Exfoliation of hexagonal boron nitride using wet-rotating disc milling

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A wet-rotating disc milling was used as a novel method to investigate the exfoliation of laminated hexagonal boron nitride (h-BN) particles. The sedimentation test after the milling showed that the relative packing density of h-BN particles treated by the wet-rotating disc milling was much lower compared to non-milled h-BN particles. Also, the particle size distributions showed that the particle size of exfoliated h-BN particle was relatively as similar as the initial particle size. Furthermore, SEM images of wet-rotating disc milled h-BN particles showed that the decrease of h-BN thickness was affected to the relative packing density after sedimentation test. The average aspect ratio of prepared h-BN particles was increased 1.8 times as compared to pristine h-BN particles. The wet-rotating disc milling process led to exfoliation of laminated h-BN particles without reducing the particle size and destroying the crystal structure. Moreover, the relative packing density of exfoliated h-BN particles was affected to rotation speed, number of pass, and distance between two rotation discs. Therefore, it was found that the exfoliation of laminated h-BN particles effectively was progressed by wet-rotating disc milling.

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1. Introduction

Laminated ceramics particles, such as hexagonal boron nitride (h-BN), have been used as fillers for polymer ceramics and composite ceramics because of its high temperature stability, a low dielectric constant, high mechanical strength, a large thermal conductivity, low hardness, and high corrosion resistance.1–3 Laminated ceramic particles such as h-BN and graphite are stacked in numerous single-layers and single-layers are formed by weak van der Waals interaction.6,17 Because the performance of polymer ceramics and composite ceramics using h-BN fillers is strongly dependent on the aspect ratio of plate-like shape, the exfoliation development of laminated ceramic particles is of importance for improvement of properties.

Since the original ‘Scotch tape method’ has been developed for exfoliation of laminated particles by Novoselove’s group,8 various exfoliation methods of laminated ceramic particles have been investigated for the application to industrial fields.9–13 In typical methods, ball milling and sonication have been widely reported for exfoliation of laminated ceramic particles. For example, Li’s group has reported the fabrication of h-BN nanosheets exfoliated by ball milling in benzyl benzoate.12 Also, Hernandez’s group has prepared graphene sheet from graphite by using high energy ultrasonication in mono- or multi-layer structures.14 However, these mechanical processes are violent methods which destroy the crystal structure of laminated particles and introduce a great lot of defects, resulting that the properties of composite are affected to be low.12,13 Furthermore, in case of ball milling and sonication methods, it is difficult to exfoliate laminated ceramic particles with high aspect ratio because the mechanical shear force is applied to the basal phase not only the edge face for the exfoliation processes of laminated ceramic particles. Therefore, it is really necessary to exfoliate laminated ceramic particles without destroying the crystal structure by applying shearing force to the edge face of laminated ceramic particles.

Recently, in chemical engineering and powder technology fields, a spinning disc processor such as wet-rotating disc milling has been developed as a new method of mixing dispersion and pulverization.15–17 In wet-rotating disc milling process, the slurry or suspension sandwiched between the parallel discs is able to add a strong shear flow at high-speed rotation of the disc. Using the effect, the homogeneous dispersion and the pulverization of agglomerated ceramic particles in slurry are achieved within a short time.

In this study, we will demonstrate to exfoliate h-BN particles using a wet-rotating disc milling by changing the mechanical conditions, such as the rotation speed, the number of pass and the distance between two rotation discs. The states of exfoliated h-BN particles will be discussed from viewpoints of lateral size, thickness, and crystal structure of h-BN particles.

2. Experimental procedure

2.1 Slurry preparation

A commercially available hexagonal boron nitride (h-BN, UHP-I, Showa Denko, Tokyo, Japan) was used as laminated ceramic particles in this work. Aqueous h-BN slurry was prepared by h-BN particles and distilled water. The solid loading of h-BN particles in slurry was adjusted to be 0.5 vol.\%.

A diagram of wet-rotating disc milling system (Disperizer CDMX-T, Sintokogio, Aichi, Japan) used in this work is shown in Fig. 1. The rotation disc (100 mm diameter), which was made from alumina-sprayed coating stainless steel, was used in order to prevent contamination during milling. The slurry was introduced between the parallel discs in the apparatus by a tube pump

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also observed by increasing the rotation speed when the numbers respectively. The decrease of the relative packing density was rpm of the rotation speed were 3.77, 3.45, 3.03, and 2.53 adjusted at 0.20 mm. In case of 10 passes, the relative packing agglomerated in slurry.

2.2 Characterization
The sedimentation tests of wet-rotating disc milled h-BN slurries were carried out in borosilicate glass tube (12.3 mm inside diameter) and allowed them to stand for 24 h. The initial slurry height was adjusted to 50 mm. After 24 h, the relative packing density was calculated from the following Eq. (1);

\[
\text{Relative packing density (\%)} = \frac{\text{Initial slurry height/Initial solid content}}{\text{Sedimentation height/Initial slurry height}}
\]

The crystallinity of wet-rotating disc milled h-BN particles was investigated by X-ray diffraction (XRD, RINT2000, Rigaku, Tokyo, Japan) with CuKα radiation. A laser particle analyzer (LA-920; HORIBA, Kyoto, Japan) was used for particle size distribution analysis of wet-rotating disc milled h-BN slurries. The thickness of wet-rotating disc milled h-BN particles was evaluated using slip-casted green compacts by a scanning electron microscopy (SEM, S-4300; Hitachi, Ibaraki, Japan). The SEM observation was carried out at the accelerating voltage of 10 kV. The thicknesses of h-BN particles were evaluated from photographic images of 150 samples.

3. Results and discussion
Figure 2 shows the relative packing densities of h-BN particles by changing the number of pass as a function of rotation speed. The distance between two discs in an apparatus was 0.10, 0.15, and 0.20 mm of the distance between two rotation discs, and the number of flow was performed at 1, 5, and 10 passes. This result showed that the relative packing densities of h-BN particles were much lower with decreasing the distance between two rotation discs. Generally, it is known that the relative packing density is very important index for statement evaluation of particles such as pulverization, crush or exfoliation.18) The relative packing density of sedimentation can be estimated from Eq. (1) as a function of initial solid contents, sedimentation height and initial slurry height. When laminated ceramic particles is exfoliated or pulverized, the relative packing density of particles will be lower because the particles packing after sedimentation is not closely as compared to spherical particles. Moreover, in the wet-rotating disc milling method, it is known that the strength of shearing flow depended on the parameters: rotation speed, distance between two discs, and viscosity of fluid.19,20) Therefore, the high shearing force generated with increasing the rotation speed and decreasing the distance between two discs led to exfoliation or pulverization of h-BN particles. On the other hand, the relative packing density of pristine h-BN particles was lower as compared to those prepared by disc rotating at 3000 and 6000 rpm, because h-BN particles were agglomerated in slurry.

In order to investigate the state of wet-rotating disc milled h-BN particles, the median particle size ($D_{50}$) of prepared h-BN particle was measured by laser particle analyzer. The median particle size was represented in Table 1. The median particle sizes of pristine h-BN and milled h-BN particles in slurries of the lowest relative packing density were 14.4 and 14.0 μm, respectively. The values of median particle size were almost similar. Furthermore, the particle size distributions of milled h-BN particles were as similar as that of pristine h-BN, meaning that h-BN particles were not crushed by wet-rotating disc milling.

As shown in Fig. 2 and Table 1, the relative packing densities of wet-rotating disc milled h-BN particles were different by affection of the rotation speed and the distance between two discs during milling despite the median particle sizes were almost similar. Therefore, the thicknesses of h-BN particles prepared from wet-rotating disc milling were measured using slip-casted green compacts by SEM images. Figure 3 represents SEM images of slip-casted green compacts observed from side direction. As shown in the SEM images, the thicknesses of h-BN particles prepared by wet-rotating disc milling was thin as compared to pristine h-BN particles. From the viewpoints of median
particle size and thickness of milled h-BN particles, the wet-rotating disc milling led to exfoliation of laminated h-BN ones. The thickness distributions of h-BN particles prepared by 10 passes of flow times at 0.20 mm of the distance between two discs were estimated from about 150 particles of SEM images. 

**Figure 4** shows the cumulative percentage as a function of h-BN thickness. The mean thickness (T50) of pristine h-BN particles, h-BN particles prepared by rotating speed of 3000, 6000, 9000 and 12000 rpm were estimated at 0.170, 0.138, 0.130, 0.121 and 0.093 μm, respectively. The thicknesses of h-BN particles were much lower with increasing the rotating speed. This is indicated that the exfoliation of laminated h-BN particles was progressed by wet-rotating disc milling method. The wet-rotating disc milling led to exfoliation of laminated h-BN particles without reducing the aspect ratio and destroying the crystal structure.

**4. Conclusion**

In this study, the exfoliation of laminated h-BN particles was investigated using wet-rotating disc milling. The states of exfoliation were affected by the rotation speed of disc and the distance between two discs. By increasing the rotation speed of disc at 0.20 mm of narrow distance between two discs in apparatus, the exfoliation of laminated h-BN particles was progressed effectively. Furthermore, the wet-rotating disc milling led to exfoliation of h-BN without destroying the particle states such as...
particle size and crystal structures. Therefore, the aspect ratio of wet-rotating disc milled h-BN particles at 12000 rpm was increased 1.8 times as compared to pristine h-BN ones.

The wet-rotating disc milled h-BN will lead to enhancement of thermal conductivity of polymer ceramics and composite ceramics because the milled h-BN with high aspect ratio forms thermal conductive path easily in the composites. Thus, this process will greatly contribute to exfoliate laminated functional ceramic particles with high aspect ratio and to improve the properties of ceramic and polymer composites.

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