The α- to β-Si₃N₄ transformation in the presence of liquid silicon

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The compacts consisted of α, β-Si₃N₄ and free silicon are heat treated in the range 1650° C to 1750° C in an argon atmosphere in order to observe the following behaviours; the α to β phase transformation and variations of the microstructure during heat treatment in silicon nitride. For the microstructural observation of the heat treated specimens, the same grains in the polished surface were investigated before and after eliminating the retained silicon by etching. The α to β phase transformation, in this case, occurs via silicon melts irrespective of added β-Si₃N₄. Both α and β phases are soluted and precipitated into molten silicon and their morphology are changed from an equiaxed shape to prismatic one. Although elongated grains are precipitated at low temperature or in the early stage of heat treatment, fine precipitated β grains are mainly observed with increasing heat treating temperature.

1. Introduction

Sintered Si₃N₄ ceramics are being considered as components in many thermochemical applications. Silicon nitride, a nitrogen compound with a highly covalent bond characteristics, has two polymorphic forms designated α- and β-phase [1]. It has long been established that the α-phase can be transformed to the β-phase by heat treatment at temperatures exceeding 1500° C [2–3, 22]. This phase transformation has been known to be reconstructive and monotropic, and it takes place readily in the presence of a suitable liquid phase.

It was reported that the α to β phase transformation and growth of elongated prismatic β grains were closely correlated [4–8]. Since the α to β transformation necessarily implied the growth of β crystals, the phase transformation and grain size were correlated [9]. Lange pointed out that the development of elongated β grains in hot pressed Si₃N₄ was of major significance to obtain high strength material [10]. However, all of the previous data on the α to β phase transformation were obtained as by-products of studies concerned primarily with the sintering of silicon nitride.

The thermal decomposition of silicon nitride occurs with increasing sintering temperature [11–13]. Therefore, the sintered Si₃N₄ ceramics may be composed of several phases: free silicon from the decomposition of Si₃N₄, α and β phases, and sintering aid compounds. Kaiser et al pointed out that some amounts of nitrogen was dissolved in a molten silicon [14], and Inomata et al reported that β-Si₃N₄ single crystals were grown from Si melts [15]. These suggest that free silicon contained in sintered Si₃N₄ may be also a suitable liquid phase for the phase transformation. In addition

to these reports, Knoch et al reported that processing parameters like β-fraction in the starting powder, applied pressure and thermal history were important factors influencing the phase transformation and correlated development of microstructure [16].

In this study, the effects of each constituent on the α to β phase transformation and variations of the microstructure are evaluated from the mixtures of α-, β-Si₃N₄, and free silicon by heat treatment in the range 1650° C to 1750° C with various times.

2. Experimental procedures

Two kinds of commercial Si₃N₄ powders were used in this investigation. One* consisted of mainly α-phase and the other was only β-phase. Both powders were composed of nearly equiaxed particles. The silicon powder used throughout the study was 99.99% pure and its mean size was 110 μm. In order to investigate the effect of Si and β-Si₃N₄ on the α to β phase transformation, the powders used for the green compacts were prepared by wet mixing the Si₃N₄ powder with 10 wt % Si in acetone for 12 h using a plastic bottle and alumina balls. Cylindrical compacts, typically of 0.5 g, were formed by uniaxial preforming and isostatic pressing at 14.3 kg mm⁻² in the absence of a binder. The specimens were then embedded in loosely packed Si₃N₄ powder contained within a graphite crucible and placed in a graphite element furnace.† The specimens were heat treated in the range 1650° C to 1750° C upto 180 min in an argon atmosphere. The heating was performed to reach at the required temperature for 1 h. Exact cooling rates were not measured, but generally the heat treated specimens cooled to below 1400° C in less than 7 min.
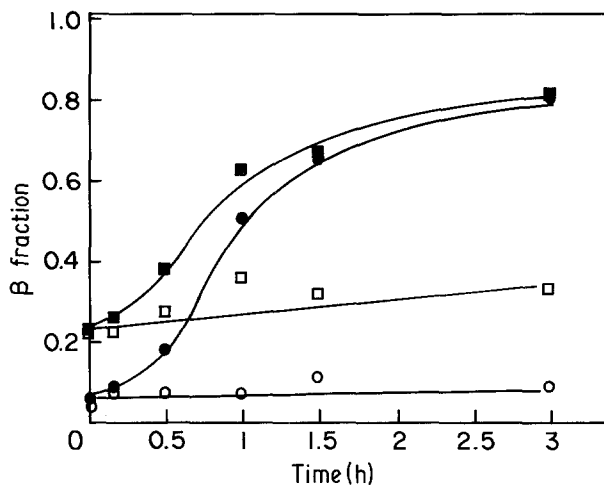
Figure 1 Beta fraction plotted against heat treating time for the α-Si₃N₄ containing 10 wt % Si and/or 10 wt %. β-Si₃N₄ heat treated at 1700° C (○ only α-phase, ● α-phase + 10 wt % Si, □ α-phase + 10 wt % β-phase, ■ α-phase + 10 wt % Si + 10 wt % β-phase).

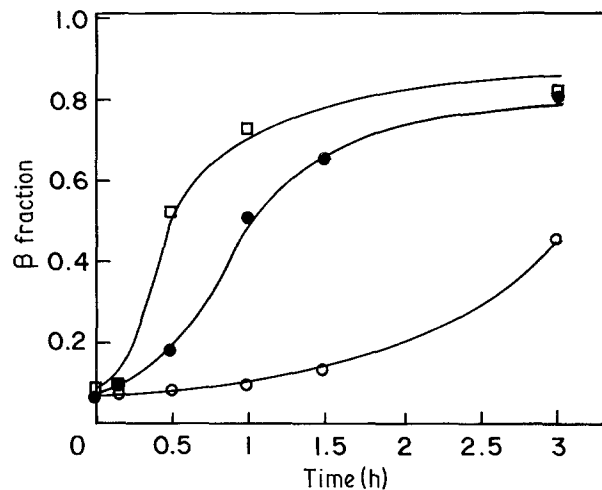*Figure 2* Beta fraction plotted against heat treating time for the α-Si₃N₄ containing 10 wt % Si heat treated at various temperatures (○ 1650° C, ● 1700° C, □ 1750° C).

For the X-ray diffraction analysis, the compacts were ground in a mortar and pestle and examined by an X-ray diffraction unit (Rigaku, Japan) using nickel filtered CuKα radiation. The β fraction was determined by comparing the intensities of α_{210} and β_{210} diffraction peaks, in a manner described by Gazzara [17]. Microstructural observation was performed using light (Zeiss, West Germany) and scanning electron microscope (ETEC Autoscan, Co, Hayward, CA USA). The specimens were prepared by mounting in bakelite and hand polishing through a sequence of 6 μm SiC abrasive paper, 1, 0.3, 0.05 μm alumina powders. Once polished, the specimens were ultrasonically cleaned. After polishing, the silicon grains with precipitated β-Si₃N₄ were observed by optical microscope. Subsequently, the retained silicon was eliminated from the specimen by etching in a concentrated HF + HNO₃ solution for 10 min. And then, the etched surface was investigated by scanning electron microscope. As above two observations were compared with the same region of the specimen before and after etching, variations of the morphology could be obviously investigated.

3. Results and discussion

3.1. Effects of added Si and β-Si₃N₄ on the α to β transformation.

Fig. 1 shows the phase transformation curves plotted against time during heat treatment of α-Si₃N₄ with and without Si and β-Si₃N₄ at 1700° C. During heat treatment, variations of the β fraction occurs dramatically. When silicon is added to α-Si₃N₄ irrespective of the addition of β-Si₃N₄, the β fraction is gradually increased. In the absence of Si, however, no α to β phase transformation is detected even after prolonged periods of heat treatment. These effects of silicon on the transformation mean that molten silicon is also acted as a suitable liquid phase for the transformation as does any sintering aid in sintered Si₃N₄. Liquid phase effects on the phase transformation in silicon nitride were reported by Bowen *et al*. They reported that the α to β phase transformation was not detected

without additives at temperatures up to 1750° C and that the transformation was occurred in compacts containing a few percent of magnesia [18].

Variations of the β fraction of the compacts composed of only α-Si₃N₄ (open circles of Fig. 1) are compared with those of compacts with the addition of 10 wt % β-Si₃N₄ (open squares of Fig. 1) in order to investigate the effects of β-Si₃N₄ on the phase transformation. The differences of the β fraction between two cases are not essentially changed during heat treatment. However, if 10 wt % silicon is added to the above two cases (closed circles and squares of Fig. 1, respectively), the transformation has taken place and variations of each curve have the similar tendency with the heat treating time. These facts suggest that addition of only β-Si₃N₄ can not influence the phase transformation and the transformation is necessarily required in the presence of a suitable liquid phase. Therefore, it is considered that the transformation takes place by solution and precipitation mechanism. This mechanism can be verified by the observation of the microstructure of the heat treated specimen. However, the fact that the presence of β-Si₃N₄ does not influence the phase transformation could not mean that β-Si₃N₄ can not be soluted and precipitated into molten silicon. This will be discussed later with observation of the microstructure in detail.

3.2. Effects of heat treating temperature on the α to β transformation

The specimens with selected composition were heat treated in the range 1650° C to 1750° C upto 3 h in order to evaluate the effects of heat treating temperature on the phase transformation. Fig. 2 shows the phase transformation curves of α-Si₃N₄ with 10 wt % Si and Fig. 3 shows those of α-Si₃N₄ with 10 wt % Si and 10 wt % β-Si₃N₄. In both cases, variations of the β fraction have a similar tendency irrespective of heat treating temperature. But the specimens heat treated at 1650° C are more slowly transformed than above 1700° C. This seems to be resulted from the differences of the dissolution rate of α-Si₃N₄ and the dispersion of Si melts at those temperatures. Since the dispersion
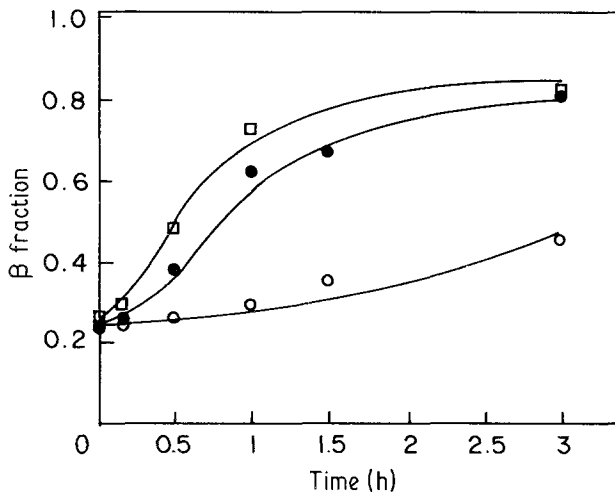
Figure 3 Beta fraction plotted against heat treating time for the α-Si_3N_4 containing 10 wt % Si and 10 wt % β-Si_3N_4 heat treated at various temperatures (O 1650° C, ● 1700° C, □ 1750° C).

of Si melts is occurred with increasing heat treating temperature, the total interface area between Si melts and the surrounding α-Si_3N_4 particles is increased. Subsequently, the materials transport required for the transformation is occurred more easily at elevated temperature. Therefore, the rate of transformation is increased with heat treating temperature. And as will be shown later, the increased rate of transformation results in the change of the size of precipitated β-Si_3N_4.

In the absence of Si, the phase transformation is not detected at each temperature as the results in the previous section. Additionally, the transformation is not also observed with only 10 wt % β-Si_3N_4. These results can be shown in Fig. 4, which is the phase transformation curves plotted against time during heat treatment of α-Si_3N_4 with and without β-Si_3N_4 in the range 1650° C to 1750° C. These results suggest that the phase transformation takes place readily in the presence of a suitable liquid phase and silicon melt is one of those liquids, and that β-Si_3N_4 does not effect the phase transformation irrespective of heat treating temperature.
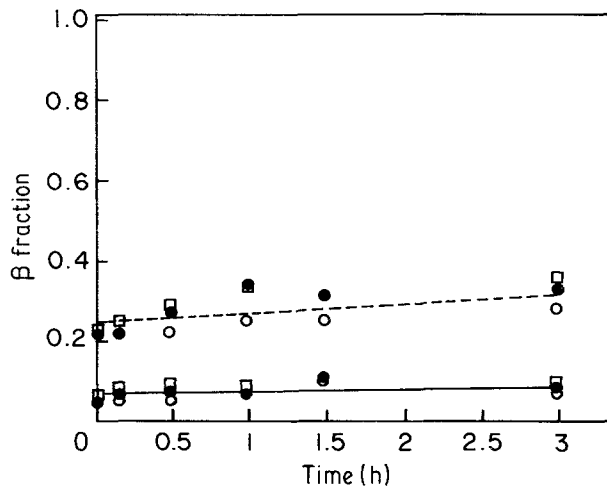
3.3. Microstructure of transformed β-Si_3N_4

When the Si_3N_4 ceramics were heat treated, it was well known that the change in morphology of Si_3N_4 particles compared with the starting powder is accompanied by solution and precipitation mechanism. However, since the morphology of precipitated β-Si_3N_4 dominates the mechanical properties of Si_3N_4 ceramics [10, 19], it is significant to understand the changes in morphology during heat treatment.

At the previous sections, it can be found that α-Si_3N_4 is dissolved and reprecipitated as β-Si_3N_4 through molten silicon. Therefore, the observation of the change in morphology of the precipitated β-Si_3N_4 via molten silicon is noteworthy. Then, α-Si_3N_4 compacts contained 10 wt % large silicon are heat treated in order to observe the morphology of the precipitated β-Si_3N_N through the molten silicon.

Fig. 5 is the microstructure of large silicon (labelled S) surrounded with fine α-Si_3N_4 (labelled N) after 0 h of heat treatment at 1700° C. Zero heat treating time means that the furnace power was turned off as soon as the temperature was reached at 1700° C. Then, it can be found that the microstructure is not changed as compared with the starting powder. With increasing heat treating time and temperature, however, it can be observed that β-Si_3N_4 is grown into Si melts.

In this study, precipitated β-Si_3N_4 grown into molten silicon is appeared with two kinds of the microstructures; one is elongated prismatic β-Si_3N_4 grains which is shown in the micrograph of Fig. 6a (labelled C). The other is fine prismatic β-Si_3N_4 shown in Fig 6d (labelled F). Fig. 6a is the optical micrograph of the polished surface of α-Si_3N_4 containing Si after 1 h of heat treatment at 1650° C. It shows that the elongated prismatic β-Si_3N_4 (labelled C) is grown into Si melts (labelled S). Figure 6b is the scanning electron micrograph of the etched surface of the same region appeared in Fig. 6a. This surface was prepared
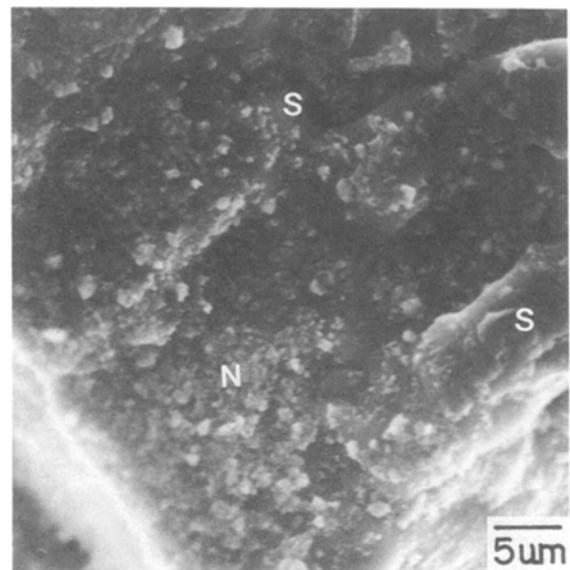

Figure 4 Beta fraction plotted against heat treating time for the α-Si_3N_4 without additives (———) and with 10 wt % β-Si_3N_4 ($\cdots$) heat treated at various temperatures.

Figure 5 Scanning electron micrograph of α-Si_3N_4 containing 10 wt % Si heat treated at 1700° C for 0 h. (S added Si, N α-Si_3N_4 matrix).
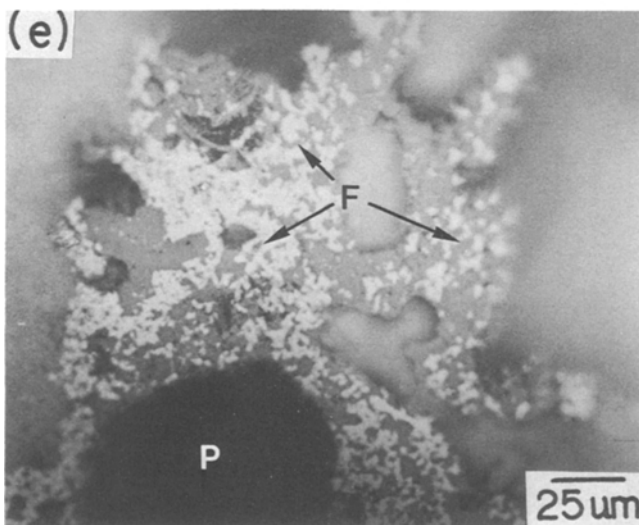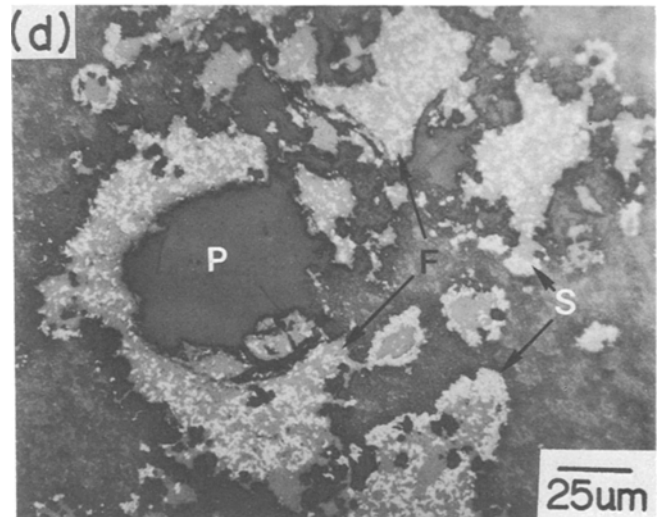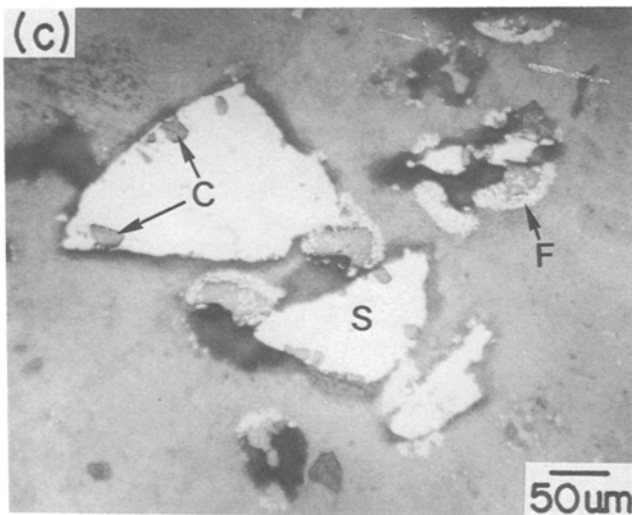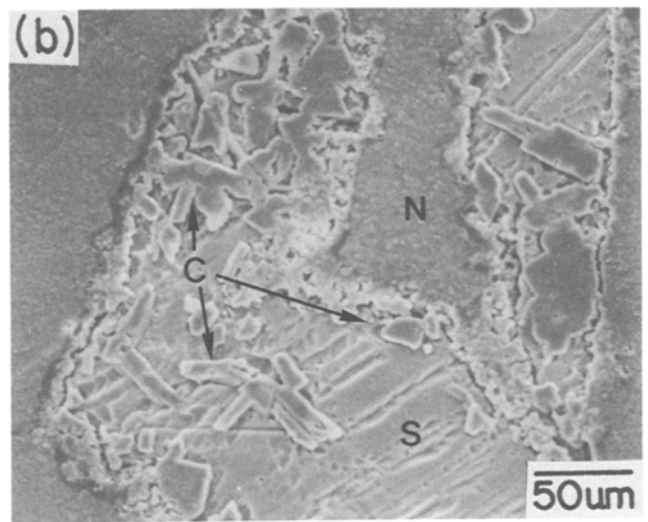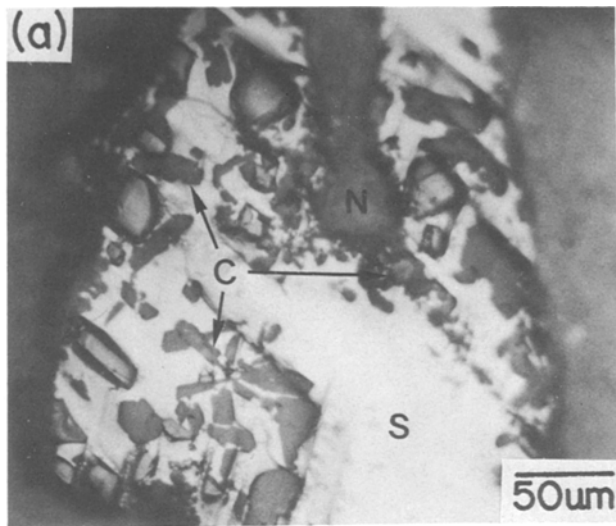
Figure 6 Micrographs of α-Si_3N_4 compact containing large Si heat treated at the various temperatures (a) and (b) 1650°C for 1 h, (c) 1700°C for 0.5 h, (d) 1700°C for 1 h, and (e) 1750°C for 0.5 h; (b) is the etched surface of (a). (N α-Si_3N_4 matrix, S added Si, C elongated grains, F fine grains, and P pore).

the specimens heat treated in the early stage of heat treatment at higher temperature (above 1700°C). Fig. 6c shows the micrograph of the elongated grains (labelled C) through molten Si (labelled S) after the specimen was heat treated at 1700°C for 0.5 h. However, at higher heat treating temperature, fine precipitated β-Si_3N_4 grains and large pores are mainly observed together, which are shown in Fig. 6d and 6e (labelled F and P, respectively). Fig. 6d is the micro-graph of the specimen after 1 h of heat treatment at 1700° C and Fig. 6e is that of the specimen after 0.5 h of heat treatment at 1750°C. In these micrographs, large pores seem to be formed by the dispersion of molten Si which is achieved with the spread of molten Si between the surrounding α-Si_3N_4 particles. This is suggested that the wetting angle of molten Si to silicon nitride is decreased with increased heat treating tem-perature as the report of Whalen *et al.* [21]. Since the dispersion of molten Si gives rise to extend the interface area between α-Si_3N_4 particles and molten Si, dissolution reaction is increased. As the result of that,

by partial etching of the specimen in HF + HNO_3 solution to eliminate the retained silicon. From the observation of both micrographs, it can be ascertained that the prismatic β-Si_3N_4 grows toward the centre from the interface between molten Si and α-Si_3N_4 particles. These phenomena are also observed in reaction bonded Si_3N_4 [20]. The elongated grains can also be observed with fine precipitated β-Si_3N_4 in
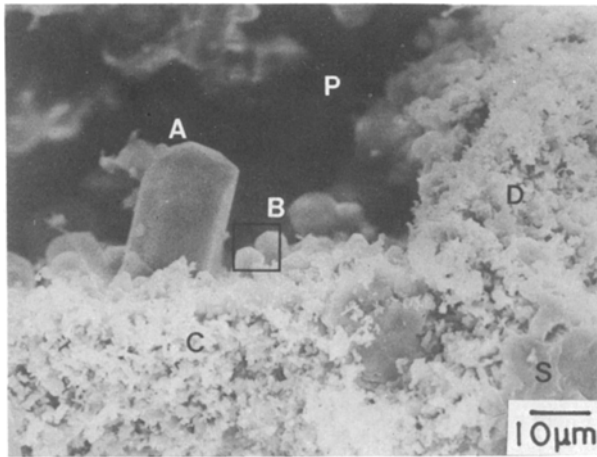
Figure 7 Typical micrograph showing the prismatic β-Si$_3$N$_4$ grown into molten silicon. (A and B enlarged grains, C and D are fine grains, P pore, and S Si.

3.4. Behaviour of β-Si$_3$N$_4$ during heat treatment

At the previous section, it was demonstrated that pre-existed β-Si$_3$N$_4$ did not influence the phase transformation. However, if β-Si$_3$N$_4$ can be dissolved in molten silicon, it is influenced by the microstructure of the heat treated specimen. Therefore, β-Si$_3$N$_4$ containing 10 wt % Si is heat treated at 1700° C for 1 h in order to evaluate the role of pre-existing β-Si$_3$N$_4$ on the formation of the microstructure of the heat treated specimen. The microstructure of the heat treated specimens are shown in Fig. 8. It can be found that another β-Si$_3$N$_4$ (labelled P) is grown into Si melts and its morphology is changed from an equi-axed shape to prismatic one (P region of Fig. 8). This means that β-Si$_3$N$_4$ is also soluted and precipitated into Si melts. Therefore, it is considered that the microstructure of the heat treated specimen with a prismatic shape results from the β-phase as well as the α-phase.

4. Conclusions

The specimens consisted of α, β-Si$_3$N$_4$ and free silicon without sintering aids occurred the α to β phase transformation. In this case, it takes place via silicon melts. This suggests that silicon melts is a suitable liquid phase for the α to β phase transformation in silicon nitride as does any sintering aid.

The size of precipitated β-Si$_3$N$_4$ depends on the heat treating temperature. At low heat treating temperature, elongated grains are precipitated through the Si melts. However, fine precipitated β-Si$_3$N$_4$ can be mainly observed with increased heat treating temperature. Microstructural variations of precipitated β-Si$_3$N$_4$ seems to result from the degree of the contact area between molten Si and α-Si$_3$N$_4$ particles with the dispersion of molten Si.

When only β-Si$_3$N$_4$ is added to α-Si$_3$N$_4$, β-Si$_3$N$_4$ cannot influence the phase transformation and the transformation is necessarily required in the presence of a suitable liquid phase. However, β-Si$_3$N$_4$ is also
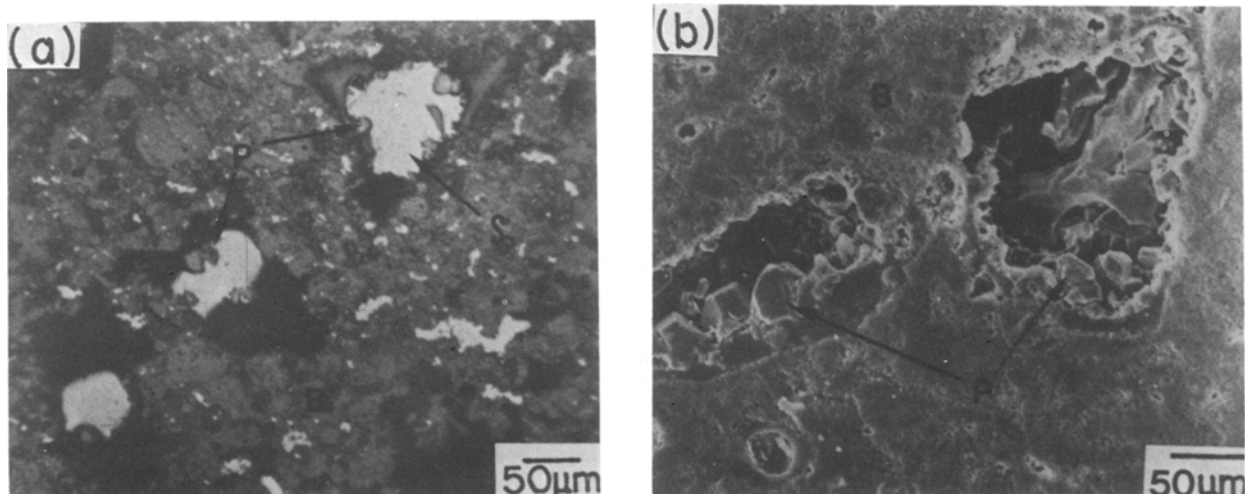
supersaturation of nitrogen in molten Si is achieved more easily and the nucleation site of precipitated β-Si$_3$N$_4$ seems to be increased. So, β-Si$_3$N$_4$ is precipitated from many grains, resulting in a finer grain size. Therefore, it is considered that the reaction between α-Si$_3$N$_4$ particles and dispersed Si melts leads to the precipitation of the fine β-Si$_3$N$_4$ grains. At lower heat treating temperature, on the other hand, the elongated grains are likely to grow by the diffusion of dissolved nitrogen in molten Si rather than by the dissolution reaction at the interface between molten Si and α-Si$_3$N$_4$ particles. Therefore, the heat treated specimens seem to have the microstructure as is shown in Fig. 7. Fig. 7 is a typical micrograph of fracture surface of α-Si$_3$N$_4$ compact containing large Si heat treated at 1700° C. The microstructure is composed of elongated grains (labelled A and B), fine grains (labelled C and D), large pore (labelled P) and Si (labelled S). According to the observation of Fig. 7, it can be ascertained that the precipitated grains have a hexagonal prismatic shape.

Figure 8 Micrographs of β-Si$_3$N$_4$ containing 10 wt % large Si heat treated at 1700° C for 1 h; (a) polished surface and (b) etched surface by conc. HF + HNO$_3$ solution. (S added Si, B β-Si$_3$N$_4$ matrix, and P precipitated β-Si$_3$N$_4$).

dissolved in molten Si and precipitated as another prismatic β-Si$_3$N$_4$.

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