Microstructure Control of Fiber-like TiN Particles in Hot Pressed Si_3N_4 -O'SiAlON-TiN Composites

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The microstructure control of TiN particles in hot pressed Si_3N_4 -O'SiAlON-TiN composites was investigated using waste-Si and sponge Ti powders, dependent upon the ball milling and attrition milling processes. The composites were composed of multi-phases, including β - Si_3N_4 , O'SiAlON and TiN phases regardless milling process used. In the composite using ball milling, TiN particles kept the original shape of sponge Ti powder and included many residual pores. Many microcracks were observed at the interfaces of Si_3N_4 /TiN interfaces due to the difference of their thermal expansion coefficients. However, in the composite using attrition milling, the morphology of TiN particles was changed to a fiber shape, without residual pores and microcracks.

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1. Introduction

Although the mechanical properties of Si_3N_4 ceramics have been remarkably improved, their applications are limited because of the high cost. From one point of view, using low-cost waste Si sludge is very effective. During the cutting process of single-crystal-Si ingots, large amounts of waste-Si sludge have been produced to make the Si wafers. For the recycling of waste-Si sludge by the filtering process, there have been some efforts to make reaction-bonded Si_3N_4 (RBSN) ceramics as the raw powders.¹⁻³⁾ The RBSN, which has some advantages such as the low cost of raw powders, easy control of dimensions and low cost of production, has been actively developed since the removal of residual Si and pores has been made possible by post-sintering processes, such as gas-pressure-sintering (GPS).^{4,5)} In recent work using waste-Si powders, we observed that many O'-SiAlON particles were detected in the GPSed-RBSN bodies due to the large amount of oxygen in the raw Si powders (13.20 mass%) compared with that of commercial-Si powders (0.18 mass%).³⁾ The existence of the O'-SiAlON phase inhibited the growth of rod-like Si_3N_4 grains during the GPS processing, so that the fracture toughness did not showed a high value. However, the hardness and high temperature properties of GPSed-RBSN using waste-Si powder was increased due to the existence of the O'-SiAlON phase.^{1,3)}

On the other hand, the TiN ceramic has been widely used as an agent for fracture toughening^{6,7)} or as an electrical conductor^{8,9)} as well as for thin film to improve the wear property.¹⁰⁾ Especially, the application of TiN as a toughening agent is basically due to the microcracking mechanism caused by the mismatch of thermal expansion coefficients between the matrix and the reinforcement.^{7,11)} In this case, an essential prerequisite is that the pre-cracks should not exist at the interface because of the strength degradation. Another important approach was to make electro-discharge-machinable ceramics by the dispersion of a TiN conductor. For the realization of this purpose, TiN particles should be fine and homogeneous in the matrix as well as in the optimized

contents. In general, the commercial TiN powders are very expensive. Furthermore, as a toughening agent, the morphology of TiN particles has no merit because they have an equiaxed shape. Recently, sponge-Ti powders also have been used as the toughening agent as well as the electrical conducting agent because of their low cost and ease of nitridation without any residual Ti phase.^{7,9,11)} However, the average size of commercial sponge Ti powders is too large compared with that of commercial TiN powders. Thus, the direct use of Ti powders brings about some residual cracks at the interfaces.

In this work, the morphology change of TiN particles in the Si_3N_4 matrix was investigated with regard to the milling method. The special focus was on the how the large-sized Ti powders were changed into the fiber-like shape and also the formation of microcracks at the Si_3N_4 /TiN interfaces.

2. Experimental Procedures

To obtain the raw Si powder, the waste Si sludge that was produced during the cutting process of single crystal Si ingot was collected by vacuum filtering and sieving. Using the waste Si powder, Si_3N_4 powder was nitrided in a flowing N_2 -10% H_2 gas mixture at 1400°C for 20 hours. The synthesized Si_3N_4 powders were ground by attrition milling and then made from sieving with 100 mesh. The obtained Si_3N_4 , sintering additives (6 mass% Y_2O_3 and 2 mass% Al_2O_3) and toughening agent (17 mass%Ti sponge powders) were mixed in with ethanol using ultrasonic power. The mixture powders were post-mixed by the ball milling for 30 hours or by the attrition milling for 30 hours, respectively. They were dried on a hot plate while stirring and then sintered by a hot press at 1850°C for 2 hours under 30 MPa pressure in the N_2 gas atmosphere. The XRD was used to examine the crystal phases of raw powders and Si_3N_4 -TiN composites over a wide scale. The internal microstructures were examined by TEM (JEOL-2010).

Fig. 1 Back scattered SEM images of Si_3N_4 -Ti powder mixtures made by (a) ball milling and (b) attrition milling.

3. Results and Discussion

Figures 1(a) and (b) show the back-scattered SEM images of Si_3N_4 -Ti mixture powders made by ball milling for 30 hours and attrition milling for 30 hours, respectively. In the images, the Ti particles are dark while Si_3N_4 powders are gray. In the Si_3N_4 -Ti agglomerates made by the ball milling, Si_3N_4 powders were comparatively coarse due to the agglomeration during the mixing process although they were fine-about 0.3–0.5 μm in diameter-as the starting powders. In particular, many large pores were included in the sponge Ti powder. However, in the mixture by attrition milling, the Si_3N_4 powders combined with the Ti powder as the attrition milling time increased; thus, they were seen as having a large, dense structure while the shape of the Ti powders was elongated, with a fiber-like morphology. This phenomenon is due to the plastic deformation by the attrition milling which has high energy.

XRD profiles of starting Si_3N_4 (a) and Si_3N_4 -Ti (b) mixture powders made by attrition milling are shown in Fig. 2. The starting Si_3N_4 powders were composed of multiple phases; *i.e.*, the intensities of the α - Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ peaks were strong while the β - Si_3N_4 peaks were weak. From the lack of detection of Si peaks in the starting Si_3N_4 powder, the Si powder was fully nitrified without any residual Si phase. From the Gazzara equation, the percent phase ratio ($\alpha/\alpha + \beta$) was 75%.¹²⁾ The detection of $\text{Si}_2\text{N}_2\text{O}$ is

Fig. 2 XRD profiles of (a) Si_3N_4 powder and (b) Si_3N_4 -Ti powder mixtures made by ball milling.

due to the high oxygen content in the waste-Si powder because their surfaces were coated with thin amorphous SiO_2 film.³⁾ In the XRD profile (b) of Si_3N_4 -Ti mixture powder, Ti peaks also were detected as well as in the α - Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$ and β - Si_3N_4 phases.

Figure 3 shows SEM images of hot pressed- Si_3N_4 -TiN composites, which were prepared by the ball milling (a) and attrition milling process (b). In the images, the arrows indicate the hot pressing direction. Many TiN particles were

Fig. 3 Back scattered SEM images of hot pressed- Si_3N_4 -TiN composites, made by the (a) ball milling process and (b) attrition milling process.

Fig. 4 XRD profile of hot pressed- Si_3N_4 -TiN composite made by the attrition milling process.

vertically arranged against the hot pressing direction. In the composite treated by ball milling, the TiN particles were an irregular shape and included some pores. However, in the sample made by attrition milling, the TiN particles had a fiber-like shape of various sizes.

Figure 4 shows an XRD profile of hot pressed Si_3N_4 -TiN composite made by the attrition milling process. The α - Si_3N_4 phase which appeared in the starting powder was not detected due to the phase transformation during the hot pressing. Also, instead of the $\text{Si}_2\text{N}_2\text{O}$ phase, the O'-SiAlON phase was detected because of some dissolution of Al in the liquid phase of Al_2O_3 and Y_2O_3 as sintering additives. The O'-SiAlON phase was also observed in the Si_3N_4 -C-fiber composite using waste Si powder.¹³⁾ From the detection of TiN peaks without any Ti peaks, it is confirmed that the fibers in the composites correspond to the TiN phase. On the other hand, there were no peaks of reaction compounds found with the exception of β - Si_3N_4 , O'-SiAlON and TiN regardless of the milling processes used.

Figures 5(a) and (b) show TEM images of hot pressed- Si_3N_4 -TiN composites made by the ball milling and attrition milling processes. The grain size of Si_3N_4 was comparatively fine less than $2\mu\text{m}$ in diameter, independent of the milling process. As indicated with arrowheads, the spherical grains are the O'-SiAlON phase, which acts as an inhibitor of Si_3N_4 grain growth.³⁾ Most of the junction regions, such as triple junctions and interfaces, were covered with an amorphous phase due to the sintering additives.³⁾ An important observation is that microcracks were not observed in the sample made by attrition milling while in the sample treated by ball

milling, some microcracks were observed at the interfaces between Si_3N_4 and TiN phases. The formation of microcracks is basically due to the difference of thermal expansion coefficients-between Si_3N_4 and TiN particles. The appearance of them is possibly closely related to the size of the TiN particles. The existence of microcracks can lead to the degradation of fracture strength of the Si_3N_4 -TiN composite. Thus, TiN particles dispersed in the Si_3N_4 matrix must be controlled with fine, or narrow size as shown in Fig. 5(b). In addition, in the Si_3N_4 -TiN composite made by ball milling, some residual pores were observed at the interior region of TiN particles. There was no special crystallographic relation between Si_3N_4 and TiN particles. On the other hand, when TiN fibers were formed in the CVD- Si_3N_4 -TiN composites,¹⁴⁾ special crystallographic orientation was usually satisfied such as $[001]_{\text{Si}_3\text{N}_4} \parallel [110]_{\text{TiN}}$.

4. Conclusions

From the study on the microstructures of hot pressed Si_3N_4 -O'-SiAlON-TiN composites using semiconductor-waste Si and sponge Ti powders, in which they were treated by different milling methods, the following results were obtained. The morphology of Ti particles in the Si_3N_4 -Ti mixtures was remarkably changed; *i.e.*, the ball milled particles kept their original shape and included many pores while the attrition milled particles were changed to a fiber shape without pores. The hot pressed composites were comprised of multi-phases including β - Si_3N_4 , O'-SiAlON and TiN phase, regardless of the milling process used. In the composite using ball milling, many microcracks were observed at the interfaces of Si_3N_4 /TiN due to the difference of their thermal expansion coefficients, but in the composite using attrition milling, their interfaces were directly bonded without any microcracks.

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Fig. 5 TEM images of hot pressed- Si_3N_4 -TiN composites, made by the (a) ball milling process and (b) attrition milling process.

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