Control of the particle-assembled structure and a novel evaluation technique for high-performance ceramics

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In this article, two techniques are described that can enhance the performance of ceramics. First, magnetic field orientation, a technique used to control the particle-assembled structure before sintering, is reviewed using c-axis Si₃N₄ ceramics as an example. Second, nondestructive internal structure observation based on optical coherence tomography (OCT) is reviewed as a novel evaluation technique using Al₂O₃ ceramics as an example.

Key-words : Magnetic field orientation, Optical coherence tomography, Graphene, Alumina, Microstructure

1. Introduction

The performance of ceramics is known to be particularly sensitive to its microstructure. The properties of ceramics inevitably degrade if their microstructures contain unintentional inhomogeneous structures such as pores, cracks, and secondary phases. The size, shape, and orientation of grains also have a marked influence on the properties of ceramics. Sintering is the densification phenomenon with reducing the surface area in a powder compact due to the diffusion of matter starting at the contact points of the particles. As such, the quality of the “particle-assembled structure” in a powder compact before sintering is essential in determining the quality of microstructure. The keys to enhancing the performance of ceramics are, therefore, controlling the particle-assembled structure to induce the formation of the desired microstructure during sintering, and using an appropriate technique to evaluate influences of the complex chain of “process factors”, as shown in Fig. 1.

This article describes two techniques that can contribute to the performance of ceramics. The first is the magnetic field orientation, which is used to control the particle-assembled structure before sintering. This technique is examined via the example of c-axis-oriented Si₃N₄ ceramics. The second technique, nondestructive internal structure observation using optical coherence tomography (OCT), is reviewed as a novel evaluation method for examining the internal structure, using Al₂O₃ ceramics as an example.

2. Magnetic field orientation

Control of crystal orientation is one of the key techniques that can be used to control the microstructure, and drastically enhances the material performance in the direction of orientation as compared to normal ceramics that are composed of randomly oriented grains. The core processes for producing crystal-oriented ceramics include particle orientation via the application of various external fields which maintains the orientation while particles accumulate, and control of anisotropic sintering shrinkage for high-densification.

Of the crystal orientation techniques that involve the application of external fields, magnetic field orientation is known to be excellent for the precise control of orientation without the need for shape constraint of raw materials and products. The author previously reported on the control of anisotropic sintering shrinkage during sintering and on the enhancement of performance via the advanced orientation of crystals in oxide and nitride ceramics. The results for the c-axis-oriented Si₃N₄ ceramics, which were fabricated in a rotating high 10 T magnetic field and subsequently sintered in 0.9 MPa N₂, are shown in Fig. 2. The fine c-axis-oriented structures resulted from the orientation of β-Si₃N₄ seeds during casting because those seeds acted as templates controlling the growth of the β-Si₃N₄ nuclei and inducing anisotropic sintering shrinkage during sintering.

However, implementing this technique for industrial applications may not be feasible because of the high magnetic fields required. Although in principle, a sufficiently high magnetic field is required to orient fine micrometer-sized particles, a lower magnetic field of below 1 T is desired for potential industrial applications. However, under magnetic fields of 1 T, the anisotropic magnetization...
energy $\Delta E$, which is the driving force of particle orientation in a magnetic field, is reduced to $1/100$ that of $10$ T, rendering particle orientation impossible by that means. Two options for obtaining a value of $\Delta E$ that can be oriented in a low magnetic field are (1) coarsening the particles or (2) enhancing $\Delta \chi$, which is the anisotropy of the magnetic susceptibility of the particles. Coarsening particles is disadvantageous in terms of sinterability. $\Delta \chi$
can be enhanced by either adding magnetic elements to the raw material, or by coating particles having a greater value of $\Delta \chi$ onto the surface of matrix particles. The former method requires consideration because coarsening the particles directly in influences the substance-specific performance. However, coating the particles can enhance $\Delta \chi$ without degrading the performance of the matrix particles. Multilayered graphene is an ideal material for application as a coating because it is a diamagnetic material having a large $\Delta \chi$, and can be thermally decomposed and removed together with organic additives during the dewaxing that is carried out before sintering.

Multilayered-graphene-coated particles were prepared using a mechanical treatment process. In the case of $c$-axis-oriented Si$_3$N$_4$, multilayered graphene was coated on the surface of rod-like $\beta$-Si$_3$N$_4$ particles synthesized using $\alpha$-Si$_3$N$_4$ (SN-E10, Ube Industry, Co., Ltd., Japan) and Y$_2$O$_3$ (RU-P, Shin-Etsu Chemical, Co., Ltd., Japan) raw powders. The morphology observation and element analysis were performed using a scanning electron microscope (SEM) (JSM-6390LV, JEOL, Japan). Figure 3 shows (A) energy-dispersive X-ray spectrometry (EDS) images of the morphology of multilayered-graphene-coated $\beta$-Si$_3$N$_4$ seeds, and (B) backscattered electron images of the multilayered-graphene-coated $\beta$-Si$_3$N$_4$ seeds observed using a low acceleration voltage in field emission SEM (FE-SEM). From the EDS analysis results shown in Fig. 3(A), carbon and silicon signals were observed in the same location, implying that carbon exists on the Si$_3$N$_4$ particles. In Fig. 3(B), a and b correspond to the topographic images and c and d show the compositional images. A visible contrast between carbon and Si$_3$N$_4$ was observed on the surface of elongated $\beta$-Si$_3$N$_4$ seeds as shown in Fig. 3(B)-c and d. The brighter and darker regions should correspond to Si$_3$N$_4$ and carbon, respectively. Peeling was observed in Fig. 3(B)-b; however, it is not evident from the contrast difference in Fig. 3(B)-d, indicating that a thin layer consisting of low-density elements had peeled off. From these results, one may conclude that the peeling was the edge of multilayered graphene which had been coated on the $\beta$-Si$_3$N$_4$ particles.

Figure 4(a) shows the topographic images of the multilayered-graphene-coated $\beta$-Si$_3$N$_4$ particle surface observed using the dynamic force microscopy (DFM) mode in the scanning probe microscope. The surface of the multilayered-graphene-coated Si$_3$N$_4$ is rough due to the coating of multilayered graphene particles. Figures 4(b) and 4(c) show the surface profiles of A-A' and B-B' respectively, indicated in Fig. 4(a). In Figs. 4(b) and 4(c), the coating particles exhibit heights of 10–70 nm and widths of several hundred nanometers. Considering the initial size (thickness: 60 nm, lateral length: 3–7 $\mu$m) of the raw multilayered-graphene particles, one may conclude that these coated particles are formed from broken multilayered graphene. To account for these dimensional differences, the raw multilayered-graphene particles are assumed to break and peel off from the coating on the surface of $\beta$-Si$_3$N$_4$ during the mechanical treatment process. However, good crystallinity of multilayered graphene on the surface of $\beta$-Si$_3$N$_4$ was suggested from the change of G/D ratio in Raman spectra before and after the mechanical treatment process.

The starting composition of raw powders was fixed at multilayered-graphene-coated $\beta$-Si$_3$N$_4$: $\alpha$-Si$_3$N$_4$:Y$_2$O$_3$: HfO$_2$:SiO$_2 = 10:82:2.5:5:0.5$ by weight. To obtain a dense microstructure composed of elongated and aligned $\beta$-Si$_3$N$_4$ grains, the sintering was performed at 1900°C for 6 h in 0.9 MPa N$_2$. The orientation of $c$-axis-oriented Si$_3$N$_4$
ceramics was evaluated using X-ray diffraction (XRD), and the microstructure was observed using SEM. Figure 5 shows XRD patterns of the \(c\)-axis-oriented Si\(_3\)N\(_4\) ceramics, which were prepared by applying static magnetic fields ranging from 0.4 T to 10 T. The measured plane was normal to the applied magnetic field. In the ceramics prepared with a magnetic field, the intensity of the (002) peak increased markedly and the intensities of other peaks derived from the (hk0) plane clearly decreased, compared with Si\(_3\)N\(_4\) ceramics prepared without a magnetic field. Of special note is that the \(c\)-axis orientation was achieved even at a magnetic field as low as 0.4 T. If settling affects the orientation, then although Si\(_3\)N\(_4\) ceramics prepared without a magnetic field should orient in-plane, the uniaxial axis orientation is impossible to achieve. As shown in Fig. 5, no orientation was observed in Si\(_3\)N\(_4\) ceramics prepared without a magnetic field. The above results indicate that a superconducting magnet is not necessary for orientating \(\beta\)-Si\(_3\)N\(_4\) particles coated multilayered-graphene particles. However, the \(c\)-axis orientation lowered in the ceramics prepared with a high magnetic field, especially at 10 T. The lower orientation at high magnetic field results from the orientation of the small quantity (~5 wt % as the value specified in a release book) of \(\beta\)-Si\(_3\)N\(_4\) particles included in raw \(\alpha\)-Si\(_3\)N\(_4\) powder. Because the orientation of \(\beta\)-Si\(_3\)N\(_4\) particles without multilayered-graphene coating in a high magnetic field is due to the intrinsic anisotropy of diamagnetic susceptibility \(\Delta \chi = |\chi_a| > |\chi_c|\) of \(\beta\)-Si\(_3\)N\(_4\), the \(a\)-axis orients parallel direction to an applied magnetic field. However, since the magnitude of \(\Delta \chi\) is very small, there was no influence on the orientation of the \(\beta\)-Si\(_3\)N\(_4\) particles in low magnetic fields.

Figure 6 shows the microstructures of the \(c\)-axis-oriented Si\(_3\)N\(_4\) ceramics prepared in a magnetic field of 1 T and sintered at 1900 °C for 6 h in 0.9 MPa N\(_2\). Densely oriented structures are observed in both the images, but the geometries observed in one image are distinctly different from those in the other image. In the plane normal to the magnetic field as shown in Fig. 6(a), most particles exhibit a hexagonal shape. In the plane parallel to the magnetic field as shown in Fig. 6(b), most particles exhibit elongated shapes and are oriented in a direction along the applied magnetic field, which is in agreement with the XRD patterns shown in Fig. 5.

Anisotropic thermal conductivity occurred between the directions parallel and normal to the applied magnetic field. A thermal conductivity value of 96 W m\(^{-1}\)K\(^{-1}\) was obtained parallel to the magnetic field, which is higher than that in the normal direction (64 W m\(^{-1}\)K\(^{-1}\)). The thermal conductivity of non-oriented specimens was 77 W m\(^{-1}\)K\(^{-1}\). This improvement in thermal conductivity results from the \(c\)-axis orientation of Si\(_3\)N\(_4\). The low magnetic field orientation technique using the multilayered-graphene coated \(\beta\)-Si\(_3\)N\(_4\) particles is therefore useful for preparing the \(c\)-axis-oriented Si\(_3\)N\(_4\) ceramics with high thermal conductivity.

Fig. 4. DFM images showing the surface of multilayered-graphene-coated \(\beta\)-Si\(_3\)N\(_4\) seeds. (a) is a topographic image, and (b) and (c) are cross-sectional images. Reproduced from Ref. 1 with permission from Advanced Powder Technology.

Fig. 5. XRD patterns of Si\(_3\)N\(_4\) ceramics including \(\beta\)-Si\(_3\)N\(_4\) seed particles (\(\alpha = 4.4\)) prepared from 0 to 10 T. Reproduced from Ref. 1 with permission from Advanced Powder Technology.
3. Nondestructive internal structure observation

Inhomogeneous structures that degrade the performance of ceramics are generated by the imperfect control of powder that occurs due to the complex chain of “process factors” (Fig. 1). To improve this control, it is necessary to clarify the morphology of the inhomogeneous structures that are present within ceramics and to elucidate their relationship with process factors. However, no direct technique is currently available that can shed light upon such relationships. To understand their relationship, a novel observation system is needed which has multifunctional features such as (1) a high-transmission light source (allowing observation at greater depths), (2) high-speed scanning, (3) high-resolution observation at micrometer scale, and (4) 3D scanning to visualize the reality of the phenomena. The authors focused on swept-source optical coherence tomography (SS-OCT) as a technique having such features.

SS-OCT can provide the depth information via the Fourier transformation of a temporally dispersed spectrum by employing a tunable laser in the near-infrared range as a light source. Figure 7 illustrates the operating principle of SS-OCT. The incident light from a tunable laser is separated by a beam splitter into reflected (reference) light and transmitted light. The transmitted light is scattered onto the surface of the sample, some of which enters the sample and passes through it via transmittance, scatters as a result of its internal structure, and ultimately exits the sample. Of the scattered light that is reflected in the beam splitter, only light (signal light) of the same wavelength and phase as the reference light reflected by the mirror and returned is detected by interference. Because of this, the internal structure can be observed without being affected by radiation, even at high temperatures. Depth scanning (A-scan) is performed at high speeds (the swept frequency of commercial SS-OCT ranges from 20 to 100 kHz). The A-scan is then repeated laterally (B-scan) to obtain an image of the cross-section. The speed of the B-scan depends on the swept frequency in the direction of the A-scan, the resolution, and the range of the scan in the lateral direction. For example, if the swept frequency, resolution, and scan range are 20 kHz, 5 μm/pixel, and 1 mm, respectively, the B-scan speed is 100 fps. This means that observation can be performed in real-time. The B-scan is also repeated in a horizontal direction (C-scan). The imaging depth depends on the coherence length of the light source and the refractive index of the material. The resolution in the direction along which the light travels is different from that normal to this direction; the former depends on the wavelength-swept width of the light source (several micrometers), and the latter is the same as that of an optical microscope.

The internal structure of Al₂O₃ ceramics with artificially induced spherical defects was observed using SS-OCT. The results are shown in Fig. 8, which is a continuous OCT image along the A-scan direction of the internal...
structure of Al$_2$O$_3$ ceramics. An interval of 2.9 μm lies between each OCT image in Fig. 8. The contrast in the OCT images indicates the presence of interfaces with different refractive indices. Such changes can be observed in Fig. 8, but the images are not clear because of noise. Grainy signals with no continuity create “speckled patterns” that are caused by the interference between signals. These patterns do not directly reflect the internal structure and should be reduced or removed by image processing to detect the true signals. Figure 9 shows the same OCT images after filtering with Image J.$^{35,37}$ If the signal to be extracted is unclear, careful consideration is necessary because excessive treatment can result in eliminating the signal reflecting the actual structure. After the images are processed (Fig. 9), clear images of clustered bright spots are observed that change continuously as the depth increases, forming a circle of bright points. The brightness within the ring darkens gradually as the depth of observation increases. This change in morphology is thought to result from reflection at the interface between the spherical defects and the particles, as well as from transmission occurring inside the pores.

Figure 10 shows a comparison of the OCT images in which (a) displays the marked locations of the clusters of bright spots observed in Fig. 9, (b) is the transmission image from the IR microscope, (c) is the reflection image from the ultrasonic microscope, and (d) is the transmission image (contrast reversed) of an X-ray CT that was captured in the same region as the OCT image. The differences between the four images are due to the used methods and the characteristics of each technique. For example, the transmission image from the IR microscope detects the transmitted light that passes through the sample to provide a two-dimensional image containing all the information gained as the sample was traversed. The transmitted light is scattered at interfaces with different refractive indices, which is then observed in the image. Images produced by the ultrasonic microscope show the reflection of the ultrasonic wave that is produced at interfaces where the density changes. The structural information that results from differences in the X-ray absorption rate is obtained in the X-ray CT. In Fig. 10(d), the region with a small amount of X-ray absorption is dark and corresponds to a void in the spherical defect. It is clear from examining the images in Fig. 10 that the same spherical group is detected in the results of all the observation techniques used. However, the inhomogeneous structure in the position indicated by the white triangles was only observed in the OCT image, in which the morphology of a “cluster of bright spots” is consistently retained in the same region as in Fig. 9. This was not detected in the images produced using the other techniques. This result suggests that the inhomogeneous structure is a plate-like thin defect such as a crack. The inhomogeneous structure is thought to have gone undetected by the other techniques because of a mismatch in the focus and problems with the spatial resolution.

Fig. 8. OCT images showing the internal structure of Al$_2$O$_3$ ceramics before image processing. Reproduced from Ref. 34 with permission from Ceramics.
The size of the defects that could originate as a fracture in the actual materials was estimated by the Griffith equation using the average bending strength and fracture toughness of the Al$_2$O$_3$ ceramics, and Al$_2$O$_3$ ceramics with small spherical defects of less than 50 $\mu$m were thus prepared for observation. Figure 11 comprises (a) OCT and (b) X-ray CT images focused on the small spherical defect in the same position that was induced in the Al$_2$O$_3$ ceramics. When compared with the X-ray CT image, it became clear that the small spherical defect can be detected by OCT even at depths greater than 0.7 mm. The size of the spherical defect, at 44 $\mu$m, showed good agreement with the 40 $\mu$m estimate using the X-ray CT image. Notable in Fig. 11(a) is that the morphology of the spherical defect...
changes depending on the direction of observation, compared with Figs. 8–10. The spherical defect appears to be a “pair of curves” in Fig. 11(a). Based on these results, OCT observation was applied for the nondestructive inspection of the Al₂O₃ ceramics.⁴⁸) Although the details are omitted in this review, the predicted mechanical strength and the position of the defect as the origin of fractures detected by OCT observation showed good agreements with the strength obtained from a three-point bending test and the SEM observation.

4. Conclusion

In this article, two techniques for improving the performance of ceramics were reviewed: magnetic field orientation, which can be used to control the particle-assembled structure before sintering, and the use of SS-OCT for nondestructive internal structure observation.

The utility of the multilayered-graphene-coated particles was demonstrated by the successful fabrication of crystal-oriented ceramics in low magnetic fields without the need for a superconducting magnet. This is a novel orientation technique that does not require the utilization of a high magnetic field. The morphology and crystalline structure of the multilayered graphene are essential factors that control the orientation of the matrix particles. The shape and surface morphology of the matrix particles are also important because of the effect that these factors have on the morphology of the multilayered graphene coating.

The usefulness of SS-OCT was suggested by the detection of artificially induced spherical defects in the Al₂O₃ ceramic. Important factors to consider when observing a sample with OCT include the sample material and structural properties as well as the equipment specifications. Comparative evaluation using other techniques is also needed to clarify the physical meaning of the OCT image due to the lack of observational data in the industrial field. The author has also performed dynamic observations during processes such as the drying and precipitating of slurry and the dry pressing or sintering of a powder compact, among others. Please refer to previous and future reports for more information concerning these results.

Acknowledgments The author gratefully acknowledges Prof. Junichi Tatami (Yokohama National University), Prof. Satoshi Tanaka, and Prof. Emer. Keiizo Uematsu (Nagaoka University of Technology) for their continuous support. The author also thanks all co-workers and students for their contributions to the original work. This work was partially supported by JSPS KAKENHI Grant Numbers 26820299 and the Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) from Japan Science and Technology Agency (JST) [grant number AS2821001e].

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Fig. 11. (a) OCT and (b) X-ray CT images focusing on a small spherical defect induced in an Al₂O₃ ceramic. Reproduced from Ref. 33 with permission from the Journal of the Japan Society of Powder and Powder Metallurgy.
Takahashi: Control of the particle-assembled structure and a novel evaluation technique for high-performance ceramics

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