Nitridation Mechanism of Si Compacts Studied by Transmission Electron Microscopy

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Microstructures of reaction-bonded Si_3N_4 bodies, which were fabricated at 1623 K, have been studied to identify the nitridation mechanism of Si compacts by transmission electron microscopy. The percent nitridation of the Si compacts gradually increases with increasing reaction time. In the sample nitrided for 36 ks, the residual Si particles showing a sharp-edged shape contain many cracks and fine-sized $\alpha\text{-Si}_3\text{N}_4$ grains around the cracks, whereas the morphology of residual Si particles in the sample nitrided for 72 ks, shows an island shape due to the nitridation, and high-density of dislocations and microcracks are observed. The sample nitrided for 108 ks is constructed with typical net-shape having about $0.4\text{ }\mu\text{m}$ fine grains. Cracks and dislocations in the Si particles play an important role to explain the nitridation mechanism of Si compacts.

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I. Introduction

Recently, Si_3N_4 ceramics with superior mechanical properties have been used as industrial materials such as high-temperature and wear parts. Furthermore, if the Si_3N_4 ceramics can be made with low cost, their industrial application will be gradually widened, according to the requiring of special material properties. Although the reaction-bonded Si_3N_4 (RBSN), which has some advantages such as low price of raw powders, easy control of dimensions and low cost of production, has been actively developed since the early 1970s, its material properties were fallen short of one's expectation⁽¹⁾⁽²⁾. However, recently, particular attention has been directed to RBSN due to the development of gas-pressure-sintering technique, i.e., because the removal of residual Si and pores as well as microstructural control have been possible by the post-sintering process⁽³⁾⁽⁴⁾. To get the superior mechanical properties of RBSN, it is necessary to make a high percent of nitridation by controlling the reaction conditions. Until now, there are many reports on the nitridation of Si compacts. At the initial stage, the rate of nitridation strongly depends on the decomposition rate of SiO_2 film attached on the Si surfaces and the diffusion rate of N_2 gas into Si_3N_4 layers which were formed on the Si particles during the nitridation. Barsoum and his coworkers studied the nitridation mechanism of Si powder compacts according to the addition of H_2 gas using $\text{N}_2\text{-4\%H}_2$ mixture gas⁽⁵⁾. It has been understood that the addition of H_2 gas during the nitridation enhanced the decomposition of the SiO_2 film due to the reducing atmosphere, so that facilitated the initial stage of nitridation. Generally, the cost of RBSN components is strong-

ly dependent on the nitridation time. For shortening of nitridation time, the use of fine-sized Si powders is desirable. However, the average particle size of the currently used Si powders is about $10\text{ }\mu\text{m}$. Furthermore, when the nitridation occurs, the nitrided Si_3N_4 layer on the Si particles gradually becomes dense as increasing the reaction time. Thus, it is expected that the diffusion of N_2 gas into interior Si side will be disturbed due to the existence of dense Si_3N_4 layer. It is necessary to study the nitridation behavior based on the microstructural approach to obtain the optimum nitridation conditions.

In the present work, the microstructures and material properties of RBSN, which were fabricated at 1623 K, were investigated to identify the nitridation mechanism of Si compacts by transmission electron microscopy (TEM).

II. Experimental Procedure

Figure 1 shows the SEM micrograph (a) and the particle size distribution (b) of irregular shaped Si particles used in the present work. The average size of Si powders used was $10\text{ }\mu\text{m}$, but large particles (about $20\text{ }\mu\text{m}$) were also observed. The Si and sintering additive (5 mass% Y_2O_3 and 2 mass% Al_2O_3) powders were thoroughly mixed in ethanol using a planetary ball mill and Si_3N_4 balls as milling media. The mixtures were dried on a hot plate while stirring. The powder mixture was pressed into pellets and CIPed at 250 MPa. The pellets, 40 mm in diameter were nitrided in flowing $\text{N}_2\text{-10\%H}_2$ gas mixture at 1623 K for 36 ks to 108 ks. The residual Si phases were identified by an optical microscope. The XRD was used to examine crystal structure of the RBSN over a wide scale. TEM samples for observations of microstructure

Fig. 1 SEM micrographs (a) and particle size distribution of Si powders.

and crystal structure were prepared from thin slices, which were mechanically polished to a thickness of about 150 μm and punched out 3 mm in diameter by an ultrasonic cutter. After polishing to a mirror plane, a back-side was polished further up to about 30 μm in thickness by a dimple grinder and finally milled with Ar ions at an accelerating voltage of 3 kV. The glancing angle was 25°. Carbon coating to prevent charge-up effects was done prior to TEM observations. The detailed crystal structures, internal microstructures were examined using TEM. TEM observation was performed with a 200 kV electron microscope (JEOL-2000FX).

III. Results

Figure 2(a)–(c) show the polished optical micrographs of RBSN bodies at 1623 K for 36 ks (a), 72 ks (b) and 108 ks (c) hours, respectively. In the image, the particles with white contrasts are residual Si phase as indicated with arrowheads, and the black contrasts are caused by the existence of residual pores. Many residual Si particles are observed with sharp grains in Fig. 2(a). The nitridation of Si particles is facilitated by increasing the reaction times. In the sample nitrided for 72 ks (Fig. 2(b)), the morphology of residual Si particles is changed with an

Fig. 2 Optical micrographs of reaction-bonded Si_3N_4 body at 1623 K. (a): for 36 ks, (b): for 72 ks, (c): for 108 ks.

island shape due to the nitridation of Si particles. However, in the sample nitrided for 108 ks (Fig. 2(c)), the contents and morphology of residual Si particles are similar to that of Fig. 2(b). This observation indicated that the nitridation of Si is saturated at 1623 K for around 108 ks.

To identify the nitridation dependence on reaction time, the crystal structures of RBSN bodies were characterized in a wide scale by using a X-ray diffraction. Figure 3(b)–(d) show typical X-ray diffraction patterns of RBSN

Fig. 3 X-ray diffraction patterns of reaction-bonded Si_3N_4 body at 1623 K. (a): raw Si powders, (b): for 36 ks, (c): for 72 ks, (d): for 108 ks.

bodies at 1623 K for 36, 72 and 108 ks, respectively. A pattern of raw Si powder is insetted in Fig. 3(a) for a comparison. In the RBSN body reacted for 36 ks, α - and β - Si_3N_4 phases coexisted as well as the residual Si phase. As seen in Fig. 3(c) and (d), the intensities of Si peaks are decreased with increasing the reaction time due to the nitridation of Si particles.

Figure 4 shows the relative density and percent nitridation values of RBSN bodies as a function of reaction time. The RBSN body reacted for 36 ks shows about 60% nitridation, but the values gradually increase as increasing of the reaction time, so that in the case of 108 ks it shows 75% nitridation. However, the increasing slope of relative density is very low, and in the RBSN body for 108 ks the value shows only 68%.

Figure 5(a) is a low magnification image showing a typical TEM image of RBSN body at 1623 K for 36 ks. From the TEM image, we can see that most of fine-sized Si particles are easily nitrided to the Si_3N_4 phase with a dark contrast, and only some amounts of large-sized Si particles still remain as a residual Si phase. The formed Si_3N_4 grains are about $0.4\ \mu\text{m}$ and between them, many pore channels are also observed as indicated with arrowheads. The white contrasts with large-sized particles correspond to the residual Si particles, in which many cracks and fine-sized particles with dark contrast are observed. The analysis of electron diffraction patterns confirmed that the fine particles are α -typed Si_3N_4 phase formed by nitridation. Figure 5(b) shows an enlarged image of a residual Si particle in the RBSN body. As indicated with arrows, many microcracks are connected with each other. An important observation is that a few of fine particles with

Fig. 4 Reaction time dependence of relative density and percent nitridation in reaction-sintered Si_3N_4 body at 1623 K.

dark contrast are observed around the cracks, and the insetted electron diffraction pattern taken from a dark circle shows the α - Si_3N_4 of [001] zone axis. In the electron diffraction, the strong-spots excepting Si_3N_4 spots are from a residual Si crystal. From the electron diffraction pattern, it is clear that when the α - Si_3N_4 grains are formed at the internal side of residual Si particles, no special crystallographic orientation between Si and Si_3N_4 crystals are observed. In addition, the strong strain field contrasts can be seen at around the cracks.

Figure 6(a) shows TEM images of RBSN body at 1623 K for 72 ks. We can see that the nitridation is promoted into interior part of Si particles compared with that for 36 ks. In the image, it is supposed that before the nitrida-

Fig. 5 (a) Typical TEM image of reaction-bonded Si_3N_4 body at 1623 K for 36 ks. The mark Si indicates the residual silicon phase. (b) Enlarged micrograph. Arrows indicate many microcracks in a residual silicon phase. Electron diffraction patterns respectively taken from the dark circled regions.

Fig. 6 (a) Typical TEM image of reaction-bonded Si_3N_4 body at 1623 K for 72 ks. (b) Enlarged micrograph. Arrowheads indicate high-density of dislocations in a residual silicon phase.

Fig. 7 (a) Typical TEM image of reaction-bonded Si_3N_4 body at 1623 K for 108 ks. The mark Si indicates the residual silicon phase. (b) Enlarged micrograph. Many Si_3N_4 grains are seen with fine contrasts. (c) Typical TEM image taken from the thick region of reaction-bonded Si_3N_4 body at 1623 K for 108 ks. The ensetted electron diffraction pattern is taken from a dark circle of rod-like grain.

tion, a dot-lined region existed with a Si particle, but, by the nitridation, the region is changed with many fine-sized Si_3N_4 particles with about $0.4 \mu\text{m}$. Between them, we can see many pore-channels and some microcracks as seen in Fig. 5(a). Figure 6(b) shows an enlarged TEM image. In the residual Si grain, we can see many dislocation lines as indicated with arrowheads. Also, many fine-sized Si_3N_4 grains are formed at around a residual Si particle.

Figure 7(a) shows a typical TEM image of RBSN made at 1623 K for 108 ks. As can be seen in this image, the

RBSN body has a typical net shape, showing many pores ranged 0.1 to $2 \mu\text{m}$ sizes. However, the frames with dark contrasts are constructed with comparatively dense. Some amounts of residual Si phase covered with densified- Si_3N_4 frame are also observed as indicated with arrowheads. Figure 7(b) is an enlarged TEM image showing a part of Si_3N_4 frame. From the image, it is confirmed that the frames are constructed with fine-sized grains about $0.4 \mu\text{m}$, and the Si_3N_4 grains have a α -typed structure. Of course, in the frame, some amounts of residual

Fig. 8 Schematic model of reaction-bonded Si_3N_4 according to the increasing of reaction times.

pores are observed as indicated with arrowheads.

On the other hand, Fig. 7(c) also shows a TEM image of RBSN body at 1623 K for 108 ks, which was taken in a thick region. It should be noticed that a few of rod-like grains as indicated with arrowheads are observed near the large-sized residual pores. The ensetted electron diffraction is taken from a rod-like grain as indicated with a dark circle. From the electron diffraction pattern, it is confirmed that the rod-like grain shows a β -type crystal structure with a [101] zone axis. However, the rod-like grains are not well observed at the thin regions because the regions are preferentially sputtered during the ion milling.

IV. Discussion

Generally, as seen in X-ray data of Fig. 3, RBSN bodies show a mixed structure with α and β types, and it is well known that α - Si_3N_4 , which is a stable phase at low temperature, is transformed to β structure at above 2073 K. Using the α to β phase transformation phenomenon, the microstructure of Si_3N_4 can be controlled with rod-like grains, and then its fracture toughness has been remarkably improved with about $8 \text{ MPam}^{1/2(4)(6)(7)}$.

Untill now, there was no detailed TEM microstructural studies which can explain the nitridation mechanism of Si compacts. It may be caused by the difficulty of TEM sample preparation because most of RBSN bodies are very brittle due to the existence of many pores. In the chemically-deposited Si_3N_4 -TiN composites, Hiraga and his coworkers made detailed studies on the atomic structure of α - and β - Si_3N_4 by high-resolution electron microscope⁽⁸⁾. Also, the TEM technique is a useful tool to identify the crystal structure and grain morphologies in the RBSN body.

From this work, although no initial reaction stage can

be clearly explained, we can obtain the important results by the TEM observation of the intermediate and final stages of the nitridation dependence on reaction time at 1623 K. Before the nitridation, as explained in the schematic diagram of Fig. 8(a), most of the Si particles are coated with the SiO_2 amorphous film. First, the SiO_2 film can be decomposed in the N_2 -10% H_2 gas atmosphere by the next equations;

At the first stage, the formed Si_3N_4 phases exist with an amorphous phase. With increasing reaction time, however, the amount of the amorphous phase changes with rod-like β - Si_3N_4 crystallines. Also, many cracks and dislocations are formed in the Si particles during ball milling because they are intrinsically a brittle phase. The ball-mill induced cracks before the nitridation can facilitate the nitridation of coarse Si particles. From the results of TEM images and electron diffraction patterns, it is confirmed that α - Si_3N_4 phases are directly formed by the nitridation of Si particles; $3\text{Si}(\text{s}) + 2\text{N}_2(\text{g}) \longrightarrow \text{Si}_3\text{N}_4(\text{s})$. In this case, cracks and dislocations in the Si particles play an important role to explain the nitridation mechanism of large sized Si particles. Generally, after the decomposition of SiO_2 film, many Si_3N_4 nuclei are formed on the surfaces of Si particles and the interior of Si near the cracks. As the nuclei gradually grow with submicron-sized α - Si_3N_4 grains, dislocation density in the Si particles increases and continuously piled up as showed in Fig. 6(b). Microcracks are generated at the pile-up regions of dislocations by the lattice mismatch between α - Si_3N_4 and Si, and these microcracks gradually penetrate into all regions of Si particles with increasing the sintering time (Figs. 8(b) and (c)). This facilitates the supply of N_2 gas into interior part of Si crystals, leading to the ac-

celeration of the nitridation process. If the nitridation dominantly occurs without cracks only by diffusion controlling mechanism of N_2 gas into Si particles or vaporization mechanism of Si particle at high temperature, for the full nitridation of Si compacts, it may take a longer time than that of the existence of many cracks in Si particles. From this point of view, the ball milling conditions are an important factor to enhance the nitridation of Si compacts. Thus, one target for further improvement in nitridation process and percent nitridation of Si compacts can be realised by controlling the ball milling process such as use of high energy mill.

Finally, it should be mentioned that the rod-like β - Si_3N_4 crystals as shown in Fig. 7(c) are only observed around comparatively large-sized pores. This indirectly means that β - Si_3N_4 grains originated from vaporization process of SiO_2 films can easily be formed if there is no compressive stress field.

V. Conclusions

From the TEM study of reaction-bonded Si_3N_4 using Si compacts about $10\text{ }\mu\text{m}$ in size, which made at 1623 K under the N_2 -10% H_2 gas atmosphere, the following results were obtained.

(1) The values of percent nitridation and relative densities are increased with increasing reaction time, and in the sample nitrided for 108 ks, their values are 75 and 68%, respectively.

(2) The morphology of residual Si particles changes from a sharp-shape to an island-shape with increasing reaction time.

(3) When the α - Si_3N_4 crystallines are formed during the nitridation, no special crystallograph orientation between Si matrix and α - Si_3N_4 is observed in the residual Si particles.

(4) In the sample nitrided for 36 and 72 ks, many cracks and fine-sized α - Si_3N_4 grains are observed, and the existence of cracks and dislocations in the Si particles plays an important role to explain the nitridation mechanism of Si compacts.

(5) The sample nitrided for 108 ks shows the frame structure having fine-sized grains with about $0.4\text{ }\mu\text{m}$, and also contains some amounts of closed pores and residual Si phases.

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