Continuous Measurement of XRD Peak Intensity of Bismuth under Magnetic Field

T Kohama and K Iwai
Department of Material, Physics and Energy Engineering, Nagoya University, Nagoya 464-8603, Japan
E-mail: kohama.takenori@g.mbox.nagoya-u.ac.jp

Abstract. A material which has a magnetic anisotropy rotates to reduce magnetization energy under a magnetic field, and finally the magnetic easy axis and the direction of magnetic field becomes the same direction. For clarification of the crystal rotation, crystal alignment behaviour of bismuth which has a magnetically anisotropic nature was examined in situ by X-ray diffraction during the static magnetic field imposition. Change of the bismuth (110) peak intensity in time was measured by X-ray diffraction to evaluate the crystal alignment. The alignment time decreased as the magnetic field strength increased. This tendency was similar to the theoretically calculated relaxation time. Aggregation of the bismuth particles decreases the driving force for the crystal alignment, which was in proportion to the magnetic susceptibility difference between the magnetically easy and hard axes. The effective difference in magnetic susceptibility for aggregated bismuth particles was estimated by measuring the alignment time of the particles under magnetic fields of various strengths. The estimated effective magnetic susceptibility difference increases with a decreasing magnetic field strength.

1. Introduction
Imposition of a magnetic field on materials has been utilized in materials processes such as crystal alignment [1], levitation [2], separation [3], and flow control of an electrically conductive material. In particular, alignment process is an attractive tool for producing functional materials, because physical properties of materials, such as the electric, magnetic, thermal, and mechanical properties, can be controlled if these properties have an anisotropic nature. With the development of the technology of superconducting magnets, crystals of nonmagnetic, magnetically anisotropic materials such as metals [4-6], ceramics [7, 8], and polymers [9] can be aligned by the imposition of a strong magnetic field. To form unidirectionally aligned crystals for a material with a magnetic anisotropy of $\chi_c < \chi_a$, a combined process involving the imposition of a magnetic field and the rotation of a sample has been proposed [9, 10]. By using this method, a bulk form of hydroxyapatite with unidirectionally aligned crystals has been produced [11]. A theoretical analysis for the optimization of this process has been performed [12]. Furthermore, crystal alignment of a tin–lead binary alloy primary phase in a magnetically preferred direction can be controlled by changing the duration of an imposed electric current and static magnetic field during solidification [13]. For optimization of these crystal-alignment processes, the rotation behaviour of crystals suspended in a solvent in a magnetic field should be clarified. Therefore, alignment behaviour of feeble magnetic material has been observed by using a laser microscope [14] and theoretical development of crystal alignment behaviour has been done [15].
In this paper, we examined the in situ crystal-alignment behaviour of bismuth particles in the presence of a static magnetic field by in situ x-ray diffraction (XRD) studies.

2. Experimental

The experimental apparatus is shown in Fig.1. Bismuth particles (2.67 g) mixed with liquid polydimethylsiloxane (4 mL) was used as a slurry in this research. The viscosity and density of the polydimethylsiloxane were 50 Pa.s and 1000 kg/m$^3$, respectively. An acrylic vessel containing the slurry was placed in the bore of a superconducting magnet for the imposition a static magnetic field on the slurry. The direction of magnetic field was vertical downward direction.

The crystallographic structure of bismuth can be considered as a hexagonal structure and bismuth crystals show anisotropy in magnetic susceptibility. The magnetic susceptibility of bismuth in the direction of the a-axis is $-1.77 \times 10^{-4}$ and that in the direction of the c-axis is $-1.24 \times 10^{-4}$, so that c-axis is parallel to the magnetic field direction if a magnetic field is imposed on the bismuth crystal. The X-ray direction in this experiment was in horizontal plane, so the XRD peak intensity in a plane parallel to the c-axis increased when the magnetic field was imposed on bismuth crystal.

The difference of magnetic susceptibility of a single crystal in easy axis and hard axis is described as “magnetic susceptibility difference”, and that for an aggregated particle is described as “effective magnetic susceptibility difference” in this manuscript. Magnetic susceptibility difference and effective magnetic susceptibility difference are expressed as $\Delta \chi$ and $\Delta \chi_E$, respectively.

The effective magnetic susceptibility difference of the bismuth particles used in this experiment was small in comparison with the magnetic susceptibility difference of a single crystal, because the bismuth particles with non-spherical shapes aggregated as shown in Fig.2. Size distribution of the bismuth particles used in this experiment was from 0.259 $\mu$m to 34 $\mu$m and the mean particle size was 8.25 $\mu$m, respectively.

The bismuth particles moves by gravitational and magnetization forces under the magnetic field. These two forces acting on the particles were evaluated. The driving force for sedimentation of the bismuth particle is the difference in density between the bismuth particles and polydimethylsiloxane, which can be expressed as follows.
where $g$ is the acceleration of gravity, $V_{Bi}$ is the volume of bismuth particles, $\rho_{Bi}$ is the density of bismuth, and $\rho_{polymer}$ is the density of polydimethylsiloxane, respectively.

This force is calculated as $2.31 \times 10^{-11}$ N for a spherical particle with a diameter of 8.25 $\mu$m.

In the presence of the magnetic field, the magnetization force affects the motion of the bismuth particles. The following equations are used to evaluate the magnetization force.

\begin{equation}
\begin{aligned}
F_r &= \mu_0 \chi_{Bi} - \chi_{polymer} \left( H_r \frac{\partial}{\partial r} H_r + H_z \frac{\partial}{\partial z} H_r \right) V_{Bi} \\
F_z &= \mu_0 \chi_{Bi} - \chi_{polymer} \left( H_r \frac{\partial}{\partial r} H_z + H_z \frac{\partial}{\partial z} H_z \right) V_{Bi}
\end{aligned}
\end{equation}

where $r$ is the radial direction, $z$ is the axial direction, $\mu_0$ is the magnetic permeability in vacuum, and $\chi_{Bi}$ and $\chi_{polymer}$ are magnetic susceptibilities of bismuth and polydimethylsiloxane, respectively.

The magnetization force is therefore proportional to the difference in magnetic susceptibility between the bismuth particles and the polydimethylsiloxane. The magnetic susceptibility of the polydimethylsiloxane is neglected in the calculation, because the magnetic susceptibility of polymers is usually of the order of $10^{-6}$ [16] which is small in comparison with that of bismuth. The calculated forces for a 8.25 $\mu$m-diameter spherical bismuth particle in the radial and axial directions are $F_r = 1.75 \times 10^{-13}$ N and $F_z = 9.73 \times 10^{-13}$ N, respectively, when the strength of the magnetic field is 3 T. Therefore, main force acting on the bismuth particles is the gravitational force.

Brownian motion acts on the bismuth particles as a thermal fluctuation. The relaxation time for the Brownian motion, $\tau_B$ is expressed as follows [17].

\begin{equation}
\tau_B = \frac{3 V_{Bi} \eta}{kT}
\end{equation}

where $\eta$ is viscosity, $k$ is Boltzmann constant and $T$ is absolute temperature, respectively.

On the other hand, the temporal variation of the angle $\theta$ for the particle rotation by the magnetic torque is theoretically expressed as follows when the inertial term can be neglected [18].

\begin{equation}
\tan{\theta} = \tan{\theta_0} \exp\left(-\frac{t}{\tau}\right)
\end{equation}

\begin{equation}
\tau = \frac{30 \eta + R^2 \sigma \mu_0^2 H^2}{5 \Delta \chi E} = \frac{\mu_0}{\Delta \chi E}
\end{equation}

where $\theta_0$ is the initial angle between the magnetic field direction and the magnetically easy axis and $\tau$ is the relaxation time for the crystal alignment, respectively, and $H$, $R$, $t$, $\theta$, and $\sigma$ are the magnetic field strength, crystal radius, time, the angle between the magnetically easy axis of the crystal and the magnetic field direction and the electric conductivity, respectively.

When the relaxation time for the Brownian motion, $\tau_B$ is equal to the relaxation time for the crystal alignment $\tau$, the critical diameter for a spherical particle, $d_c$ can be obtained as follows under the assumption that the effect of the electrical conductivity can be neglected.

\begin{equation}
d_c = \left( \frac{3 \mu_0 kT}{2 \pi \Delta \chi E B^2} \right)^{\frac{1}{3}}
\end{equation}

The critical particle sizes in the cases of $B=0.5$ T and $B=1$ T magnetic fields are calculated to 0.246 $\mu$m and 0.155 $\mu$m, respectively when the effective magnetic susceptibility difference $\Delta \chi_E$ is $5.3 \times 10^{-6}$ and $T$ is 300 K. The effective magnetic susceptibility adopted here is one-tenth of the single crystal value. Therefore Brownian motion might slightly affect the alignment behavior under these
magnetic fields because the minimum size of the bismuth particles used in this experiment was 0.259 μm.

The XRD results with and without a 2 T magnetic field are shown in Fig. 3. The (110) peak increased by imposing a magnetic field, whereas the (104) peak relatively decreased. This well agrees with the theoretical prediction mentioned above while aggregated bismuth particles were used in the experiment. Therefore, the (110) peak intensity of the bismuth crystal was chosen as an index of the crystal alignment. And its temporal change was measured for various strengths of the magnetic field. The results are shown in Fig.4 with a fitting curve. The (110) peak intensity did not change with time under the no magnetic field although it showed a small fluctuation. This means that sedimentation of the bismuth particles in this experiment can be neglected. And the magnetization forces in radial and axial directions can therefore be ignored in this experiment, since these forces are smaller than the force caused by the density difference. The fluctuations observed here are might be caused by thermal fluctuation. On the other hand, the intensity of the (110) peak measured under a 1 T magnetic field increased gradually with time and it reached a plateau after a certain time. That is, the bismuth particles in the polydimethylsiloxane rotate to the magnetically preferred direction. We defined the alignment time in this experiment as the period from the insertion of the sample into the bore of the magnet to the time at which the (110) peak intensity reached 90% of its maximum value. The 90% value is also indicated in Fig.4(b) as the horizontal line.

Table 1 shows the alignment time in the several different magnetic field strengths. The alignment time decreases with increasing magnetic field strength. In particular, it decreases markedly between the 1 T and 2 T. The alignment time at fields of more than 2 T may be weakly dependent on the strength of the magnetic field, but this is not clear from this experiment.
3. Discussion

The relaxation time was calculated by using equation (4) and was compared with the measured alignment time. The results are shown in Fig. 5. The real alignment time exists between two measurement times whose interval is about 30 seconds as shown in the Fig. 4. Therefore this interval is adopted as the range of error bar in Fig. 5. The relation between the magnetic field strength and the measured alignment time is similar to the relation between the magnetic field strength and the

![Figure 5. Comparison of calculated alignment time and measured one](image)

![Figure 6. Estimated effective magnetic susceptibility difference of the bismuth particles](image)
The imposition of the magnetic field was theoretically calculated to one radian based on the random distribution of the particles. The effective magnetic susceptibility difference, $\Delta \chi$, was then estimated from equations (3) and (4), by assuming that the final and initial angles were $0.1^\circ$ (0.0017 radians) and $57.3^\circ$ (1 radian), respectively. According to the final angle, it should be theoretically decided under the consideration of thermal fluctuation while the $0.1^\circ$ was adopted here. The alignment times shown in Table 1 were also used in the calculation. Figure 6 shows the calculated effective magnetic susceptibility difference of the bismuth particles under the different magnetic field strength.

Horizontal line in Fig.6 is the magnetic susceptibility difference of bismuth single crystal, $\Delta \chi$. The estimated effective magnetic susceptibility difference, $\Delta \chi_{E}$, has roughly a tendency to decrease with the increase in the magnetic field strength. This is because only particles with a large value in effective magnetic susceptibility align in the magnetically preferred direction under a weak magnetic field, whereas particles with not only a large value in effective magnetic susceptibility difference but also a small value in effective magnetic susceptibility difference also align in the magnetically preferred direction under a strong magnetic field.

However, slight increase in the effective magnetic susceptibility measured between 1T and 2T cannot be explained only from the viewpoint of the measuring time error.

To confirm the accuracy of the evaluated effective magnetic susceptibility, we calculated the effective magnetic susceptibility difference under the different initial angles of $1^\circ$ (0.017 radians), $10^\circ$ (0.17 radians), $57.3^\circ$ (1 radian), $80^\circ$ (1.4 radians) and $89^\circ$ (1.6 radians). The final angle was fixed to $0.1^\circ$ (0.0017 radians). Table 2 shows the calculated values of the effective magnetic susceptibility difference under different initial angles. The effective magnetic susceptibility difference weakly depends on the initial angle. The error due to the initial angle difference was estimated within 43% if it was between $10^\circ$ (0.17 radians) and $80^\circ$ (1.4 radians) in this experiment. The error bars in Fig.6 are evaluated by taking account of fluctuation of initial angle, whose minimum and maximum valued are assumed to be $10^\circ$ and $80^\circ$, respectively. The error induced by the measuring time is small in comparison the error induced by the initial angle in every experimental condition. For more accurate measurement of the effective magnetic susceptibility difference, we should align the particles to a certain angle in the experiment. This is our future work.

### Table 2. Effect of initial angle on effective magnetic susceptibility difference

| Initial angle $\theta_0$ / degree | 0.5T | 1T    | 1.5T   | 2T    | 3T    |
|----------------------------------|------|-------|--------|-------|-------|
| 1                                | $1.1 \times 10^{-5}$ | $2.6 \times 10^{-6}$ | $2.9 \times 10^{-6}$ | $3.1 \times 10^{-6}$ | $1.1 \times 10^{-6}$ |
| 10                               | $2.1 \times 10^{-5}$ | $5.3 \times 10^{-6}$ | $5.7 \times 10^{-6}$ | $6.2 \times 10^{-6}$ | $2.3 \times 10^{-6}$ |
| 57.3                             | $3.1 \times 10^{-5}$ | $7.8 \times 10^{-6}$ | $8.4 \times 10^{-6}$ | $9.1 \times 10^{-6}$ | $3.3 \times 10^{-6}$ |
| 80                               | $3.7 \times 10^{-5}$ | $9.2 \times 10^{-6}$ | $1.0 \times 10^{-5}$ | $1.1 \times 10^{-5}$ | $4.0 \times 10^{-6}$ |
| 89                               | $4.8 \times 10^{-5}$ | $1.2 \times 10^{-5}$ | $1.3 \times 10^{-5}$ | $1.4 \times 10^{-5}$ | $5.1 \times 10^{-6}$ |

calculated relaxation time, although the measured alignment time is longer than the calculated relaxation time under the same strength of magnetic field. This is mainly because the effective magnetic susceptibility difference in the experiment is small in comparison with that of single crystal. Actually, the forty five times increase in the value of the relaxation time agrees well with the measured alignment time except the result under the 0.5T magnetic field, as shown in Fig.5.

The average angle between the direction of the magnetic field and the c-axis, $\theta$, immediately after the imposition of the magnetic field was theoretically calculated to one radian based on the random distribution of the particles. The effective magnetic susceptibility difference, $\Delta \chi$, was then estimated from equations (3) and (4), by assuming that the final and initial angles were $0.1^\circ$ (0.0017 radians) and $57.3^\circ$ (1 radian), respectively. According to the final angle, it should be theoretically decided under the consideration of thermal fluctuation while the $0.1^\circ$ was adopted here. The alignment times shown in Table1 were also used in the calculation. Figure 6 shows the calculated effective magnetic susceptibility difference of the bismuth particles under the different magnetic field strength.

4. Conclusion

By using XRD analysis, we examined the alignment behaviour of bismuth particles in order to elucidate their rotational behaviour when suspended in a solvent in a static magnetic field. The following is the main result that we obtained.

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
# The effective magnetic susceptibility difference of aggregated particles, $\Delta \chi_E$ can be estimated by measuring the alignment time of the particles in a magnetic field.

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