Three-dimensional alignment of FeSi₂ with orthorhombic symmetry by an anisotropic magnetic field

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Abstract. This paper presents the three-dimensional alignment of β-FeSi₂ particles in a resin under an anisotropic magnetic field. The alignments obtained under a static magnetic field and a rotating magnetic field proved that the magnetic susceptibilities of β-FeSi₂ are \( \chi_c > \chi_b > \chi_a \). The magnetic anisotropy was sufficiently large under a magnetic field of 10T for the crystallographic alignment. Under an anisotropic magnetic field (oscillating magnetic field), a-, b- and c-axes of β-FeSi₂ particles suspended in a resin were aligned each other. A pseudo single crystal β-FeSi₂ with the orthorhombic structure was fabricated by the oscillating magnetic field.

1. Introduction
Development of cryogen-free superconducting magnets enables us to use a relatively high magnetic field exceeding 2T for materials processing. One of the applications in materials processing is fabrication of the crystallographically aligned materials, in which a certain crystallographic orientation aligned each other. Para- and diamagnetic materials of which crystal symmetry is lower than the cubic symmetry have the magnetic anisotropy, while the ferromagnetic materials even with the cubic symmetry have the anisotropy. The uni-axial alignment under a magnetic field has been extensively studied [1-16]. Even in the coarsening process, the aligned structure was achieved [17,18]. Thus, the uni-axial alignment has been achieved for various materials.

Recently, the three-dimensional alignment, in which a-, b- and c-axes of grains were aligned each other, has been realized [19,20]. The magnetic susceptibilities of a-, b- and c-axes are different each other for a material with low symmetry like orthorhombic structure. An elliptic magnetic field, in which the direction of the magnetic field rotates with the modulated angular velocity, is used for the three-dimensional alignment. The time-average intensity of the elliptic magnetic field becomes anisotropic. When a crystal cannot follow the rotation, the crystal tends to rotate in accordance with the time-averaged magnetic field. As a result, the crystallographically aligned structure is formed in accordance with the magnetic anisotropy. Until now, the three-dimensional alignment has been obtained only for L-alanine [20]. Although the mechanism was essentially explained in the previous study [19], the fundamental of the alignment is explained in the next section for describing the experimental procedures.
The $\beta$-FeSi$_2$ intermetallic compound with the orthorhombic symmetry has received considerable attention because of its high potential as optoelectronic and thermoelectric materials. Since $\beta$-FeSi$_2$ intermetallic compound is produced through the peritectoid reaction, it is rather difficult to produce a single crystal. The single crystals are desired for evaluating intrinsic physical properties and for improving material performance. In this paper, the three-dimensional alignment of $\beta$-FeSi$_2$ particles in a resin under an anisotropic magnetic field is presented as a preliminary study for fabricating a bulk single crystal by the magnetic alignment. In addition, the magnetic anisotropy of $\beta$-FeSi$_2$ is evaluated by using a static magnetic field and a rotating magnetic field.

2. Motion of magnetized particles under an anisotropic magnetic field

2.1. Crystallographic alignment under a static magnetic field

Magnetic susceptibilities of a single crystal are generally given by equation (1),

$$ \chi = \begin{pmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{22} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix} $$

(1)

The magnetic energy is also given by equation (2).

$$ U = -\int_0^H \mathbf{M} \cdot d\mathbf{H} $$

(2)

The crystallographic alignment is described by considering motion and rotation of a crystal under a magnetic field. The crystals move and/or rotate in a favourable direction to minimize the magnetic energy.

In the case of a paramagnetic crystal with the cubic symmetry, the magnetic susceptibilities are $\chi_{11} = \chi_{22} = \chi_{33}$. Since the magnetic susceptibility is isotropic, the magnetization does not depend on crystal orientation. Thus, the crystallographical alignment is not obtained.

The magnetic susceptibilities becomes $\chi_{11} = \chi_{22} = \chi_a, \chi_{33} = \chi_c$ for a crystal with the hexagonal or the tetragonal symmetry. Under a static magnetic field, the magnetization for the crystal is expressed by

$$ \mathbf{M} = \begin{pmatrix} \chi_a & 0 & 0 \\ 0 & \chi_a & 0 \\ 0 & 0 & \chi_c \end{pmatrix} \mathbf{H} $$

(3)

As shown in equation (3), the magnetization, $\mathbf{M}$, is not always parallel to the magnetic field, $\mathbf{H}$. The imposed magnetic field and the induced magnetization cause a torque on the crystal, given by equation (4).

$$ \mathbf{T} = \mathbf{M} \times \mathbf{H} $$

(4)

In the case that $\chi_c$ is larger than $\chi_a$, c-axis tends to be parallel to the magnetic field and a- and b-axes distribute in a plane perpendicular to the magnetic field. The imposition of a static magnetic field results in the uni-axial alignment in which the crystallographic orientation with the maximum magnetic susceptibility aligns each other.

2.2. Crystallographic alignment under a rotating magnetic field

In the case that $\chi_a$ is larger than $\chi_c$, for the hexagonal and the tetragonal symmetry, c-axis randomly distributes on a plane perpendicular to the magnetic field, because the magnetic susceptibility in any crystal orientation on the a-b plane is the same.

The uni-axial alignment can be achieved for the hexagonal or the tetragonal crystal with $\chi_a > \chi_c$ by using a rotating magnetic field. Here, one considers that a crystal with $\chi_a > \chi_c$ is suspended in a fluid under a rotating magnetic field with a constant angular velocity. When the angular velocity is sufficiently high, the crystal cannot follow the change of magnetic field direction. In this situation, the
crystal rotates in accordance with the time-averaged magnetic field. Since the average intensity of the rotating magnetic field is constant on a plane perpendicular to the rotation axis, a- and b-axes randomly lie on the plane and c-axis is aligned along the rotation axis. Namely, the rotating magnetic field achieves the uni-axial alignment in which the crystallographic orientation with the minimum magnetic susceptibility aligned along the rotation axis.

2.3. Crystallographic alignment under a oscillating magnetic field

The magnetic susceptibilities of a crystal with the orthorhombic symmetry are

\[
\chi = \begin{pmatrix}
\chi_a & 0 & 0 \\
0 & \chi_b & 0 \\
0 & 0 & \chi_c \\
\end{pmatrix}.
\]  

(5)

Here, one consider the case of \(\chi_a > \chi_b > \chi_c\). When the angular velocity of the rotating magnetic field is periodically modulated, the time-average magnetic field becomes elliptic. For example, the intensities of the time-averaged magnetic field in x-, y- and z- directions become \(H_x > H_y > H_z\). If the angular velocity is sufficiently high, the crystal rotates in accordance with the time-average magnetic field. As a result, the three-dimensional alignment in which a-, b- and c-axes of crystals are aligned each other can be achieved by the elliptic magnetic field. The detail of the three-dimensional alignment has been studied [19].

3. Experimental procedure

3.1. Preparation of \(\beta\)-FeSi\(_2\) particles

Mother alloy of 33.3at%Fe-66.7at%Si was made by arc melting. The ingot was annealed at 1173K for 24h to increase volume fraction of \(\beta\)-FeSi\(_2\) intermetallic compound. After annealing, the other phases such as FeSi and FeSi\(_2\) (high temperature phase) were observed only in the grain boundary region. The ingot was crashed mechanically into the particles (average diameter: 2.2 \(\mu\)m). The particle size was sufficiently smaller than the grain size in the ingot. Thus, most of the \(\beta\)-FeSi\(_2\) particles consisted of a single grain of \(\beta\)-FeSi\(_2\). The \(\beta\)-FeSi\(_2\) particles were suspended in a resin. Volume fraction of \(\beta\)-FeSi\(_2\) particles was 0.2%. The crystallographic alignment was examined by X-ray diffraction.

Since the magnetic susceptibility of the FeSi compound is much higher than that of \(\beta\)-FeSi\(_2\), even small amount of the FeSi compound remaining in the crashed particles remarkably increases the apparent magnetic susceptibility of the specimen. However, most of the crashed particles did not contain the FeSi compound. The motion of the \(\beta\)-FeSi\(_2\) particles is dominantly controlled by the magnetic property of \(\beta\)-FeSi\(_2\). Thus, the overall trend in the alignment of the \(\beta\)-FeSi\(_2\) particles is not influenced by the remaining FeSi compound.

3.2. Magnetic fields

Since the magnetic properties of \(\beta\)-FeSi\(_2\) were not known, the magnetocrystalline anisotropy was examined by using a static magnetic field and a rotating magnetic field. As mentioned in the previous section, the orientation of the maximum magnetic susceptibility can be identified by imposing a static magnetic field. The static magnetic field of 10T was horizontally imposed. The resin was cured under the static magnetic field by adding a curing agent. The curing specimen was placed for more than 6h under a magnetic field.

The orientation of the minimum magnetic susceptibility can be identified by using a rotating magnetic field. In this study, the specimen was rotated at the constant angular velocity (9rpm). As the resin cured, the viscosity of resin remarkably increased. The \(\beta\)-FeSi\(_2\) particles did not follow the
change of the magnetic field direction and consequently the rotation was controlled by the time-averaged magnetic field.

Figure 1 shows a schematic illustration of the elliptic magnetic field used in this study (It is referred to as the oscillating magnetic field). The rotating direction was periodically changed. The rotating speed was 9 rpm and the oscillation angle was 30 degrees.

![Figure 1](image1.png)

**Figure 1.** Oscillating magnetic by changing the rotation direction periodically.

![Figure 2](image2.png)

**Figure 2.** (a) Configuration of the specimen in the magnet, (b) stereopropjection of (004) plane in the specimen cured under a static magnetic field of 10T and the stereopropjection of (220) and (202) planes in the specimen cured under the rotation magnetic field (10T).
4. Crystallographic alignment under a magnetic field

4.1. Alignments under the static magnetic field (10T) and the rotating magnetic field

Figure 2(a) shows the configuration of the specimen in the magnet bore. The axis $H_1$ is the direction of the static magnetic field. As shown in figure 2(b), the diffraction of (004) plane was clearly observed around the $H_1$ axis. Thus, the [001] direction (c-axis) is parallel to the static magnetic field. The clear alignment indicates that the magnetic susceptibility of the c-axis is maximum among those of a-, b- and c-axes. In addition, the difference in the magnetic energy, $(1/2)(\chi_c - \chi_{a,b})H^2V$, is sufficiently large, comparing to the thermal energy, $kT$. Here, $V$ is the volume of $\beta$-FeSi$_2$ particle.

The alignment of the $\beta$-FeSi$_2$ particles under the rotating magnetic field is shown in figure 2(c). Since the angular velocity was constant, the time-averaged intensity of the magnetic field is the same on the $H_1$-$H_2$ plane. The diffractions of (220) and (202) planes lie around the axis $H_3$ (the rotation axis). The tilt angle between the diffraction and the rotation axis was approximately 52 degrees. According to the crystal structure of $\beta$-FeSi$_2$ intermetallic compound, the diffraction pattern indicates that the [100] direction (a-axis) was parallel to the rotation axis. Thus, the magnetic susceptibility of the a-axis is minimum.

The alignments under the static magnetic field and the rotation magnetic field proved that the magnetic susceptibilities of the $\beta$-FeSi$_2$ are $\chi_c > \chi_b > \chi_a$. Furthermore, the differences in the magnetic energy, $(1/2)(\chi_c - \chi_b)H^2V$ and $(1/2)(\chi_b - \chi_a)H^2V$, are sufficiently large under the magnetic fields. Thus, the anisotropy in the magnetic susceptibilities of the $\beta$-FeSi$_2$ satisfied the requirement for the three-dimensional alignment.

4.2. Alignment under the oscillating magnetic field

To achieve the three-dimensional alignment, the oscillating magnetic field was imposed on the $\beta$-FeSi$_2$ particles suspended in the resin. The stereographic projection of (220) and (202) planes is shown in figure 3. The distributions of (220) and (202) planes showed that the c-axis is parallel to the axis $H_1$, the b-axis parallel to the axis $H_2$ and the a-axis parallel to the axis $H_3$. The result indicated that a pseudo single crystal of $\beta$-FeSi$_2$ was fabricated by imposing the oscillating magnetic field.

Degree of the alignment was evaluated by measuring the half maximum full-width (HMFW) of the diffraction peaks of (220) and (202) planes. The values of HMFW ranged from 4 degrees to 10 degrees. The modification of oscillating magnetic field (oscillating angle, angular velocity, modulation of angular velocity etc.) is expected to improve the degree of the three-dimensional alignment.

5. Summary
The magnetic anisotropy of $\beta$-FeSi$_2$ was identified by using the static magnetic field (10T) and the rotating magnetic field (10T, 9rpm). The alignments obtained under the static magnetic field and the rotating magnetic field proved that the magnetic susceptibilities of FeSi$_2$ are $\chi_c > \chi_b > \chi_a$. The oscillating magnetic field achieved the three-dimensional alignment of $\beta$-FeSi$_2$ particles in the resin. Namely, a pseudo single crystal of $\beta$-FeSi$_2$ was fabricated by the oscillating magnetic field.

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