The Control of Crystal Orientation in Non-magnetic Metals by Imposition of a High Magnetic Field

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(Received on November 29, 2002; accepted in final form on January 28, 2003)

High magnetic filed can affect not only ferromagnetic materials but also non-magnetic ones. In general, materials have a crystal magnetic anisotropy where a magnetic susceptibility is different in each crystal direction. So that the utilization of this property can control the crystal orientation by imposition of the high magnetic field. Up to now, the possibility of magnetic orientation by imposition of the high magnetic field has been studied, it was said that existence of crystal magnetic anisotropy and a low viscosity are essential. Then, substance which has crystal magnetic anisotropy can control the crystal orientation by heating up to liquid and solid zone which is a low viscosity.

It is found that the high magnetic field can control the crystal orientation of Zinc or Bismuth–Tin alloy, non-magnetic material, by reheating in a solidification process. These experimental results can be explained by taking into account of a magnetic energies due to the crystal magnetic anisotropy. And, we discuss a theoretical analysis on the magnetic rotation of non-magnetic metal crystals by taking account of Lorenz force which acts in of molten metals.

KEY WORDS: high magnetic field; crystal orientation; solidification process; non-magnetic material.

1. Introduction

Recently, thanks to the superconducuting technology, it has become possible to get a high magnetic field with relatively wide space even in a small-scale laboratory. By using a high magnetic field, a lot of new phenomena and functions have been found, giving us useful hints for creating new materials so that a new science and technical field called “Materials Science of a High Magnetic Field”,1) can be expected to emerge.

Under a high magnetic field, various magnetic effects become tangible in not only ferromagnetic materials but also non-magnetic ones such as paramagnetic and diamagnetic, on which the effect of a magnetic field has been considered to be negligible hitherto. The magnetization force resulted from a magnetic field is classified into two kinds. One is known as the force in which a magnet pulls ferromagnetic and paramagnetic materials and repels diamagnetic ones and the other as the force in which materials are rotated to a magnetic field direction, such as a compass rotating to the north direction due to the earth magnetic field. The former force is mainly usable for magnetic separations,2) magnetic levitations3) and measurements of magnetic susceptibility of materials.2) The latter is applicable for alignment of crystal orientations and texture structures on the basis of susceptibility difference due to crystal and shape magnetic anisotropies. It is important that these two functions work in not only magnetic materials but also non-magnetic materials under a high magnetic field. Especially, a large number of materials have the crystal magnetic anisotropy where the magnetic susceptibility is different in each crystal direction so that they may have the possibility to align to a preferred direction. Since the material properties strongly depend on their crystal orientations, controlling of them may provide an improvement of material characteristics. Therefore, the possibility of magnetic transportation and rotation of non-magnetic materials has been examined under several processes such as solidification,4) electro-deposition,5) vapor-deposition6) and solid phase reaction.7) Now the application of a high magnetic field has been recognized as one of the useful technologies in materials processing.

In the solidification process of metals, Mikelson et al.8) reported that the macrostructure of Al–Cu and Cd–Zn alloys, which are non-magnetic materials, aligned to the magnetic field direction during solidification. However, details on the method for evaluating the orientations of crystals and textures are not clearly written in this report. Yasuda et al.9) reported that the crystal orientation of a BiMn alloy, which is a ferro-magnetic material, aligned to the magnetic field direction by heating the specimen which was prepared by rapid quenching, up to a liquid–solid zone in the magnetic field.

In this research, a method is proposed where the crystal orientation of non-magnetic metals can be aligned in the solidification process without any need for pre-processing. Such a method has not been raised up hitherto. Further-
more, the theoretical analysis on the rotation of polymer fibers which is theoretically done by Yamato et al.\textsuperscript{10} is extended to the rotation of non-magnetic metal crystals by taking account of the Lorenz force which acts in molten metals.

2. Theory

2.1. Crystal Orientation Control by Magnetic Field

When a non-magnetic substance is magnetized in a magnetic field, the energy for magnetization of the substance is given by Eq. (1).

\[ U = -\int_0^{B/\mu_0} MdB \] ..........................(1)

in which \( M \) is the magnetization, \( B \) and \( B_a \) are the imposed magnetic flux density and the magnetic flux density in the substance, respectively and \( \mu_0 \) is the permeability in vacuum (4\( \pi \times 10^{-7} \) [H/m]). The principle of crystal orientation using a magnetic field is that a torque rotates a crystal to take a stable crystal orientation so as to decrease the magnetization energy.

Both zinc and bismuth have a hexagonal crystal structure with a magnetic anisotropy where the magnetic susceptibility is different in each crystal direction. The magnetic susceptibility along \( c \)-axis, \( \chi_c \), and that along \( a \)- or \( b \)-axis, \( \chi_a \) or \( \chi_b \), respectively and \( \mu_0 \) is the permeability in vacuum (4\( \pi \times 10^{-7} \) [H/m]). The theoretical expression of the magnetic torque \( T \) caused by the imposed magnetic field and the torque \( \tau \) caused by the crystal magnetic anisotropy works on the particle. The principle of crystal orientation using a magnetic field is that a torque rotates a crystal to take a stable crystal orientation so as to decrease the magnetization energy.

By Eq. (3), we get \( U \), and let the particle take a stable crystal orientation so as to decrease the magnetization energy.

\[ \mathbf{B} = B \cos \theta \mathbf{i} + B \sin \theta \mathbf{j} \] ....................(3)

The magnetization \( \mathbf{M} \) arises in the particle is described by Eq. (4).

\[ \mathbf{M} = \chi_i \mathbf{i} + \chi_j \mathbf{j} \] ....................(4)

2.2. Rotation of Crystal

2.2.1. Magnetic Torque

The rotation of a crystal particle arises from the torque caused by the imposed magnetic field. When the particle is precipitated in a melt, the magnetization \( \mathbf{M} \) arises in it due to the imposed magnetic field and the torque caused by the crystal magnetic anisotropy works on the particle. The theoretical expression of the magnetic torque \( \mathbf{T} \) is derived as follows.

A non-magnetic particle is placed under a magnetic field in \( x \)-\( y \) coordinate, as shown in Fig. 2, where \( x \)-axis is defined to be the direction of an easy magnetization axis with the magnetic susceptibility \( \chi_x \), and \( y \)-axis is defined to be the direction of a difficult magnetization axis with the magnetic susceptibility \( \chi_y \), and the angle between \( x \)-axis and the imposed magnetic field direction is \( \theta \). Then the imposed magnetic flux density is expressed by Eq. (3).

\[ \mathbf{B} = B \cos \theta \mathbf{i} + B \sin \theta \mathbf{j} \] ....................(3)

The magnetization \( \mathbf{M} \) arising in the particle is described by Eq. (4).

\[ \mathbf{M} = \chi_i \mathbf{i} + \chi_j \mathbf{j} \] ....................(4)

Therefore, the magnetic torque \( \mathbf{T} \) that acts on volume \( V \) of the particle is derived as Eq. (5).

\[ \mathbf{T} = V \mathbf{M} \times \mathbf{B} = \frac{V(\chi_x - \chi_y)B^2 \sin 2\theta}{2\mu_0} \mathbf{i} \] ..........................(5)

Hence, the \( z \)-component of the magnetic torque \( \mathbf{T} \) is obtained as Eq. (6)

\[ T = \frac{1}{2\mu_0} V\Delta\chi B^2 \sin 2\theta \] ..........................(6)

where \( \Delta\chi = \chi_x - \chi_y \).

2.2.2. Lorenz Force

In the coordinate system shown in Fig. 3, let the particle...
that is placed in \((r, \phi, \theta)\) rotate in the \(xy\)-plane, where \(x\)-axis is the direction of the imposed magnetic field. The imposed magnetic flux density \(B\), the rotation velocity \(v\) of the particle and the rotation radius \(a\) are expressed as follows:

\[
B = Bi_x, \tag{7}
\]

\[
v = r \sin \theta \sin \phi \frac{d\theta}{dt} i_x + r \cos \theta \sin \phi \frac{d\phi}{dt} i_y \tag{8}
\]

\[
a = r \cos \theta \sin \phi i_x + r \sin \theta \sin \phi i_y \tag{9}
\]

Then, Lorenz force as an electromagnetic force is induced by the interaction of the current and the given magnetic field, is given as Eq. (10).

\[
J = \sigma v \times B = -\sigma Br \cos \theta \sin \phi \frac{d\theta}{dt} i_z \tag{10}
\]

Then, Lorenz force as an electromagnetic force is induced by the interaction of the current and the given magnetic field. The force that acts on the particle to suppress its rotation is given by Eq. (11).

\[
F = J \times B = \sigma B^2 r \cos \theta \sin \phi \frac{d\theta}{dt} i_z \tag{11}
\]

Then, the torque caused by Lorenz force is derived as Eq. (12).

\[
a \times F = \sigma B^2 r^2 \cos^2 \theta \sin^2 \phi \frac{d\theta}{dt} i_z \tag{12}
\]

If the particle shape is assumed to be spherical, the torque \(L\) that acts on the particle with a radius \(r\) is obtained as Eq. (13) by integrating Eq. (12) over the particle volume.

\[
L = \int \sigma B^2 r^2 \cos^2 \theta \sin^2 \phi \frac{d\theta}{dt} dV = \frac{4}{15} \pi r^5 \sigma B^2 \frac{d\theta}{dt} \tag{13}
\]

2.2.3. Equation of Rotational Motion

When a particle rotates in a liquid, the liquid viscosity induces a rotating torque \(R\) that prevents its rotation

\[
R = 8\pi \eta r^3 \frac{d\theta}{dt} \tag{14}
\]

where \(\eta\) is the viscosity.

Considering the three torques described above, the equation of a rotational motion caused by a magnetic field is given as Eq. (15).

\[
\frac{2}{5} \rho r^5 \frac{d^2 \theta}{dt^2} + 8\pi \eta r^3 \frac{d\theta}{dt} + \frac{4}{15} \pi r^3 \sigma B^2 \frac{d\theta}{dt} = -R - L - T \tag{15}
\]

Substituting Eqs. (6), (13) and (14) into Eq. (15), Eq. (16) is derived

\[
\frac{4}{15} \pi r^3 \sigma B^2 \frac{d\theta}{dt} = \frac{2}{5} \rho r^5 \frac{d^2 \theta}{dt^2} + 8\pi \eta r^3 \frac{d\theta}{dt} \tag{Inertia force} \tag{Viscous force} \tag{Lorenz force}
\]

(Magnetization force)

The ratio of the inertia force term to the sum of the viscous force and the Lorenz force terms can be approximately expressed as Eq. (17)

\[
8\pi \eta r^3 \frac{d\theta}{dt} + \frac{4}{15} \pi r^3 \sigma B^2 \frac{d\theta}{dt} \approx \frac{3\rho r^5}{2\pi(30\eta + r^3 \sigma B^2)} \tag{17}
\]

where \(\tau\) shows a characteristic time. By substituting the physical properties of zinc \((\rho = 6.575 \text{ kg/m}^3), \eta = 3.85 \times 10^{-3} \text{ Ns/m}^2\), \(\sigma = 2.68 \times 10^6 \text{ [1/\Omega m]}\) into Eq. (17), the interval in which the inertia force term predominantly works under the \(B = 1\text{T}\) is evaluated as \(10^{-4} \text{s}\) when the particle radius is \(100 \mu\text{m}\), and \(10^{-6} \text{s}\) when the particle radius is \(10 \mu\text{m}\). Thus, the inertia term can be neglected and Eq. (16) is more simplified to Eq. (18).

\[
8\pi \eta r^3 \frac{d\theta}{dt} + \frac{4}{15} \pi r^3 \sigma B^2 \frac{d\theta}{dt} + \frac{2}{3\mu_0} r^3 \Delta \chi B^2 \sin 2\theta = 0 \tag{18}
\]

The solution of Eq. (18) is given as Eq. (19)

\[
\tan \theta = \tan \theta_0 \exp \left( -\frac{t}{\tau} \right), \quad \tau = \frac{30\eta + r^3 \sigma B^2}{5\Delta \chi B^2} \frac{1}{\mu_0} \tag{19}
\]

where \(\theta_0\) is an angle between the imposed magnetic field and the easy magnetization axis at \(t = 0\). The dimensionless numbers of \(T^*\), \(\alpha\) and \(\beta\) are defined as followings.

\[
T^* = \frac{t}{r^2 \rho \eta}, \quad \alpha = \frac{r^2 \sigma B^2}{30\eta}, \quad \beta = \frac{5\rho \Delta \chi}{\mu_0 \eta \sigma}
\]

By using the above dimensionless numbers, Eq. (19) is expressed as Eq. (20).

\[
\tan \theta = \tan \theta_0 \exp \left( -\frac{\beta}{1+\alpha} T^* \right) \tag{20}
\]

If the initial angle at time \(t = 0\) is \(\theta_0 = 90^\circ\), the particle will not rotate forever so that the initial angle is given as \(\theta_0 = 89^\circ\). By using Eq. (20), the rotation time is defined as the interval time that it takes for the particle to rotate from \(\theta_0 = 89^\circ\) to \(\theta = 1^\circ\). The angle of \(1^\circ\) is considered to be substantially zero. The relations between the interval time and dimensionless numbers of \(\alpha\) and \(\beta\) are shown in Figs. 4(a) and 4(b). The relations between the magnetic flux density and the rotation time are shown in Fig. 5. It is understood that the particle finishes rotating within one second when a magnetic field of more than 1T is imposed, and the rotation time decreases with increasing the magnetic flux density. The relations between the particle radius and the rotation time are shown in Fig. 6. It is understood that the rotation time decreases with decrease of the particle radius. If
The rotation time does not depend on the particles with a radius less than 10^{-5} m. This result can be interpreted from Eq. (18) as the following. The Lorenz force term is a function of five powers of the radius and the viscous force and the magnetization force terms are a function of three powers of the radius, respectively. Thus, the Lorenz force term becomes predominant and the rotation time depends on the radius substantially when the particle radius is large, but the Lorenz force is negligible when the particle radius becomes small. This is the reason why the dependence of the rotation time on the particle radius becomes small when the viscous force and the magnetization force terms have the same powers of the particle radius.

\[ A = \frac{8\pi \eta r^3}{15 \pi r^5 \sigma B^2} = \frac{30 \eta}{r^2 \rho} \quad \text{(21)} \]

By substituting \( \eta = 1.0 \times 10^{-3} \text{[N s/m}^2] \) and \( \sigma = 1.0 \times 10^{7} \text{[1/}\Omega \text{m]} \) which are the physical properties of metals into Eq. (21), the particle radius is evaluated as 5 \( \mu \text{m} \) at which the viscous and the Lorenz force terms give the same contribution under \( B = 1 \text{T} \). The viscous force term becomes predominant for the particles with radii less than 5 \( \mu \text{m} \) as shown in Fig. 7.

Fig. 4. Relations between angle and rotation time.

Fig. 5. Relations between angle and rotation time.

Fig. 6. Relations between rotation time and radius.

Fig. 7. Relations between dimensionless number \( A \) and radius.

Fig. 8. Schematic view of experimental apparatus.
3. Experiment

3.1. Zinc Film

3.1.1. Experiment

Figure 8 shows the schematic view of the experimental apparatus. A water-cooled pipe was inserted in the bore of a superconducting magnet, and an alumina crucible with a heater was set inside the pipe. A zinc film (10 × 28 mm²) prepared by dipping a steel plate in a molten zinc bath was set on a stainless steel pipe, which was inserted from the upper part of the magnet bore. The sample plane was adjusted at the position with the maximum magnetic flux density in the direction parallel or perpendicular to the magnetic field. A thermocouple was inserted through the midair part of the stainless steel pipe, and the temperature of the sample was measured by the thermocouple connected with the plane. The crucible was filled with argon gas to prevent the oxidation of the sample and the temperature was kept in liquid–solid zone of zinc for 3 min. The furnace was then cooled down by shutting off the heater.

3.1.2. Results and Discussion

The X-ray diffraction patterns of the sample on which the magnetic field was imposed in perpendicular direction are shown in Fig. 9. The peak of (101) plane was detected stronger in the sample obtained under no magnetic field. On the other hand, when a magnetic field of 12 T was imposed, the peak of (101) decreased, and the peak of (002) equivalent to c-plane appeared stronger. The X-ray diffraction patterns of the sample on which the magnetic field was imposed in parallel direction are shown in Fig. 10. The peak of (101) detected stronger in the sample obtained under no magnetic field, similar to the previous result shown in Fig. 9. However, when a magnetic field of 12 T was imposed, the peak of (101) decreased, and the peak of (100) equivalent to a, b-plane appeared stronger. That is, regardless of the imposing direction of the magnetic field, the zinc crystals aligned to the direction estimated from the viewpoint of the magnetization energy.

The magnetic orientation works only when the magnetization energy is larger than a thermal energy \( kT \) \(^{14} \). This condition can be described as Eq. (22)

\[
\frac{\lambda_i}{2\mu_0} B^2 > kT \quad \text{(22)}
\]

where \( k \) is Boltzmann constant. The condition that a particle radius should be larger than 20 nm is derived from Eq. (22) by using physical properties and experimental conditions adopted in this experiment. The other hand, if a rotation time is assumed to be one second, the particle radius is evaluated as less than 100 \( \mu \text{m} \) from Eq. (19). Therefore, the particle radius of zinc that is expected from the magnetization energy and the equation of motion is the range from 20 nm to 100 \( \mu \text{m} \).

3.2. Bismuth–Tin Bulk Alloy

3.2.1. Experiment

Bismuth–5mass% tin alloy, which is an eutectic alloy, was used as the specimen. Figure 11 shows the schematic view of the experimental apparatus. The specimen was heated up to 300°C in argon atmosphere at the rate of 300°C/h, and kept for 30 min. Then it was cooled down to 255°C at the rate of 180°C/h, and stirred at 255°C for 3 min and then cooled to the room temperature in the furnace. The specimen was cut in the direction perpendicular to that of the magnetic field and its surface was polished to examine the crystal structure by use of XRD.
3.2.2. Results and Discussion

The X-ray diffraction patterns of bismuth–tin alloy are given in Fig. 12. The peak of (00n) scarcely appeared in the case of 0 T, but the peaks of a,b-plane (hkl) and (012) increased in the case of 12 T. This result agrees with the theoretical estimation mentioned in Sec. 2.1.

A method to evaluate the degree of crystalline orientation from the intensity of X-ray diffraction lines obtained by X-ray diffraction analyzer (XRD) is proposed here as given in Eq. (23).

\[ \theta_f = \frac{\sum (I_{hkl} \times \theta_{hkl})}{\sum I_{hkl}} \] ...............(23)

where \( \theta_f \) is defined as the facial angle measured from c-plane, \( \theta_{hkl} \) is the facial angle between \((hkl)\) and (00n) planes, \( I_{hkl} \) is the intensity of \((hkl)\) plane obtained from the X-ray diffraction pattern. The facial angle \( \theta_f \) is reduced to 0° when all crystals are oriented to c-plane and to 90° when oriented to a,b-plane.

The facial angle of bismuth crystal is shown in Fig. 13. In the case of 0 T, the bismuth crystal tilted only 4° from the c-plane. The reason could be explained as follows; as the alloy solidifies inward from mold wall, a,b-axis, which is the priority growth orientation, grows in the parallel direction to the heat flow. On the other hand, in the case of 12 T, the crystal inclined to 60°. This result agrees with the theoretical prediction. However, it is not 90° corresponding to the case where all crystals aligned to the magnetic field direction. This experimental result can be attributed to the interruption caused by heat flow as follows; tips of dendrite arms that grow from the mold wall break off by agitation and disperse in the molten metal. As the a,b-axis of the crystal corresponding to the priority growth orientation is stable in the direction of the magnetic field, the tips of dendrite arms dispersed in the molten metal align to the magnetic field direction and grow. However, the preferred crystal orientation for the magnetic field direction is perpendicular to that of the heat flow from the mold wall so that all of the crystals can not align to the magnetic field direction.

By taking the same procedure mentioned in Sec. 3.1.2, the particle radius of bismuth that is expected from the magnetization energy and the equation of motion is the range from 10 nm to 1 mm.

4. Conclusion

The control of crystal orientation by imposition of a magnetic field has been studied through experimental and theoretical works. The following results have been obtained.

(1) The equation of motion for a particle rotating in a molten metal under the imposition of a magnetic field has been derived. An analytical solution is obtained under the condition of neglecting the inertia force term.

(2) It takes less than one second for a particle to rotate to the direction of an easy magnetization axis under a magnetic field of 1 T.

A method for crystal orientation of non-magnetic materials which does not need any preprocessing has been proposed and the usefulness of the method is shown through experiments. The following results were obtained.

(a) When a zinc film which was prepared by dipping a steel plate in zinc bath was heated up to a solid–liquid zone under the magnetic field, the orientation of zinc crystals in the film could align.

(b) When a bismuth–tin bulk alloy was heated up to a solid–liquid zone under the magnetic field, the orientation of bismuth crystals could align.

Acknowledgement

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research on Priority Areas (B) (2), 10211203.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Unit</th>
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<tbody>
<tr>
<td>A</td>
<td>Dimensionless number</td>
<td>[-]</td>
</tr>
<tr>
<td>a</td>
<td>Rotation radius of a particle</td>
<td>[m]</td>
</tr>
<tr>
<td>B</td>
<td>Imposed magnetic flux density</td>
<td>[T]</td>
</tr>
<tr>
<td>B_m</td>
<td>Magnetic flux density in material</td>
<td>[T]</td>
</tr>
<tr>
<td>F</td>
<td>Lorenz force per unit volume</td>
<td>[N/m³]</td>
</tr>
<tr>
<td>i_x</td>
<td>Unit vector in the direction of ( x )</td>
<td>[]</td>
</tr>
<tr>
<td>i_y</td>
<td>Unit vector in the direction of ( y )</td>
<td>[]</td>
</tr>
<tr>
<td>i_z</td>
<td>Unit vector in the direction of ( z )</td>
<td>[]</td>
</tr>
<tr>
<td>J</td>
<td>Current density</td>
<td>[A/m²]</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
<td>[J/K]</td>
</tr>
<tr>
<td>L</td>
<td>Torque due to Lorenz force</td>
<td>[Nm]</td>
</tr>
<tr>
<td>M</td>
<td>Magnetization</td>
<td>[A/m]</td>
</tr>
<tr>
<td>N</td>
<td>Demagnetizing factor</td>
<td>[-]</td>
</tr>
<tr>
<td>R</td>
<td>Torque due to viscosity</td>
<td>[Nm]</td>
</tr>
<tr>
<td>r</td>
<td>Radius of a particle</td>
<td>[m]</td>
</tr>
<tr>
<td>t'</td>
<td>Characteristic time</td>
<td>[s]</td>
</tr>
<tr>
<td>T</td>
<td>Magnetic torque</td>
<td>[Nm]</td>
</tr>
<tr>
<td>T_z</td>
<td>z-Component of ( T )</td>
<td>[Nm]</td>
</tr>
<tr>
<td>U</td>
<td>Magnetic energy</td>
<td>[Nm]</td>
</tr>
</tbody>
</table>
\( V \): Volume of substance \[m^3\]
\( v \): Rotation velocity of substance \[m/s\]
\( \eta \): Viscosity \[N\,s/m^2\]
\( \theta \): Angle between directions of imposed magnetic field and easy magnetization axis \[\text{[°]}\]
\( \theta_0 \): Value of \( \theta \) in \( t=0 \) \[\text{[°]}\]
\( \mu_0 \): Permeability in vacuum \[H/m\]
\( \rho \): Density \[kg/m^3\]
\( \sigma \): Electric conductivity \[1/\Omega\,m\]
\( \sigma_0 \): Relaxation time \[s\]
\( \phi \): Angle between \( r \) and \( z \)-axis \[\text{[°]}\]
\( \chi \): Magnetic susceptibility of a substance \[\text{[°]}\]
\( \chi_1 \): Magnetic susceptibility in the direction of easy magnetization axis \[\text{[°]}\]
\( \chi_2 \): Magnetic susceptibility in the direction of difficult magnetization axis \[\text{[°]}\]

REFERENCES