Control of microstructure and mechanical properties of sintered aluminum nitride through addition of aluminum nitride whiskers

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ABSTRACT
Aluminum nitride (AlN) usually exhibits a microstructure consisting of equiaxed grains. However, these grains do not allow for the positive control of the microstructure and mechanical properties of AlN. In this work, we attempted to control the microstructure of AlN through the addition of whiskers and investigated the relationship between the microstructure and mechanical properties. The sintered AlN showed a microstructure consisting of large, rod-like grains, which originated from the whiskers. Furthermore, the microstructure varied with the size and amount of whiskers added, and so did the flexural strength and fracture toughness. The flexural strength and fracture toughness of the whisker-added AlN samples ranged from 197 to 267 MPa and 5.4 to 6.4 MPa m$^{1/2}$, respectively. In contrast, those of AlN without whiskers were 336 MPa and 3.1 MPa m$^{1/2}$, respectively.

1. Introduction
Ceramic substrates, such as those of alumina, silicon nitride (Si$_3$N$_4$), and aluminum nitride (AlN) are used for power devices [1,2]. Of these, AlN has the advantage of high thermal conductivity but shows low strength and fracture toughness. For instance, AlN substrates joined with copper plates on both sides often form cracks after thermal cycling tests. This is due to the low fracture toughness of AlN [3]. Hence, to increase the applicability of AlN as a substrate for power devices, it is essential to improve its reliability, that is, its fracture toughness, in order to prevent crack formation. Although many studies have attempted to increase its fracture toughness, the improvements have not been significant.

Recently, we attempted to improve the fracture toughness of AlN based on a method for the microstructural control of Si$_3$N$_4$ to ensure high fracture toughness [4–9]. The microstructure of Si$_3$N$_4$ consists of rod-like grains. Thus, Si$_3$N$_4$ is similar to a whisker-reinforced composite. These rod-like grains form spontaneously during sintering. Therefore, Si$_3$N$_4$ is sometimes referred to as a self-reinforced composite. Toughening mechanisms such as crack deflection, grain bridging, and grain pull-out are induced by these rod-like grains [4,5]. In addition, further microstructural control to improve the fracture toughness is possible through the addition of seed particles [6,8] or the alignment of the rod-like grains [7,9]. However, it is difficult to form rod-like grains in AlN, for example, through the choice of sintering additives [10] or by the addition of coarse grains [11].

The promising next approach to explore is the addition of AlN whiskers. Recently, prototype AlN whiskers have become available commercially. It is expected that the addition of whiskers would produce a composite-like microstructure. Furthermore, the alignment of the added whiskers by tape casting is expected to result in a highly anisotropic microstructure in AlN, which, in turn, would help ensure higher fracture toughness along the alignment direction. We had explored the above-described strategy in a previous study [12,13]. A highly anisotropic microstructure, in which the rod-like grains were aligned, was realized in sintered AlN, resulting in a fracture toughness as high as 6.7 MPa m$^{1/2}$. Thus, the potential of using microstructure control through the addition of whiskers to improve the fracture toughness of AlN had been confirmed.

In this study, we focused on the following two factors: the size of whiskers used and the isotropy of the sintered AlN. The AlN whiskers used in the previous study contained various sizes of whiskers, which were generated during the whisker synthesis and disentanglement process. In the present study, the whiskers were separated into two categories based on their size, namely, large and small, and the effects of the whisker size and amount on the microstructure and mechanical properties were investigated. The AlN sample produced in the previous study had a highly anisotropic microstructure, since the aim of the study was to...
ensure high fracture toughness. An anisotropic microstructure would also exhibit anisotropic mechanical properties and thus would be unsuitable for substrates. Therefore, in this study, we employed uniaxial press forming, instead of tape casting, to ensure a more isotropic microstructure.

2. Materials and methods

The AlN whiskers used were provided by U-MaP Co. Ltd., Japan. Before use, the received whiskers were mechanically disentangled using wet type disk mill equipment with 50 µm disk spacing and a rotation speed of 10,000 rpm. These were labeled as whiskers—original (W-O). The W-O sample was then dispersed in ethanol and settled for 30 min. The large whiskers sank to the bottom while the smaller ones remained dispersed in the ethanol; both were collected separately. The separated whiskers were labeled whiskers—large (W-L) and whiskers—small (W-S). The size and shape of the whiskers were examined through laser diffraction analysis (LDA) under wet-dispersion conditions, particle image analysis (PIA) under dry-dispersion conditions, optical microscopy (OM), and scanning electron microscopy (SEM).

The sintered AlN samples were produced using the following procedure. The AlN raw powder used was H-grade and was provided by Tokuyama Corp. Japan. It contained oxygen of 0.8 mass %. The average sizes of the primary and secondary (agglomerates) particles were 0.4 and 3 µm, respectively. Y2O3 was chosen as the sintering additive. The AlN raw powder, Y2O3 powder and AlN whiskers were mixed in different proportions; the mixing ratios and their labels are listed in Table 1. The powder mixture was then subjected to uniaxial press molding. This was followed by cold isostatic pressing at 100 MPa. Next, the pressed body was placed in a carbon crucible coated with boron nitride powder, and sintered at 1900°C for 2 h in nitrogen. This yielded sintered specimens with dimensions of 45 × 35 × 5.5 mm³ and φ12 × 3.5 mm². Finally, rectangular specimens with dimensions of 4 × 3 × 45 mm³ and disc-shaped specimens with dimensions of φ12 × 2 mm² were cut from the former and latter sintered bodies.

| Table 1. Powder mixtures provided for sample fabrication. Type and amount of added AlN whiskers are mentioned. Y2O3 and AlN whiskers were added to AlN raw powder with outer percentage. |
|-----------------------------------------------|
| AlN Whisker Type | NA | WO3 | WS3 | WL3 | WLS |
| AlN Whisker addition | No Addition | 0 | 3 | 5 | 3 |
| / mass % | 100 | 5 |
| AlN raw powder | 5 |
| / mass % | 5 |

The phases and degree of anisotropy of the sintered specimens were examined by X-ray diffraction (XRD) analysis. Thermal conductivity measurements were performed by the laser flash method (ISO 18,755) using the disc-shaped specimens. Specific heat capacity of AlN, 740 J/kg K, was used for calculation. The flexural strength was measured by the flexural test method (ISO 14,704) in the four-point flexural mode; the upper and lower spans were 10 and 30 mm, respectively. The fracture toughness was measured by the single-edge pre-cracked beam method (ISO 15,732) in the three-point bending mode; the span was 16 mm. The microstructure of the fractured surfaces as well as the chemically etched surfaces of the sintered AlN was observed by SEM. To observe the whiskers in the sintered specimen, the chemical etching was done for a duration of 1 day, using a 10 mass % KOH solution.

3. Results and discussion

3.1. Whiskers

Optical micrographs of the whiskers used are shown in Figure 1. W-O contained rod-like whiskers and fine equiaxed particles. The particles were generated during the whisker synthesis and mechanical disentangling processes. W-S contained smaller whiskers and fine particles, while W-L contained larger whiskers and only a few fine particles. The oxygen contents of W-O, W-S, and W-L were 4.1, 5.8, and 0.9 mass %, respectively. This implies that the smaller whiskers and fine particles were more oxidized than the larger whiskers. As some of the whiskers had a higher oxygen content, the whiskers were added in a small amount, and the amount of excess oxygen in the mixed powder was less than 0.2 mass %.

The fine particles were examined by LDA, and the results are shown in Figure 2. LDA is suitable for the detection of fine, equiaxed particles but not for rod-like whiskers. Thus, only the relative amount and size of the fine particles are known. Two peaks were observed in the cases of W-O and W-S, while only one peak was seen in the case of W-L. From the LDA, OM and SEM results, it can be concluded that the peaks at approximately 1 µm correspond to the fine particles. Further, the peaks on the right (i.e., those at approximately 1.5 µm) correspond to the rod-like whiskers. However, these data for whiskers have errors. The amount of fine particles in W-S should be larger than that in W-O. On the other hand, W-L was mainly composed of whiskers and contained only a few fine particles.

The shape of the whiskers was determined using PIA. Photographs of individual whiskers were taken, and an image filter was applied to exclude the fine particles, agglomerates, and overlapping whiskers.
More specifically, the following were filtered: particles with diameters less than 1.5 μm (threshold for fine particles and whiskers) and those with diameters greater than 25 μm (no whiskers larger than 25 μm were found in the OM and SEM images; those that met this condition were agglomerates), shapes with aspect ratios of less than 2 (these were not whiskers), and overlapping whiskers (these were distinguished based on their outline). After filtering, 4000–7000 individual whiskers were counted in W-O, W-S, and W-L, and their diameters and length distributions were determined. The results are shown in Figure 3.

The diameter and length distributions of W-O were centered around smaller and larger values than those of W-S and W-O, respectively. The cumulative diameter and length at 10, 50, and 90 vol% are listed in Table 2.

### 3.2. Sintered bodies

Regardless of the amount and size of the whiskers added, all the sintered bodies exhibited densities of $3.27 \times 10^3$ to $3.30 \times 10^3$ kg/m$^3$ and thermal conductivities of 187 to 204 W/mK, as shown in Table 3. These values are comparable to those of typical AlN. Thus, the addition of the AlN whiskers did not have an adverse effect on the sinterability and thermal conductivity.

The XRD patterns of NA and WL5 are shown in Figure 4. The patterns were taken from the top (T) and side (S) planes, which were perpendicular and parallel to the uniaxial pressing direction. Peaks related to the main phase (AlN) and secondary phases (Y$_2$O$_3$ and Al$_2$Y$_2$O$_5$) were detected. The positions and heights of their peaks are indicated in Figure 4. The presence of these phases was reasonable. The AlN peaks in the patterns of NA-T and NA-S were similar, indicating that the AlN sample sintered without whiskers was isotropic. On the other hand, WL5 showed weak anisotropy and so did the other three whisker-added AlN samples. The intensities of the (100) and (002) peaks, which were related to the prismatic and basal planes of AlN, were compared. The intensity ratio of the peaks, (100)/(002), became higher in WL5-T, and lower in WL5-S, compared to NA. This suggests that the AlN whiskers were slightly aligned perpendicular to the pressing direction.
Table 2. Cumulative diameter (D) and length (L) at 10, 50, and 90 vol% of whiskers.

| Material | D_{10} / µm | D_{50} / µm | D_{90} / µm | L_{10} / µm | L_{50} / µm | L_{90} / µm |
|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| W-O      | 3.1          | 4.5          | 8.4          | 14.1         | 29.1         | 54.1         |
| W-S      | 2.6          | 3.7          | 6.4          | 11.8         | 23.7         | 45.9         |
| W-L      | 3.7          | 5.5          | 9.7          | 19.4         | 39.1         | 71.9         |

Table 3. Densities and thermal conductivities of the sintered AlN samples.

| Material | Density (g/cm³) | Thermal Conductivity (W/m K) |
|----------|-----------------|-----------------------------|
| NA       | 3.30            | 195                         |
| WO3      | 3.29            | 204                         |
| WS3      | 3.28            | 187                         |
| WL3      | 3.29            | 190                         |
| WL5      | 3.27            | 188                         |

Figure 4. X-ray diffraction patterns of the sintered AlN samples. Positions and intensities of the peaks from the phases, AlN (JCPDS 25–1133), Y₂O₃ (JCPDS 41–1105) and Al₆Y₂O₁₉ (yttrium aluminum monoclinic, YAM, JCPDS 34–0368) are shown at the bottom. Only major peaks from Y₂O₃ and YAM are shown.

The microstructures of the sintered AlN samples are shown in Figures 5 and Figures 6. The fractured surfaces and the chemically etched surfaces of the AlN samples were observed by SEM. Both small grains and large grains were found in the fractured surfaces (Figure 5). The shape of large grains was more clearly observed in the chemically etched surfaces (Figure 6). As the etching was conducted under an over-etching condition, small grains were etched away, and the shapes of large grains were emphasized.

It was found that their microstructure changed significantly with the addition of the whiskers. NA exhibited a microstructure consisting of equiaxed grains with a size of ~5 µm. In contrast, the microstructures of the whisker-added AlN samples consisted of large grains greater than 10 µm in size and small grains with a size of ~5 µm. The size and shape of the small grains were similar to those of the grains in NA. Therefore, it can be concluded that the small grains originated from the raw AlN powder. Large grains were found only in the whisker-added AlN samples, and most of the large grains had rod-like shape, therefore, they were originated from AlN whiskers.

Most of the added whiskers had diameters of less than 10 µm (see D_{90} in Table 2). However, the large grains in the sintered AlN samples had diameters of more than 10 µm. The length of the large grains in the sintered AlN samples was less than 100 µm, which is similar to that of the added whiskers (see L_{90} in Table 2). Therefore, it can be concluded that the added whiskers thickened but did not undergo significant elongation after sintering. However, this conclusion is based on initial observations, and a quantitative analysis is underway.

The microstructures of the whisker-added AlN samples varied with the type and amount of whiskers added. WO3 showed a microstructure consisting of small and large grains. The microstructural changes of other samples were evaluated using WO3 as the reference.

WS3 also consisted of small and large grains, although with a lower proportion of small grains compared to WO3. Moreover, the sizes of rod-like grains were not extremely large. The difference in microstructure was caused by the whiskers. W-S contained smaller, shorter whiskers compared with those seen in W-O. Therefore, for the same sample weight, the number of whiskers in W-S was higher than that in W-O. The larger numbers of whiskers acted as seed grains for grain growth. This could be the reason the microstructure of WS3 had smaller rod-like grains compared to WO3. Both W-O and W-S contained fine equiaxed particles of approximately 1 µm. These fine particles did not seem to affect the microstructure formation. If the fine particles acted as seed grains, WO3 would have a microstructure with less small grains. WL3 exhibited a microstructure consisting of small and large grains, similar to that of WO3. Most of the large grains were rod-like in shape, and sizes of them were larger than those in WO3. The amount of the large grains was smaller than that in WO3. W-L contained larger and longer whiskers, and number of the whiskers was small, compared to W-O. This resulted in the microstructure of WL3. WL5 showed a microstructure similar to that of WL3. However, the amount of the large grains seemed to increase with the addition of a greater amount of W-L.

The flexural strength and fracture toughness values of the sintered AlN samples are shown in Figure 7. The flexural strength decreased and the fracture toughness increased with the addition of the whiskers. For example, the flexural strength and fracture toughness of NA were 336 MPa and 3.1 MPa m^{1/2}, respectively, and these changed to 202 MPa and 5.8 MPa m^{1/2} in WO3.
WS3 showed a similar flexural strength (197 MPa) and a slightly lower fracture toughness (5.5 MPa m$^{1/2}$) compared with those of WO3. WL3 showed the highest flexural strength (267 MPa) among the whisker-added AlN samples, and its fracture toughness also remained high at 5.4 MPa m$^{1/2}$. Finally, WL5 showed the highest fracture toughness at 6.4 MPa m$^{1/2}$, but its flexural strength was low (214 MPa).

All the whisker-added AlN samples showed fracture toughness values greater than 5 MPa m$^{1/2}$. To the best of our knowledge, fracture toughness values this high have only been reported in the case of whisker-added, tape-casted AlN [12,13], and this is the first instance of such high values being observed in nearly isotropic AlN.
To elucidate the reasons for the observed high fracture toughness, the fractured surfaces were examined in detail. The fractured surfaces of NA and WL5 are shown in Figure 8; these images were taken from tilted surfaces. It can be seen from Figures 5, Figures 6 and Figures 8 that, in NA, fracture occurred mainly at the grain boundary. Thus, the primary fracture mode was intergranular fracture. Crack deflection, which is an important toughening mechanism for ceramics, were not remarkable, since NA consisted of small, equiaxed grains. On the other hand, a large number of fractured grains were observed in WL5. Therefore, in this case, the primary fracture mode changed to transgranular fracture. Furthermore, the fractured surface became rough, and a large number of large grains, which caused crack deflection, were observed. Thus, in the case of this sample, the toughening mechanism was activated by the large rod-like grains. As mentioned, the high fracture toughness values of the whisker-added AlN samples were in keeping with their fractured surfaces.

Even though the number of samples used in this study was limited, the flexural strength and fracture toughness seemed to exhibit a trade-off relationship. In the case of silicon nitride [14], high fracture toughness is related to a microstructure with large, rod-like grains, which aid the toughening mechanisms. However, the interactions between the large, rod-like grains have an effect similar to that of defects, resulting in a decrease in the flexural strength. A microstructure consisting of fine, rod-like grains is preferable for high flexural strength. However, it also results in poor fracture toughness. A similar relationship was observed in the case of the AlN samples in this study. For example, WL3 showed higher flexural strength and lower fracture toughness values than those of WL5, in which larger amount of the same whiskers added. This is the assumption from the limited samples. Thus, further quantitative analysis must be required to clarify the relationship among added whisker size and amount, microstructure, and mechanical properties.

4. Conclusions

In this study, we showed that the addition of AlN whiskers is a promising technique for controlling the microstructure and mechanical properties of sintered AlN. Sintered AlN samples containing different types of AlN whiskers were fabricated, and the microstructures and mechanical properties of the samples were investigated. After the addition of the whiskers, microstructures consisting of large grains with sizes greater than 10 µm and small grains with a size of ~5 µm were formed. Some of the large grains were rod-like in shape. Thus, they originated from the added whiskers. The microstructure of the samples changed with the type and amount of whiskers added, and so did their mechanical properties. In general, the addition of the whiskers improved the fracture toughness (5.4–6.4 MPa m$^{1/2}$) but lowered the flexural strength (197–267 MPa) compared with those of AlN without whiskers (3.1 MPa m$^{1/2}$ and 336 MPa, respectively).

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Figure 8. Fractured surfaces of the AlN samples (a) without (NA) and (b) with (WL5) whiskers. The sample surfaces were tilted to allow for morphology to be observed.
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