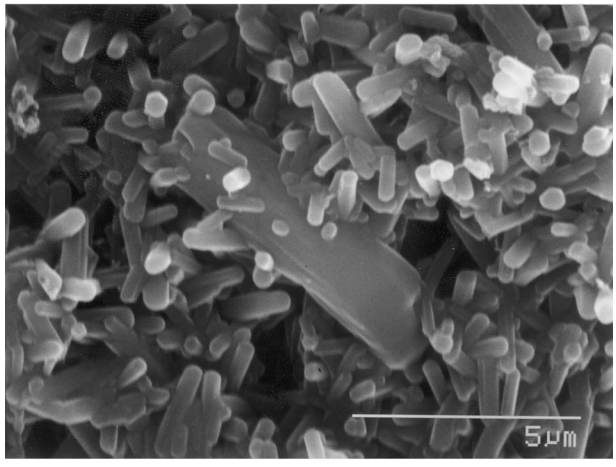

(b)

Fig. 8. Fracture surfaces of the M-specimen obtained after the heat-treatment at 1760°C for (a) 0 h and (b) 30 min.

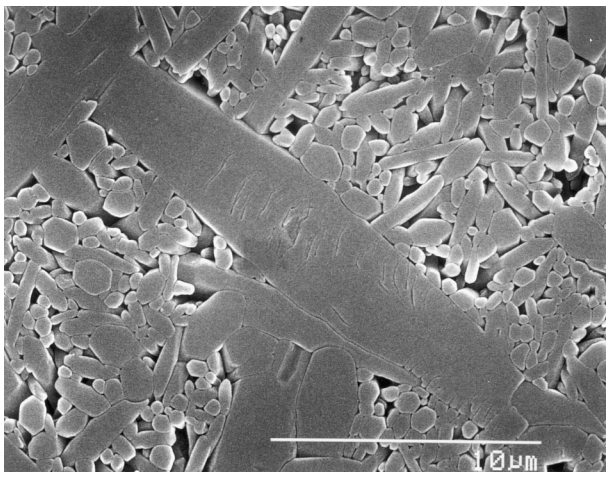

Fig. 9. Polished surface of the M-specimen obtained after the heat-treatment at 1760°C for 3 h.

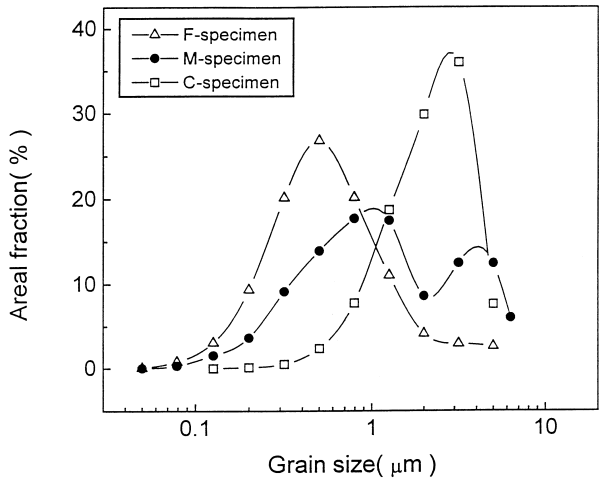

Fig. 10. Areal fraction as a function of grain size for the specimens sintered at 1760°C for 3 h.

4. Conclusion

This investigation has shown that the specimen prepared with fine α-Si_3N_4 powders exhibits much faster α/β-transformation compared to that prepared with coarse α-Si_3N_4. On the other hand, the growth kinetics of β-Si_3N_4 grains during the transformation stage at the expense of α-Si_3N_4 was observed to be much faster than that after the completion of phase transformation. As a consequence, the size and size distribution of β-Si_3N_4 grains are critically dependent on those of initial α-Si_3N_4 powders.

When the specimen was prepared with fine α-Si_3N_4 powders containing a small fraction of coarse α-Si_3N_4 powders, the duplex microstructure consisting of a few extensively grown large grains in fine-grained matrix was produced. The coarse α-Si_3N_4 particles remaining without transformation until the later stage of sintering are expected to induce an extensive growth of some β-Si_3N_4 grains. A practical significance of the result is that the Si_3N_4 ceramics with increased fracture toughness could be obtained by sintering at relatively low temperature.

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