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A quantitative evaluation method for particle orientation structure in alumina powder compacts

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Abstract

A quantitative evaluation method was developed to analyze weak-moderate particle orientation in alumina green compacts based on the optical anisotropy measured with a polarized light microscope. Alumina compacts of various structures were prepared in high magnetic fields 0–10 T by a casting method. The compact was made transparent with an immersion liquid, and the retardation of polarized light through it was measured quantitatively using a polarized light microscope with a Berek compensator. The degree of particle orientation was defined as the ratio of birefringence of the compact to that of alumina single crystal perpendicular to the *c*-axis. The degrees of orientation thus evaluated were compared to those calculated from X-ray diffraction analysis for samples with high orientation, and were found to agree very well.

Keywords: Microstructure-prefiring; Optical microscopy; X-ray method; Al_2O_3; Oriented particles

1. Introduction

The powder packing structure in a green compact must be fully characterized in processing of ceramics since it governs sintering behavior, microstructure development and thus characteristics and properties of sintered bodies. Characterization of particle orientation structure is essential. Recent papers reported that controlled particle orientation in polycrystalline ceramics improved mechanical, electrical and magnetic properties remarkably.[1–3,20,21] Particle orientation structure also causes troubles in processing, such as anisotropic shrinkage and/or cracking during sintering.[4–11] In the alumina system, however, extreme difficulty is often encountered in the evaluation of particle orientation with X-ray diffraction analysis. The relevant diffraction peaks of major crystalline faces are very weak, which allow reliable evaluation only for highly oriented structures. The change of diffraction peak cannot be detected in many powder compacts where the orientation is moderate to low. The particle orientation becomes apparent only after sintering and grain growth.[7] Alumina is one of the most important ceramics and a convenient characterization method is urgently needed to evaluate particle orientation.

In previous papers, we have proposed a semi-quantitative method to characterize particle orientation with a polarized light microscope for alumina compacts made by slip casting or injection moulding processes.[8,12] Alumina compacts show optical anisotropy when *c*-axes of particles are oriented. In the method, the green compacts are made transparent by addition of adequate immersion liquid[13] and the orientation structure was observed in the transmission mode of a polarized light microscope. To develop a quantitative evaluation method for orientation, it is important to establish the relationship between the orientations evaluated by this new characterization technique and the conventional X-ray method.

This paper presents a quantitative evaluation method for particle orientation structure for an alumina green compact using polarized optical microscopy. The validity of this method is demonstrated by comparing the results obtained by this method to that evaluated with the X-ray diffraction analysis on a well-oriented particle compact, for which the evaluation is possible by both methods.

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Nomenclature

d thickness of a thinned compact (nm)
f degree of orientation (%)
f_{cal} degree of orientation calculated from sum of birefringence of particles (%)
$I_{\mathrm{max\_random}}$ maximum intensity of random structure in rocking curve (arb.unit)
I_{modified} modified intensity of rocking curve (arb.unit)
$I_{\mathrm{orientation}}$ intensity of orientation structure in rocking curve (arb.unit)
I_{random} intensity of random structure in rocking curve (arb.unit)
$\Delta n_{\mathrm{cal\ compact}}$ theoretical birefringence of a compact
$\Delta n_{\mathrm{compact}}$ birefringence of a compact
$\Delta n_{\mathrm{particle}}$ theoretical birefringence of a particle
$P(\alpha)$ probability of particles (%)
R_{compact} retardation of a compact (nm)
R_{particle} retardation of a particle (nm)
$R_{\mathrm{single\ crystal}}$ retardation of a single crystal (nm)

Greek letters
α inclination angle between direction of magnetic field and c-axis of particle (degree or radian)
γ rotation angle of particles by spherical polar coordinate (degree or radians)
ε reflective index of extraordinary light
$(\varepsilon - \omega)$ birefringence of single crystal (0.0075)
ζ inclination angle between light wave direction and c-axis of particle (degree or radian)
θ diffraction angle with XRD (degree or radian)
ρ relative density of a compact (%)
ω reflective index of ordinary light

2. Experimental procedure

2.1. Preparation of compact

Compacts with various particle orientation were prepared in high magnetic fields.[14,15] Three commercial α-alumina powders (AA1, AA05, AA03, Sumitomo Chemical Co., Japan) were used as raw materials. The alumina powders were nearly monodispersed and their shapes were spherical; particle diameters were 1.3, 0.7 and 0.5 μm. The powder was mixed with distilled water and a dispersant (ammonium polyacrylate; Seruna D305, Chukyoyushi Japan). The volume fraction of powder was 20–30 vol%. The mixture was ball milled for 24 h to make a slurry and was poured into cylindrical moulds. After drying in high magnetic fields (0–10 T) provided by a superconductor magnet, the compact was calcined at 1273 K to remove the dispersant and to fix the packing structure of particles.

2.2. Evaluation of particle orientation in compact

The degree of particle orientation was evaluated on transparent green compacts with a polarized light microscope. We assumed that retardation of a compact R_{compact} could be written as follows:[8]

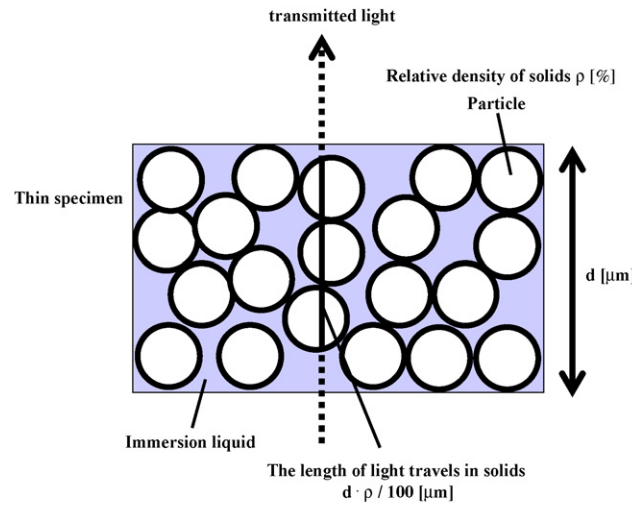


Fig. 1. Illustration of specimen.

$$R_{\mathrm{compact}} = d\frac{\rho}{100}\Delta n_{\mathrm{compact}} \tag{1}$$

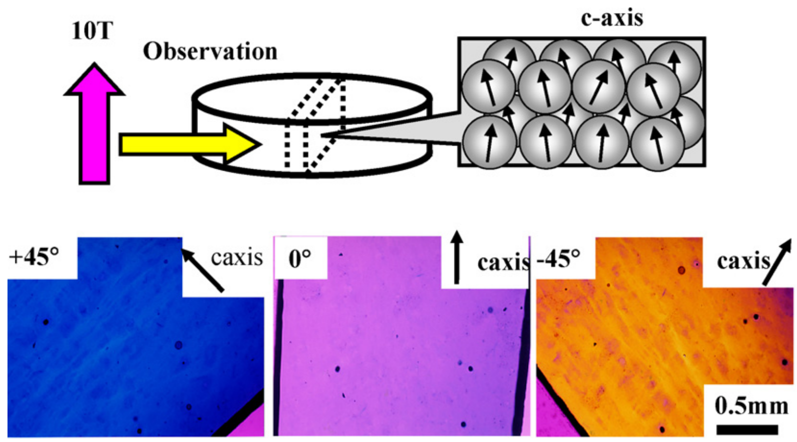
where $\Delta n_{\mathrm{compact}}$ is the birefringence of compact, d the measured thickness of a thinned compact and ρ is the relative density; the product $d\rho/100$ corresponds to the net length of the solid through which the light travels (see Fig. 1). The relative density ρ was measured with a Hg-porosimeter, and was about 60% for all compacts. The degree of particle orientation f is defined as the ratio of birefringence of compact $\Delta n_{\mathrm{compact}}$ and that of single crystal $\Delta n_{\mathrm{single\ crystal}}$, as follows:

$$f = \frac{\Delta n_{\mathrm{compact}}}{\varepsilon - \omega} \times 100 = \frac{\Delta n_{\mathrm{compact}}}{0.0075} \times 100 \tag{2}$$

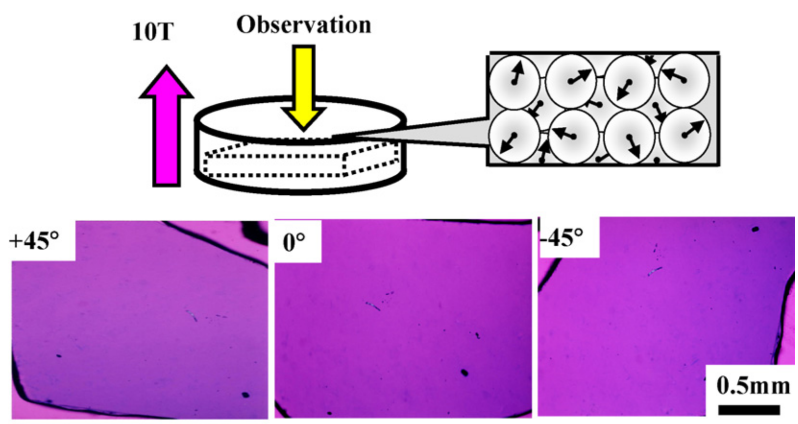
where the term $(\varepsilon - \omega)$ is the birefringence of single crystal along a-axis and is 0.0075 for alumina[16] observed perpendicular to c-axis.

The birefringence $\Delta n_{\mathrm{compact}}$ was measured as follows. A thinned sample (typically 0.3 mm thick) was made transparent by addition of adequate immersion liquid (methylene iodide with sulfur, refractive index, RI = 1.77) having the same refractive index as alumina (RI = 1.76–1.77). The liquid eliminates the reflection of light at the liquid/alumina interface, and lets all light go through the particle.

A polarized light microscope was used to observe the optical anisotropy in a green compact with a white light under a cross-nicols. A sensitive tint plate (R = 530 nm) was used to overview the structure of particle orientation. The image shows a repeated change of colour, i.e., yellow/pink/blue with the rotation of the sample, when the particles are orientated. The change is due to the interference which depends on the retardation of the compact and the sensitive tint plate. A compensator of the Berek type[17] was used for quantitative measurement of retardation.



(a)



(b)

Fig. 2. Polarized light micrograph of compact made in a high magnetic field: (a) perpendicular to the magnetic field, and (b) parallel to the magnetic field.

2.3. X-ray diffraction analysis

Highly orientated alumina compact prepared specially in a high magnetic field was used to examine orientation by X-ray diffraction (XRD; MO3XHF, MacScience Japan) with Cu Kα radiation. The conventional $2\theta/\theta$ scan was used to obtain the X-ray diffraction profile. The $\{0\,0\,l\}$ orientation factor F was calculated by the Lotgering method.[18] The Rocking curve analysis was also made to determine the distribution of preferred orientation.[19]

3. Results and discussions

3.1. Evaluation of degree of particle orientation in a green compact

Fig. 2 shows the polarized light microphotographs taken for cross-sections parallel and perpendicular to the magnetic field (arrows in Fig. 2). The slurry was of the solid loading 30 vol% and the particle diameter 0.5 μm. The thin sample prepared parallel to the magnetic field showed a repeated change of colour from blue to pink and then to yellow with its rotation for every 45° as shown in Fig. 2(a). Other thin samples prepared normal to the magnetic field did not show a colour change and was always pink (Fig. 2(b)). These changes of colour suggest the particle orientation shown schematically in the figure.

Fig. 3 shows the photograph for a green compact prepared in the same way as that shown in Fig. 2 except the applied magnetic field. No change of colour was found regardless of the rotation of the sample, showing the absence of retardation in the polarized light.

Fig. 4 shows the retardation as a function of thickness for a specimen with a specific particle orientation. There is a linear relationship between the retardation R_{compact} and the thickness of specimen d. The correlation coefficient was 0.970. Clearly, the slope of line gives the birefringence of compacts $\Delta n_{\text{compact}}$ accurately. Interface effect between particles and pore, if any, are not significant in the present system. The degree of particle orientation can be calculated with Eq. (2) and was 37% for the specimen shown in the figure. The maximum degree of particle orientation was 95% among specimens used in this study.

Fig. 5 shows X-ray diffraction patterns of a compact with an exceptionally high degree of orientation, which was prepared in a high magnetic field 10 T with slurry of very low solid load-

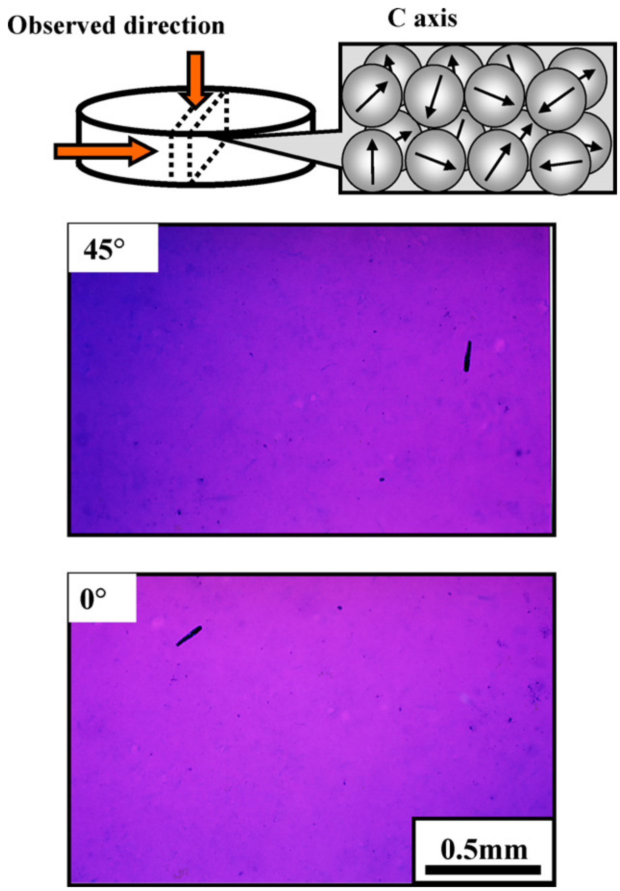


Fig. 3. Polarized light micrograph of randomly oriented compact.

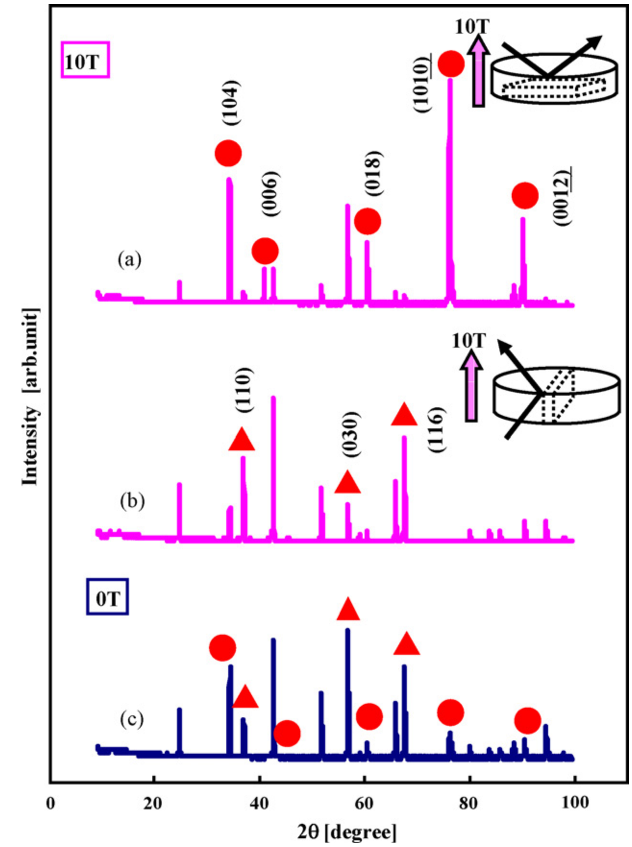


Fig. 5. X-ray diffraction patterns for (a) the surface parallel to magnetic field, (b) perpendicular to magnetic field, and (c) the randomly oriented sample without magnetic field.

ing. Faces perpendicular and parallel to the magnetic field were examined. The diffraction pattern of a compact prepared without a magnetic field is also shown in Fig. 5(c). Markedly enhanced diffraction peaks were noted relevant to *c*-planes (0 0 *l*) for the surface of the specimen perpendicular to the magnetic field, such as (0 0 6) and (0 0 1 2) planes. The diffraction peak was also enhanced for the planes nearly parallel to *c*-plane such as (1 0 1 0). In contrast, intensities for (*h k* 0) planes such as (1 1 0) and (0 3 0) planes were high on faces parallel to the magnetic field. These results are consistent to the structure of particle orientation shown in Fig. 2.

Fig. 6 shows the relationship between the degrees of particle orientation determined by the present optical method and the Lotgering method.[18] In the region of high orientation, good, but non-linear correlation was noted between the results of these

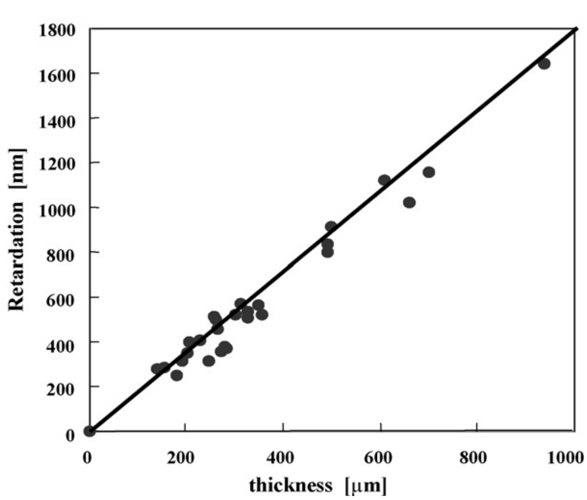


Fig. 4. Relationship between retardation and sample thickness.

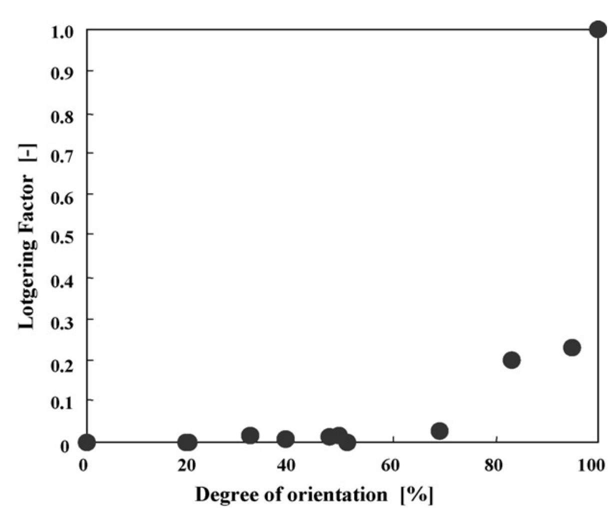


Fig. 6. Relationship between orientation degree measured by polarized light microscopy and Lotgering factor.

two methods. The optical method has merit in the determination of weak-moderate orientation of particles in alumina compacts. The value of Lotgering factor approaches zero rapidly when the degree of orientation was less than about 50% in the optical method. The Lotgering factor was only 0.23 in the compact which has degree of orientation 95% in the optical measurement. The Lotgering method is best suited for evaluating orientations of very high degree, as are often encountered in the field of thin film deposition. However, the method is not adequate for evaluating orientation in particulate systems with low to moderate degrees of orientation. It should also be emphasized that the Lotgering factor is just a semi-quantitative measure of orientation.

3.2. Verification of degree of particle orientation from birefringence

The optical method is clearly much more sensitive than the X-ray method in identifying the orientation of alumina particles. It also has a clearer physical meaning compared to the Lotgering method. Before its broad application, it is important to justify the observed retardation in terms of the packing structure of particles. In this section, the retardation measured optically is compared with that calculated by simulation with the Rocking curve of X-ray diffraction analysis.

Consider a case where the compact is examined from a direction perpendicular to the magnetic field as shown in Fig. 2(a). The retardation of the compact is assumed to be given by the sum of the retardation for each particle $\sum R_{\text{particle}}$ in the compact, and the degree of orientation f_{cal} is given as follows:

$$f_{\text{cal}} = \frac{\sum R_{\text{particle}}}{R_{\text{single\_cristal}}} \times 100 = \frac{\Delta n_{\text{cal\_compact}}}{0.0075} \times 100 \quad (3)$$

Birefringence of the compact $\Delta n_{\text{cal compact}}$ is calculated by summing the product of the frequency of oriented particles and the birefringence of each particle $\Delta n_{\text{particle}}$, as follows:

$$\Delta n_{\text{cal\_compact}} = \sum \Delta n_{\text{particle}}\,\text{frequency} \quad (4)$$

First, the birefringence of particle $\Delta n_{\text{particle}}$ is calculated for the case of inclined angle α and rotation angle γ for c-axis as shown in Fig. 7(a). An angle α is defined as the inclination angle from the direction of the magnetic field, and the rotation angle γ against the direction of observation in a spherical polar coordinate. Fig. 7(b)–(e) shows some typical directions of particles for various α and γ. Fig. 7(b) shows that a particle has a birefringence $\Delta n_{\text{particle}}$ 0.0075, when its c-axis is oriented along the magnetic field (incline angle α is 0°) for the rotation angle $\gamma = 0$–$360°$. Fig. 7(c)–(e) shows ray surfaces of a particle, when inclination angle α is 40° and rotation angles γ are 0°, 90° and 270°, respectively. Theoretical birefringence is given by the equation:

$$\Delta n_{\text{particle}} = \omega - \frac{\omega\varepsilon}{\sqrt{\omega^2 \sin^2\zeta + \varepsilon^2\cos^2\zeta}} = 1.7685 - \frac{1.7685 \times 1.761}{\sqrt{1.7685^2 \sin^2\zeta + 1.761^2\cos^2\zeta}} \quad (5)$$

where ζ is inclination angle between the polarized light and c-axis, which is given by $\zeta = \cos^{-1}(\sin\alpha \sin\gamma)$. The values 1.7685 and 1.761 in this equation are refractive indices of ordinary light and extraordinary light at $\alpha = 90°$, respectively. Fig. 8 plots expected birefringence $\Delta n_{\text{particle}}$ for various α for intervals of every 5° in the range from 0° to 40° and γ from 270° to 90°. The expected birefringence $\Delta n_{\text{particle}}$ is a function of rotation angle γ, and has the minimum values at 270° and 90° in γ. The expected birefringence $\Delta n_{\text{particle}}$ has the maximum and a constant value 0.0075 at 0° in γ, since the incident polarized light

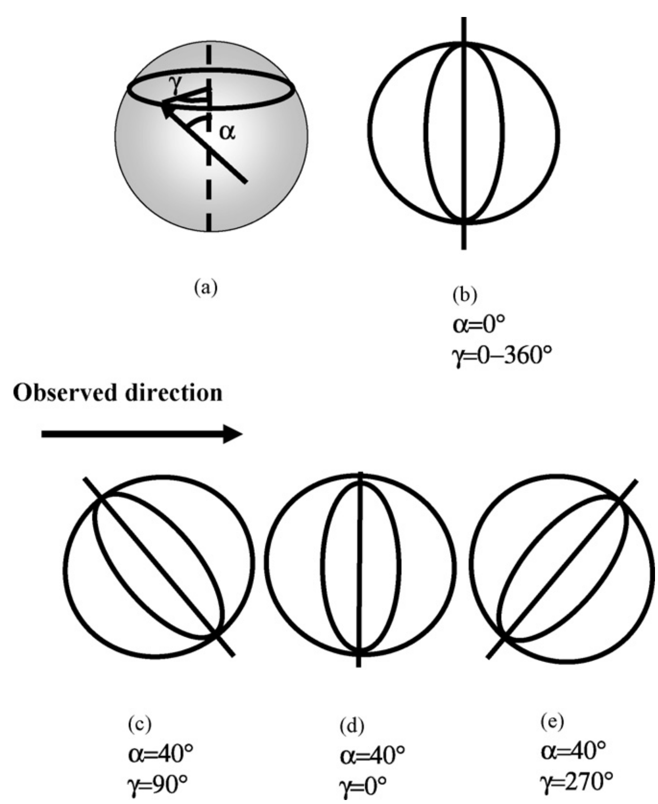


Fig. 7. Directions of particles with inclination angle α and rotation angle γ.

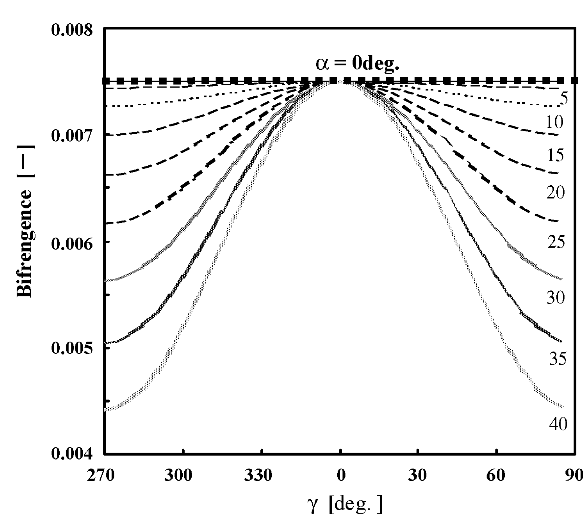


Fig. 8. Theoretical bifrengence as function γ.

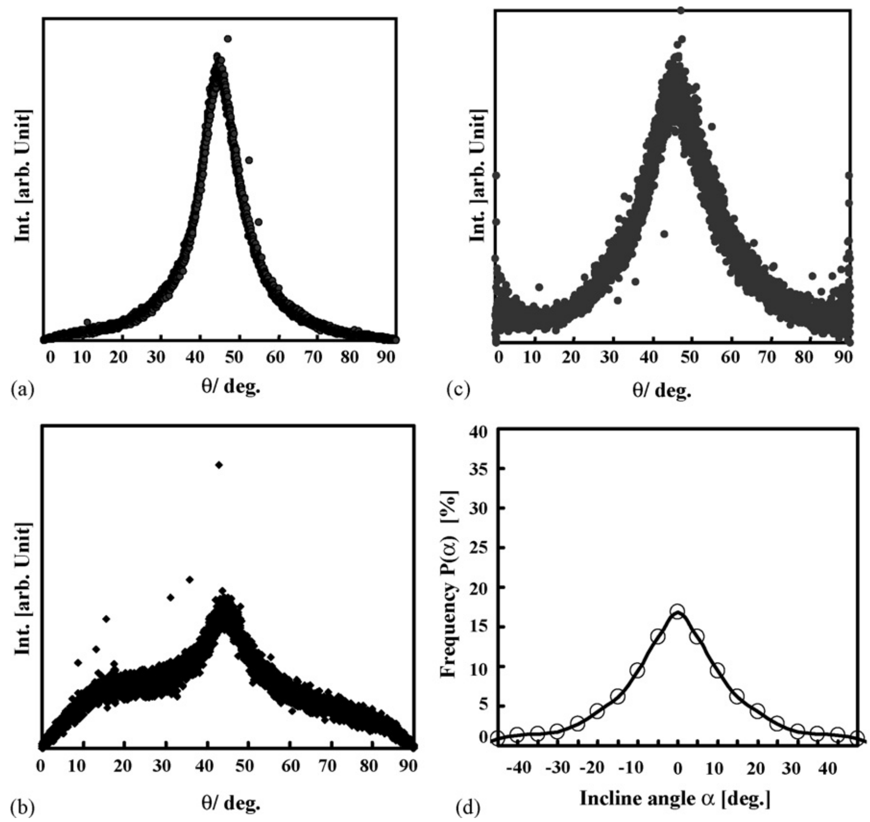


Fig. 9. Rocking curves of (0 0 1̲ 2̲) plane: (a) oriented sample, (b) randomly oriented sample, (c) modified rocking curve of orientation sample, and (d) orientation distribution of *c*-plane.

is perpendicular to *c*-axis. $\Delta n_{\text{particle}}$ is 0.0044 at $\gamma = 90^\circ$, 270° and $\alpha = 40^\circ$ as shown in Fig. 7.

The rocking curve of *c*-plane of the compact was used to determine the frequency of particles orientated at specific angles relative to the magnetic field. Fig. 9 shows the rocking curves of (0 0 1̲ 2̲) plane in compacts which have the degrees of particle orientation 89% and zero. A sharp peak was noted at 45.34° (=2θ/2) in the compact with highly oriented particles (Fig. 9(a)). In the specimen without a specific orientation, a rocking curve had a tableland shape with a small broad peak at the central angle (about 45° (=2θ/2)) (Fig. 9(b)) and not of the expected flat shape. This apparent tableland shape is due to the defocusing phenomenon, caused by multiplex diffraction. To compensate this anomaly of X-ray apparatus, the measured rocking curve was modified with the curve of random structure as follows:

$$I_{\text{modified}} = \frac{I_{\text{orientation}}}{I_{\text{random}}/I_{\text{max\_random}}} \tag{6}$$

where I_{modified} is modified intensity, $I_{\text{orientation}}$ and I_{random} are intensities for oriented and random structures, respectively. $I_{\text{max\_random}}$ is the maximum intensity for a random structure. Fig. 9(c) shows a modified rocking curve for the oriented structure. The frequency $P(\alpha)$ of particles with *c*-axis oriented along magnetic field is given be by the following equation:

$$P(\alpha) = \frac{I_{\text{revise},\alpha}\,\mathrm{d}\alpha}{\sum I_{\text{revise},\alpha}\,\mathrm{d}\alpha} \times 100 \tag{7}$$

Fig. 9(d) shows $P(\alpha)$ calculated with Fig. 9(c). The direction of magnetic field corresponds to the incline angle zero. The *c*-axes orients to the direction of magnetic field for 18.2% of particles in a compact.

Spherical polar coordinates are used when describing 3D distribution of orientation. The probability of particles for specific orientation is proportional to the area in unit sphere described in Fig. 10(a) and (b), where the unit area is given by $\sin\alpha\,\mathrm{d}\gamma\,\mathrm{d}\alpha$. Product of $P(\alpha)$ and $\sin\alpha\,\mathrm{d}\alpha\,\mathrm{d}\gamma$ represents probability at the angle α and γ. The probability at α only, $2\pi P(\alpha)\sin\alpha\,\mathrm{d}\alpha$ is given by integrating γ from 0 to 2π. Fig. 9(c) shows distribution of probability in 3D as a function of α. Equation (4) is rewritten by using probability in 3D as follows:

$$\Delta n_{\text{cal\_compact}} = \frac{\int_{-\pi/2}^{\pi/2}\int_0^{2\pi} \Delta n_{\text{particle}}(\alpha,\gamma)P(\alpha)\sin\alpha\,\mathrm{d}\gamma\,\mathrm{d}\alpha}{\int_{-\pi/2}^{\pi/2} 2\pi P(\alpha)\sin\alpha\,\mathrm{d}\alpha} \tag{8}$$

Fig. 11 shows the product of theoretical birefringence $\Delta n_{\text{particle}}$ and probability based on Eq. (8) as a function of incline angle α. Birefringence of the compact $\Delta n_{\text{cal\_compact}}$ is given by integration for the curve, and is 0.006887.

The degree of orientation of the compact f_{cal} which is estimated from the ratio of calculated birefringence of compact $\Delta n_{\text{cal\_compact}}$ and that of single crystal 0.0075 according to Eq. (3) is 92%. This calculated degree of orientation $f_{\text{cal}} = 92\%$for the model agreed with $f = 89\%$ of experimental value (Fig. 12).

Fig. 12 shows the relation between the degrees of orientation evaluated by the present method with polarized light microscopy

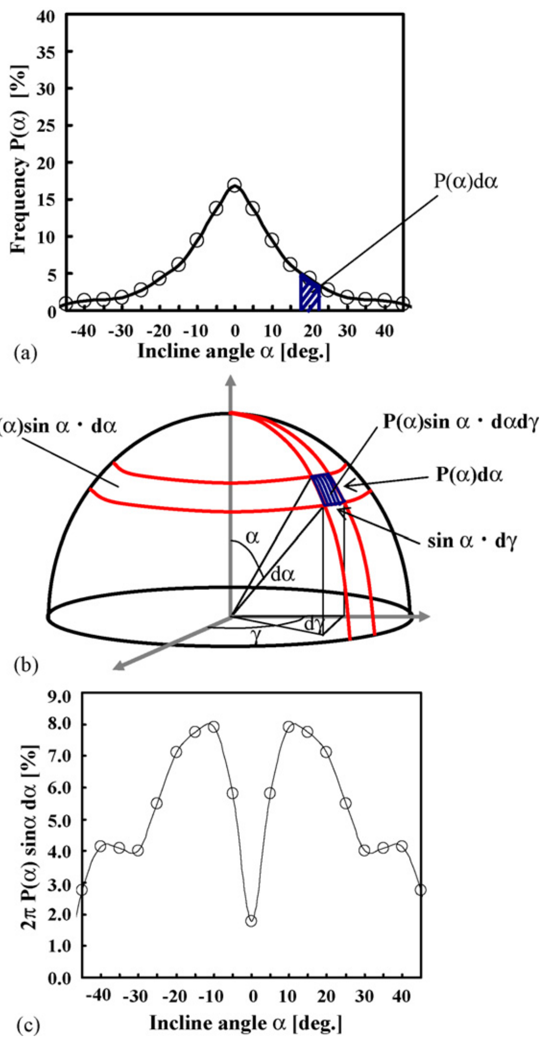


Fig. 10. Scheme of spherical polar coordinate to explain distribution in 3D: (a) orientation distribution for *c*-axes of particles in 2D, (b) spherical polar coordinate, and (c) orientation distribution for *c*-axes of particles in 3D.

and the calculated value $\Delta n_{\mathrm{cal\_compact}}$. The degree of orientations also agreed with all the result calculated for the model for other compact. A very high correlation coefficient 0.9952 was obtained, showing the validity of the present model.

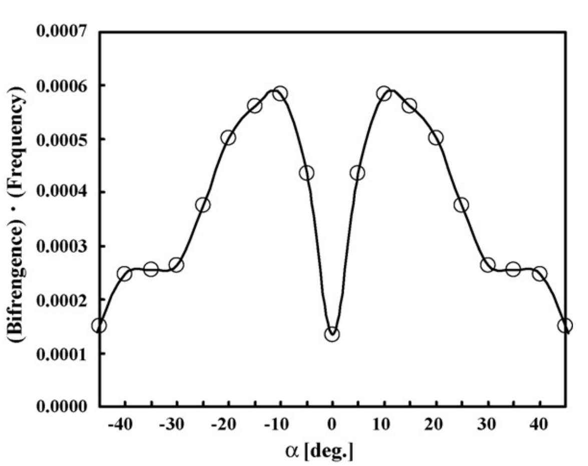


Fig. 11. Relationship between (bifrengence) (frequency) and *α*.

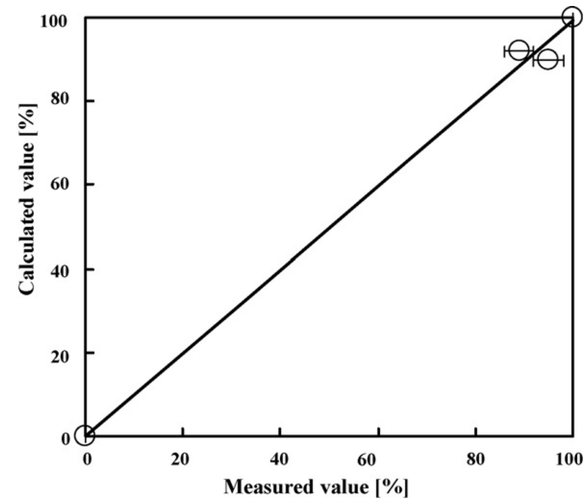


Fig. 12. Relationship between calculated and measured orientation degree.

This method is applicable for determining the orientation in optically anisotropic systems when specimens are transparent and optically colorless. Results in this study suggested that orientation distribution is directly related to degree of orientation determined by the polarized light microscopy. The degree of orientation determined in this study should be well correlated to various properties in polycrystalline systems, other than the optical property. Important property such as piezo-electricity should be linearly correlated to the degree of orientation determined in this method.

The Lotgering method is widely used to evaluate orientation structure. But, the Lotgering factor is only semi-quantitative because it represents crystals of specific direction and those of only slightly mis-oriented do not contribute to the diffraction peak. This method provides little information about crystal orientation in the structure. The polarized light microscopy gives comprehensive information, including not only oriented particles but also mis-oriented particles. Our method can provide useful data for analysis of orientation structure in understanding processing and texture relationships.

4. Conclusions

A quantitative characterization method was developed for evaluating particle orientation structure in a green compact with polarized microscopy using anisotropic optical characteristics. The compact was produced by a casting method in high magnetic field 10 T. The compact was soaked in an immersion liquid that made compacts transparent. A polarized light microscope was used to observe the transparent thinned compacts. Birefringence of the compact was measured by a quantitative evaluation method for particle orientation structure. The degree of orientation was determined from the ratio of birefringence of a compact and single crystal 0.0075. Furthermore, the degree of orientation evaluated with birefringence agreed with X-ray diffraction results for the sample with a well-oriented structure. The result demonstrated validity of the novel characterization method.

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