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Synthesis of β-Si_3N_4 particles from α-Si_3N_4 particles

Takehiko Hirata*, Katsunori Akiyama, Tatsuo Morimoto

Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd. 8-1 Sachiura 1-chome, Kanazawa-ku, Yokohama, 236-8515, Japan

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Abstract

This report describes an investigation of the synthesis of β-Si_3N_4 particles from α-Si_3N_4 particles. The β fraction of Si_3N_4 particles was found to depend on temperature, heating time, and the type of crucibles in which the Si_3N_4 particles were heated. When Si_3N_4 particles were heated in a crucible made of carbon, most α-Si_3N_4 particles converted to β-Si_3N_4 after heating at 2000°C for 90 min in an atmosphere of N_2 of 9 kgf/cm^2. The morphology of the resulting β-Si_3N_4 particles appeared as a whisker shape. When Si_3N_4 particles were heated in a crucible made of boron nitride, most α-Si_3N_4 particles converted to β-Si_3N_4 after heating at 2000°C for 480min in an atmosphere of N_2 of 9kgf/cm^2. The resulting morphology was equiaxed. It is suspected that the transformation occurs via the gas phase and is affected by the partial pressure of oxygen in the atmosphere.

Keywords: Aspect ratio; Phase transformations; Si_3N_4

1. Introduction

Ceramics have been considered for application in hot structural parts such as blades for gas turbines,[1] but have not been used because of their current brittleness. It is therefore necessary to develop high toughness ceramics. In order to enhance the fracture toughness of ceramics, attempts including transformation toughening[2] particulate reinforcement,[3] and whisker/fiber reinforcement[4] have been undertaken. However, it has been difficult to obtain a dense sintered body of particle- or whisker-reinforced ceramics. Si_3N_4 ceramics in which elongated rod-like β-Si_3N_4 grains are developed in situ exhibit relatively high toughness and strength,[5] and it is comparatively easy to obtain a dense sintered body. In order to realize such Si_3N_4 ceramics, Kawashima et al.[6] produced Si_3N_4 at a higher temperature at which β-Si_3N_4 grains become coarse. At this higher temperature, however, pores are formed in the sintered body by glassy phase vaporization. Hirao et al.[7] produced Si_3N_4 ceramics by adding elongated β-Si_3N_4 grains obtained by means of growth from a melt flux followed by acid rinse treatments. But, β-Si_3N_4 grains produced using these methods include impurities composed of Y and F or S,[8] and these impurities decrease the strength at higher temperatures. Accordingly, β-Si_3N_4 must be produced so as to be free of inclusions. We have developed a systematic method to produce β-Si_3N_4 by means of growth from α-Si_3N_4 without any additives, so that the purity of the derived β-Si_3N_4 is extremely high.

2. Experimental procedures

The raw Si_3N_4 powder (UBE Industries, SN-E10) was made by heat treatment of silicon-diimide, the average particle size of which was 0.2μm, with a purity of 99.97%. The raw powder contained 3% β-Si_3N_4. The powder was heated at various temperatures in crucibles made of carbon or boron nitride. In order to prevent the decomposition of Si_3N_4, the powder was heated in an atmosphere of 9 kgf/cm^2 N_2 gas. The ratio of β-Si_3N_4 was evaluated by XRD (Rigaku Ltd., Model: Rotaflex RU-300, operating conditions: 40 kV, 100mA) using the equation.[9]

* Corresponding author. Tel.: +81-45-771-1222; fax: +81-45-771-3879.

E-mail address: hirata@atrc.mhi.co.jp (T. Hirata).

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$$\left(1-\left(1.4434\times\frac{I\beta(101)}{I\beta(101)+I\alpha(201)}-0.4434\right.\right.$$

$$\left.\left.\times\left(\frac{I\beta(101)}{I\beta(101)+I\alpha(201)}\right)^2\right)\right)\times 100$$

The morphologies of the powders were observed by scanning electron microscope (SEM, JEOL Ltd., Model: JSM-T330A).

3. Results and discussion

Fig. 1 shows the β-ratio of Si_3N_4 powders heated in the carbon crucibles at temperatures from 1800 to 2000°C for 240 min. Below 2000°C, the β-ratio and morphology of Si_3N_4 particles were unchanged. On the other hand, most Si_3N_4 converted from α to β by heating at 2000°C, producing whisker-like particles.

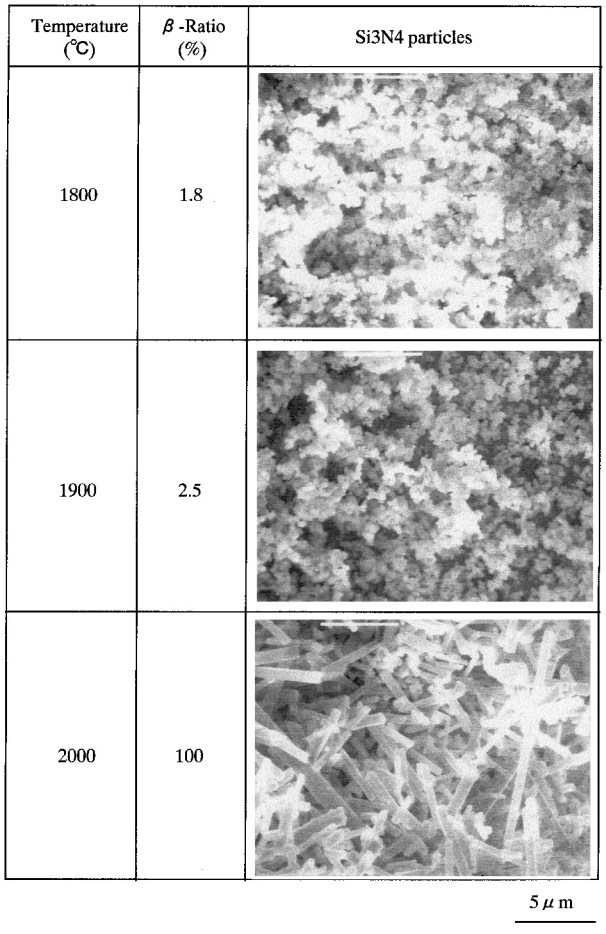

Fig. 1. Scanning electron micrographs of Si_3N_4 particles after heat treatment (holding time: 240 min, atmosphere: 9 kgf/cm^2 N_2, crucibles: carbon).

Tanaka et al.[10] investigated hot isostatic press sintering of Si_3N_4 without additives, and showed that the α–β transformation of Si_3N_4 occurred from 1750°C. They demonstrated that this is caused by solution–reprecipitation of Si_3N_4 through the liquid phase, composed of SiO_2. Fig. 1 shows that the α–β transformation occurred at a temperature of 2000°C, and it is therefore supposed that the α–β transformation observed in this study is caused by a different mechanism from solution–reprecipitation of Si_3N_4 via the SiO_2 liquid phase. Sarin[11] has demonstrated that transformation of Si_3N_4 is reconstructive and requires either a liquid phase or a vapor phase; it is consequently surmised that the transformation discussed here occurred via the vapor phase.

Fig. 2 shows the relationship between the β-ratio and holding time at 2000°C in the carbon crucible. Most α-Si_3N_4 had converted to β-Si_3N_4 after heating for 90 minutes or longer at 2000°C. Fig. 3 shows the change in the morphologies of the Si_3N_4 particle during heat treatment. α-Si_3N_4 particles become whisker-like β-Si_3N_4, with an aspect ratio of 20 or less.

Fig. 4 shows the relationship between the β-ratio and holding time at 2000°C in the boron nitride crucible. The kinetics of the α–β transformation are lower compared to those of Si_3N_4 which is heated in a carbon crucible. Most α-Si_3N_4 had converted to β-Si_3N_4 after heating for 480 minutes or more. Fig. 5 shows the morphologies of Si_3N_4 particles during heat treatment in the boron nitride crucible. The aspect ratio of Si_3N_4 particles heated in the boron nitride crucible is smaller than that of particles heated in the carbon crucible.

As noted previously, the morphology of β-Si_3N_4 synthesized in the carbon crucible was whisker-like.

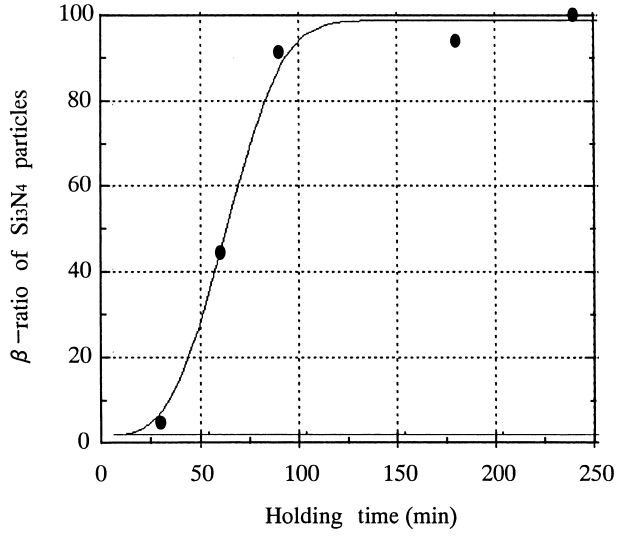

Fig. 2. Dependence of β-ratio of Si_3N_4 particles on holding time (temperature: 2000°C, atmosphere: 9 kgf/cm^2 N_2, crucible: carbon).

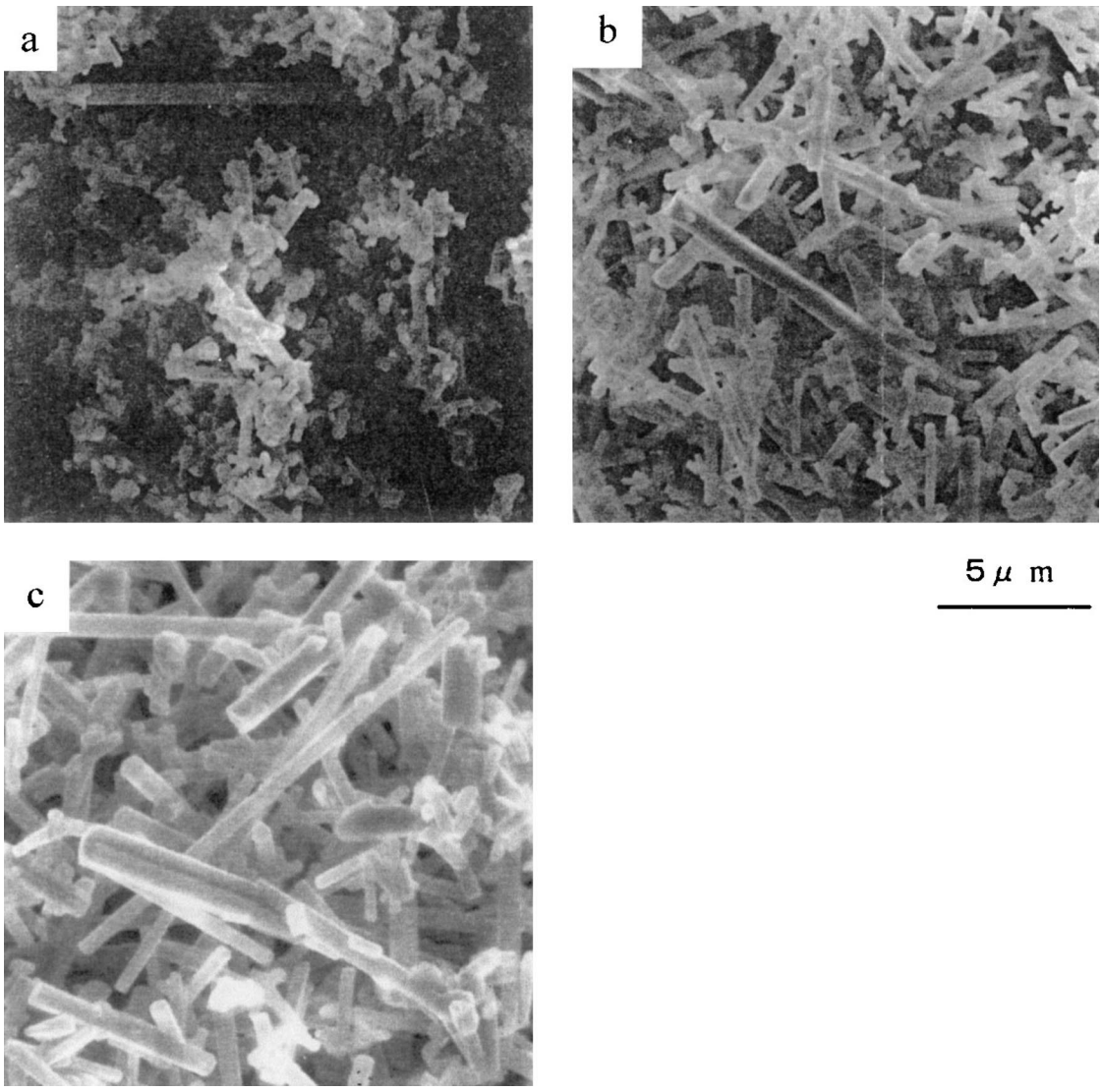

Fig. 3. Scanning electron micrographs of Si_3N_4 particles after heat treatments in the crucibles made of carbon at 2000°C for (a) 60 min, (b) 90 min (c) 240 min.

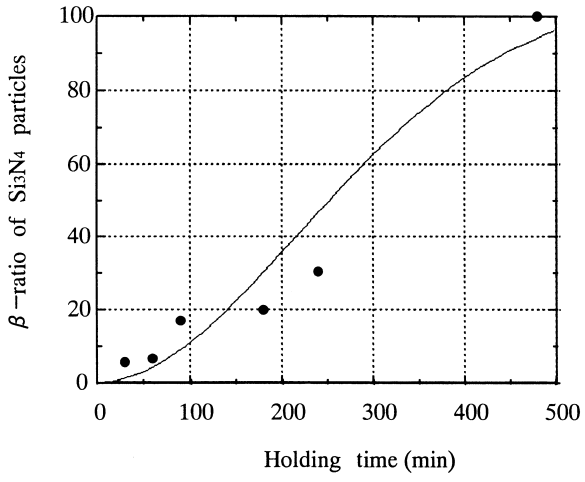

Fig. 4. Dependence of β-ratio of Si_3N_4 particles on holding time (temperature: 2000°C, atmosphere: 9 kgf/cm^2 N_2, crucible: boron nitride).

Generally, whiskers of ceramics such as SiC are grown using the vapor–liquid–solid (VLS) mechanism.[12] α-Si_3N_4 particles include SiO_2 at the particle surface and it is considered that this SiO_2 is converted to Si in the carbon crucible because the partial pressure of oxygen is relatively low. It is therefore supposed that the β-Si_3N_4 whisker-like particles in this study were grown through this Si liquid and that the transformation mechanism is VLS. Fig. 6 shows the relationship between $\log(\log(\frac{1}{1-y}))$ and log(time), in which y represents the ratio of transformation. Fig. 6 shows that $\log(\log(\frac{1}{1-y}))$ is in proportion to log(time), which means that the transformation of Si_3N_4 obeys the Johnson–Mehr equation $y = 1 - \exp(-(at)^n)$. When Si_3N_4 is heated in the boron nitride crucible, the n value is near 1.5[13] which means the transformation is controlled by a diffusion process. When Si_3N_4 is heated in the carbon crucible, the n value is near 3[13] which means the transformation is

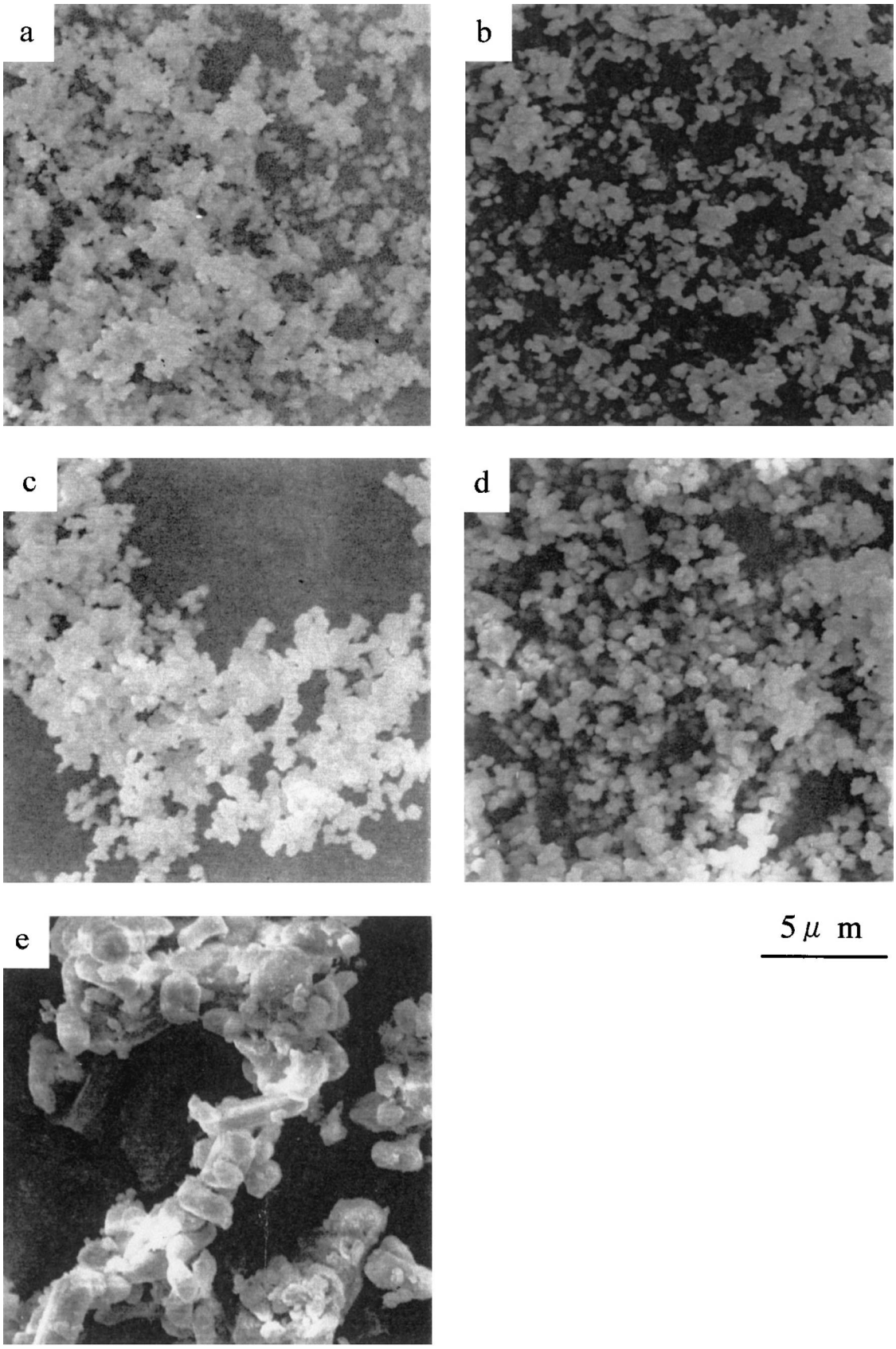

Fig. 5. Scanning electron micrographs of Si_3N_4 particles after heat treatments in the crucibles made of boron nitride at 2000°C for (a) 30 min, 60 min, (d) 240 min, and (e) 480 min.

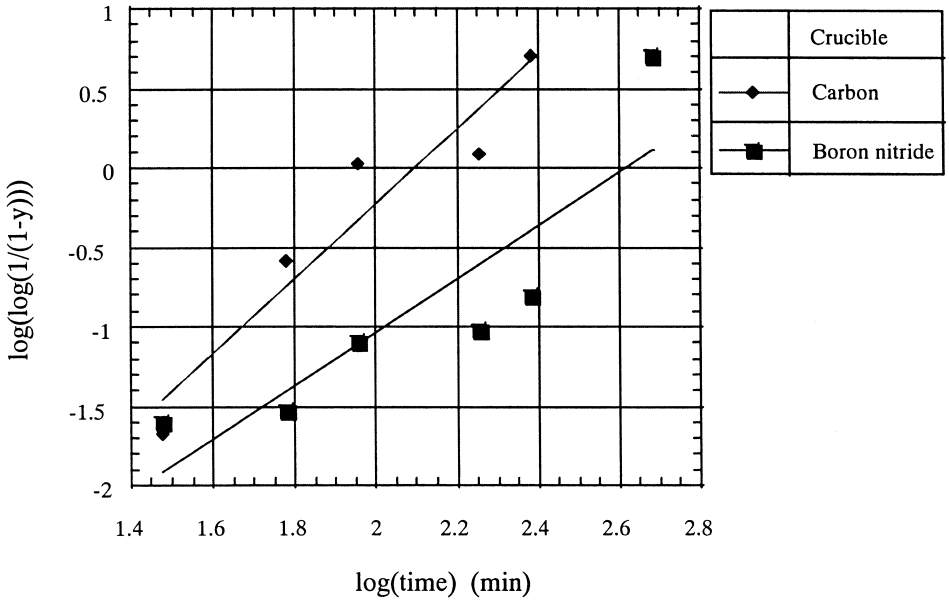

Fig. 6. Relation between log(log(1/(1-y))) and log(time).

controlled by reactions at the surface of the particles. Thus, in the carbon crucible, transformation occurred at the edges of rod-like particles, and was controlled by the reaction of Si_3N_4; in the boron nitride crucible transformation occurred over the entire surface of the Si_3N_4 particles, and was controlled by the diffusion of Si_3N_4.

4. Conclusions

In the project reported here, we investigated the synthesis of β-Si_3N_4 particles from α-Si_3N_4 particles. Results were as follows:

1. The β-ratio of Si_3N_4 particles depends on temperature, heating time, and the type of crucible in which Si_3N_4 particles are heated.
2. When Si_3N_4 particles were heated in a crucible made of carbon, most α-Si_3N_4 particles converted to β-Si_3N_4 particles after heating at 2000°C for 90min in an atmosphere of N_2 of 9kgf/cm^2. The morphology of the resulting β-Si_3N_4 appeared as a whisker shape.
3. When Si_3N_4 particles were heated in a crucible made of boron nitride, most α-Si_3N_4 particles converted to β-Si_3N_4 after heating at 2000°C for 480 min in an atmosphere of N_2 of 9kgf/cm^2. The resulting morphology was an equiaxed shape.
4. It is suspected that the transformation is caused via the gas phase of Si_3N_4 and affected by the partial pressure of oxygen in the atmosphere.

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