High-Density β-$FeSi_2$ crystals with 3D alignment fabricated by an oscillating magnetic field

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Abstract
This paper demonstrates three-dimensional alignment of β-$FeSi_2$ in sintered bulk specimens. The three-dimensional alignment was achieved by using an oscillating magnetic field during slip-casting under a magnetic field of 6T. Sintering using direct electric current heating was performed in various conditions. The degree of alignment did not significantly degrade during sintering process. Apparent density became as high as 97%. The degree of alignment tended to increase as grain size increased.

Keywords: Magnetic orientation, crystallographic alignment, magnetic anisotropy, anisotropic magnetic field

Introduction

Single crystals are desired to measure physical properties and to improve materials performance. Not a few compounds are produced through the solid-solid reaction, of which rate is extremely small, comparing to that in the melt growth. Thus, it is often difficult or nearly impossible to fabricate single crystals for the compounds by melt growth processes and solidification processes. One of the possible solutions is to fabricate materials with crystallographically aligned texture by using magnetic fields.

Crystals with lower symmetry lattice structure (*i.e.* hexagonal, orthorhombic symmetry) exhibit magnetic anisotropy. If a magnetic field with sufficient intensity is applied, a certain crystallographic orientation tends to align to reduce the magnetic energy. For example, the uni-axial alignment has been realized by imposing static magnetic fields for various kinds of materials such as metallic, inorganic and organic substances [1-11]. The aligned structure with micro-meter scale was also fabricated by irradiating laser on the surface of non-equilibrium solid solution of Bi-Mn alloys [12].

The three-dimensional alignment has paid much attention, because the three-dimensional alignment [13] leads to fabrication of pseudo single crystals. The magnetic susceptibilities of a-, b- and c-axes are different each other for a material with low symmetry like the 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. When crystals suspended in a viscous fluid cannot follow the magnetic field rotation, they are likely to rotate in accordance with the time-averaged magnetic field. If the conditions (magnetic field intensity, rotation speed, viscosity, size and density of crystalline particle and magnitude of magnetic anisotropy) satisfies the requirement, the three-dimensional alignment is achieved in accordance with the magnetic anisotropy. For example, the three-dimensional alignment has been obtained for L-alanine [13, 14] and β-$FeSi_2$ (the orthorhombic structure) [15, 16]. However, the aligned crystals suspended in a resin or textured compacts with lower density were obtained. From a viewpoint of application, it is strongly desired to fabricate t bulk materials, which consist of a single phase, with the three-dimensional alignment. Thus, it is a critical issue to fabricate the three-dimensionally aligned bulk materials.

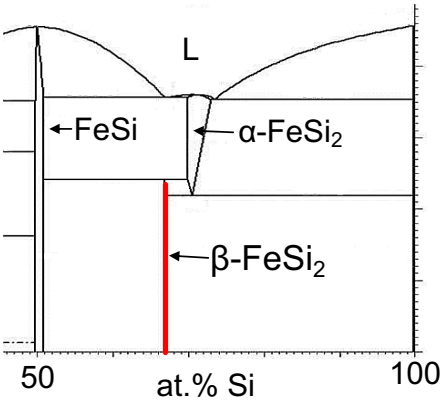


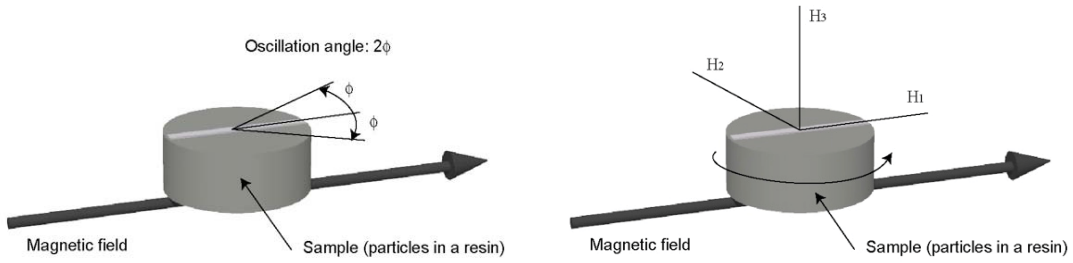
Figure 1 Phase diagram of Fe-Si system.

Intermetallic compound β-FeSi2, which is produced through the peritectoid reaction (solid-solid reaction) as shown in Fig.1, has received considerable attention because of its high potential as optoelectronic and thermoelectric materials. The single crystals are

desired for measuring intrinsic physical properties and for improving materials performance. A motivation of this study is to fabricate the three-dimensionally aligned $FeSi_2$ with higher density. We will demonstrate processing of bulk β-$FeSi_2$ with higher density.

Experiments

Mother alloy with composition of 33.3at%Fe-66.7at%Si was made by conventional arc melting. The ingot was annealed at 1173K for 24h to proceed the solid-solid reaction. After annealing, the ingot was mechanically crashed into the particles (diameter: 2.2 μm, ranging from sub-μm to 20μm). Since grain size of β-$FeSi_2$ in the ingot was sufficiently larger than the crashed particle diameter, most of particles consist of a single grain of β-$FeSi_2$ phase.



(a) (b)

Fig. 2. Oscillating magnetic field by changing the rotation direction periodically. (a) Definition of the oscillating angle and (b) definition of axes in accordance with the oscillating magnetic field.

Figure 2 shows a schematic illustration of oscillating magnetic field (referred to as the oscillating magnetic field). The rotating direction was periodically changed. In this study, the oscillation angle 2φ and rotation speed were 135 degrees and 9 rpm, respectively. The procedures for the alignment is essentially the same as those in the previous works [14,15].

The β-$FeSi_2$ particles (10 vol%) was suspended in ethylene glycol (viscosity is 20 times larger than that of water). Ultrasonic vibration was imposed for 15min for homogenization. The slurry was cast into a mold of which bottom was made of plaster (inner diameter: 5mm). A time-dependent magnetic field (6T in H_1 direction) was imposed during slip-casting. It took 12-24 hours to remove the fluid (ethylene glycol) from the bottom plaster plate. Sedimented particles (refer to as a precursor) was obtained. Dimension of precursor was 5mm in diameter and 1-2 mm in thickness.

Molds made of graphite or WC were used for sintering. The precursor was once sintered at 1073K for 10min -30min to produce a green compact. The green compact was sintered at 1073 K to increase apparent density. of β-$FeSi_2$. Pressure of sintering ranged from 50 to 200 MPa.

Since magnetic susceptibilities of β-$FeSi_2$ are $\chi_c > \chi_b > \chi_a$ [15], the following relationship is expected for the three-dimensional alignment; H_1 // c-axis, H_2 // b-axis and H_3 // a-axis.

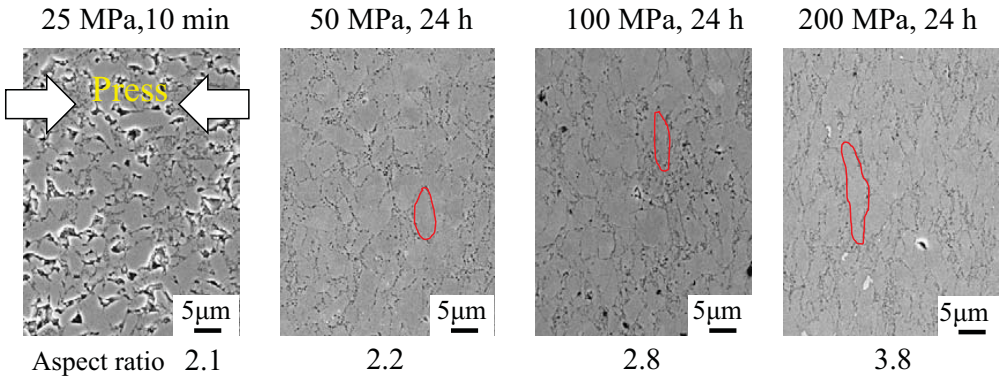
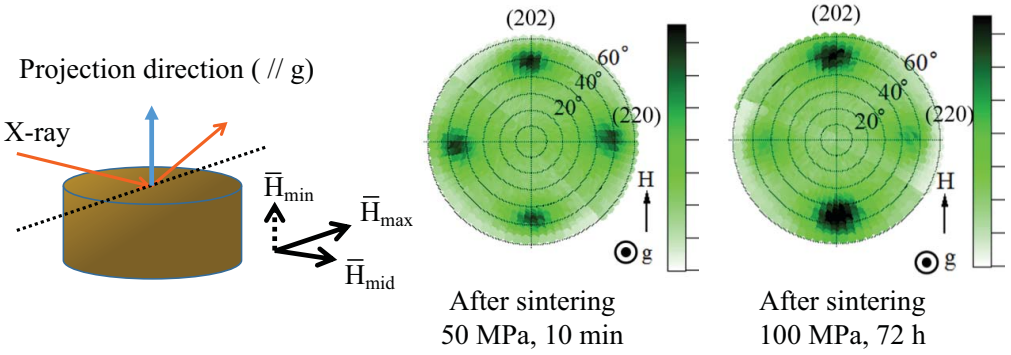


Figure 3 Microstructure of sintered specimens. Press axis is indicated by arrows on the photograph. Average aspect ratio of grains is also shown below the microstructure.



(a) (b)

Figure 4 (a) Configuration of measurement of crystallographic orientation and (a) distribution of normal vectors of (220) and (202) planes. Four peaks on the projection indicate the three-dimensional alignment.

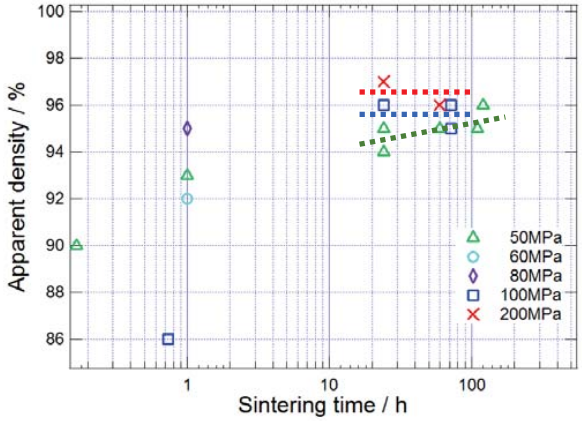


Figure 5 Apparent density change as a function of sintering pressure and duration.

Results and discussion

Figure 3 shows microstructure of sintered specimens. Pressure and sintering duration are listed in the figure. Although porosity was clearly observed at 25MPa, dense specimens were produced at a pressure more than 50MPa. In addition, aspect ratio of grains increased with increasing pressure of sintering. The change suggested that brittle deformation of β-$FeSi_2$ grains occurred during sintering and consequently contributed to decrease in porosity. Crystallographic alignment was measured by X-ray diffraction, as shown in Fig. 4. Diffraction of (220) and (202) peaks are plotted in Fig. 4(b). When the three-dimensional alignment is achieved, four peaks appears on the stereo projection. As shown in Fig. 4(b), the four peaks were clearly remained after sintering even for 72h under a pressure of 100MPa. Thus, β-$FeSi_2$ compacts with the three-dimensional alignment was fabricated by the proposed processes.

Figure 5 shows apparent density, which should be unity for β-$FeSi_2$ single crystal, as a function of sintering time. Apparent density increased with increasing sintering duration and pressure. Apparent density was less than 96% for 1hour-sintering at any pressure.

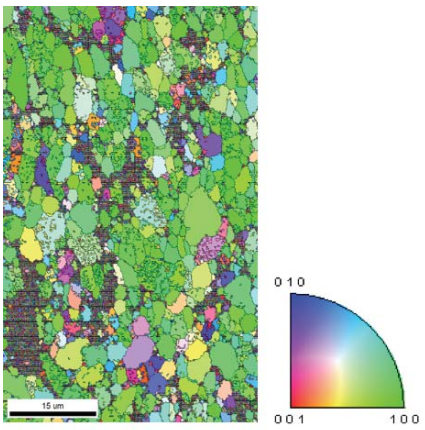
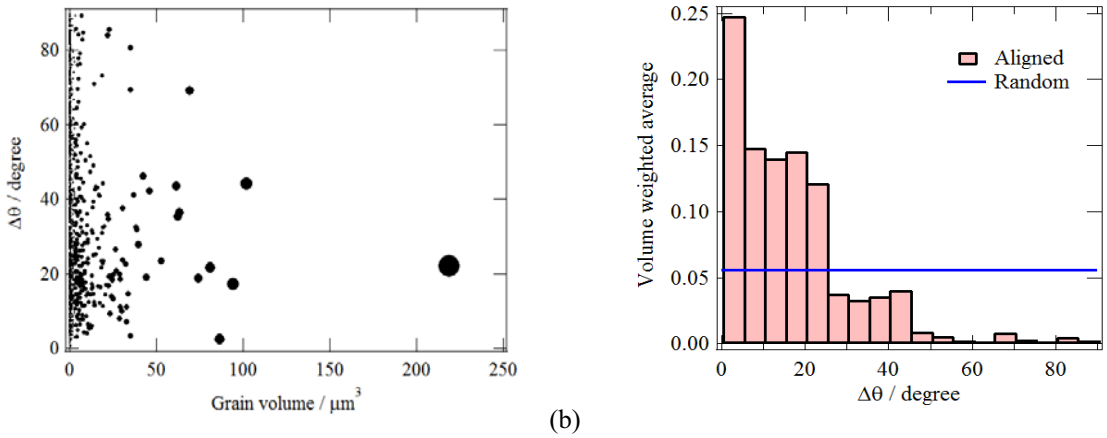


Figure 6 Inverse pole figure of the compacts sintered for 72 h, 100 MPa. The cross-section is perpendicular to the rotation axis (H_3 in Fig. 1)



(a) (b)

Figure 7 (a) Relationship between the misalignment (Δθ) and grain volume estimated by grain diameter and (b) volume-weighted histogram. The misalignment Δθ is the angle between [100] and H_3 defined in Fig. 1. Size of marks in (a) is proportional to grain volume.

Appropriate sintering condition (duration > 24hours, pressure > 100MPa) achieved dense compact with the three-dimensional alignment.

Figure 6 shows inverse pole figure of a compact sintered for 72 hours under 100 MPa. Green color indicates that normal direction of (100) plane is perpendicular to the cross-section (H_1-H_2 plane). The crystallographic orientation in the sintered compact agreed with the expected one. However, there are some grains with different colors such as blue, violet and pink. A misalignment (Δθ) was defined as angle difference between <100> direction and H_3 direction. Figure 7(a) shows the relationship between the misalignment (Δθ) and grain volume (estimated from grain diameters on the cross-section). Mark size is proportional to grain volume. The misalignment was likely to decrease with increasing grain volume. The tendency suggested that larger particles tend to have higher alignment in the precursor and was still observed in the sintered compacts. Although some grains have relatively high misalignment, misalignment for most of grains was less than 20 deg and clear alignment was observed in grain-scale aspect, as shown in Fig. 7(b).

Conclusions

We tried to fabricate bulk β-$FeSi_2$ compacts with the three-dimensional alignment. The alignment was initially obtained by slip-casting under the oscillating magnetic field (maximum 6T). The crystallographic alignment remained even after sintering. This study showed the sintering condition (temperature: 1073 K, pressure: 50-200 MPa and duration: 24 hours or more) for the three-dimensional alignment of β-$FeSi_2$ compacts. The apparent density was as high as 97%.

Acknowledgement

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