Formation of Crystallographically Aligned BiMn Grains by Semi-solid Processing of Rapidly Solidified Bi-Mn Alloys under a Magnetic Field

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Alignment of the BiMn grains during solidification under a magnetic field was examined for Bi-Mn alloys (20, 30, 40 and 50 at%Mn). During the conventional peritectic solidification, the BiMn grains produced through the peritectic reaction did not align because of difficulties of the grain rotation. Rapid solidification produced the finely distributed BiMn grains in the Bi-rich matrix or the Bi-BiMn eutectic structure at off-eutectic compositions. Heating the rapidly solidified structure resulted in the semi-solid state even for Bi-50 at%Mn alloy, in which no semi-solid state containing BiMn phase in equilibrium. The BiMn grains suspended in the semi-solid state rotated in the favorable direction. Growth of the BiMn grains following the rotation achieved c-axes alignment of the BiMn grains. The semi-solid state, which is controlled by the initial microstructure obtained by the rapid solidification, is significantly useful for the magnetic alignment.

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1. Introduction

In solidification processing, the electromagnetic force induced under a magnetic field less than 7.96 × 10^5 A/m (1T) has been used to reduce convection. Superconducting magnets developed recently can provide relatively high static magnetic fields of the order of 7.96 × 10^6 A/m (10T) in room temperature bore for long term. At high magnetic fields, the magnetization force that originates due to interaction between the induced magnetization and external magnetic field can also be used even for paramagnetic and diamagnetic materials. For example, diamagnetic water was levitated at a magnetic field of about 1.59 × 10^7 A/m (20T).1-2) Another example is the textured structure of the superconducting oxide, Y-Ba-Cu-O system produced under a magnetic field.3-10) Since the YBaCuO shows anisotropy for critical current density, it is advantageous to obtain crystallographically aligned polycrystalline.

Achievement of the aligned structure cannot always be obtained during solidification even for materials with large magnetic anisotropy energy. In the previous study,11) c-axes of the BiMn grains did not align during solidification through the peritectic reaction, although the BiMn exhibits a large magnetic anisotropy (c-axis is the easy magnetization axis).12) On the other hand, the magnetically aligned structures of the Bi-Mn alloys were obtained by remelting the rapidly solidified Bi-50 at%Mn alloy13) and by annealing the rapidly solidified Bi-Mn alloys under a magnetic field up to 7.96 × 10^6 A/m (10T).13) The study13) implied that the semi-solid processing has potential to achieve the aligned structure even for the materials in which the aligned structure is not obtained by conventional solidification under a magnetic field. Furthermore, it has been suggested that the semi-solid state can be applied to fabrication of the micro-magnetic devices.14) Thus, it is of interest to achieve the aligned structure obtained by remelting the rapidly solidified alloy. However, there is no extended study on the aligned structure formation in the Bi-Mn system by using the remelting procedure.

The study presents the alignment of the BiMn grains in the Bi-20, 30, 40 and 50 at%Mn alloys by two solidification procedures. One is the semi-solid solidification of the rapidly solidified Bi-Mn alloys. The other is the solidification through the peritectic reaction. Comparing the alignment obtained by the semi-solid processing to that obtained by the conventional solidification, the study presents applicability of the semi-solid processing of the rapidly solidified Bi-Mn alloys. Mechanism of the aligned structure formation in the peritectic Bi-Mn system is also discussed.

2. Experiments

Rapidly solidified particles with compositions of Bi-20, 30, 40 and 50 at%Mn were produced by rotating-water-atomization technique.15) Cold press under a pressure of 250-300MPa produced compacts made of the rapidly solidified particles. The compacts was 6-8 mm in diameter and 5-10 mm in length.

Figure 1 shows phase diagram of Bi-Mn system16) and temperature profiles for solidification. Two different solid-
ification procedures were performed as shown in Fig. 1. In the first procedure (referred as semi-solid processing), the compacts made of the rapidly solidified particles were heated up to 573 K at a heating rate of 0.1 K/s and then were cooled at a cooling rate of 0.1 K/s. The temperature of 573 K is above the Bi-BiMn eutectic temperature but below the liquidus temperatures for the Bi-Mn alloys used in the present study. Thus, heating the rapidly solidified structure up to temperatures above the Bi-BiMn eutectic temperature resulted in the semi-solid state. In the other procedure (referred as peritectic solidification processing), the compacts were heated up to 733 K at a heating rate of 0.1 K/s and were cooled at a cooling rate of 0.026 K/s. As shown in Fig. 1, the specimens were completely melted and the BiMn grains were produced through the peritectic reaction in the Bi-30, 40 and 50 at% Mn alloys.

X-ray diffraction and magnetization measurement were done to estimate degree of the alignment of BiMn grains. Observation of the microstructure was done using a SEM and an optical microscope. DSC was also performed to characterize melting behavior of the rapidly solidified particles during the heating procedure. Heating rate was 20 K/min.

3. Results and Discussion

Figure 2 shows macrostructures of the rapidly solidified Bi-Mn alloys. For the Bi-30 at%Mn alloys (Fig. 2(a)), BiMn grains (gray) were uniformly distributed in the Mn supersaturated Bi matrix (white). For the Bi-20 at%Mn and 30 at%Mn alloys, primary Mn phase was not apparently observed in the rapidly solidified structure. The primary Mn phase appeared in the Bi-40 at%Mn and 50 at%Mn alloys. The Mn grains with diameters of 1-3 μm were observed in the rapidly solidified Bi-50 at%Mn alloy (Fig. 2(b)). Between the Mn grains, the Bi-BiMn eutectic structure was observed. Volume fraction of BiMn grains was approximately 50%. The microstructure indicated that the coupled growth of Bi and BiMn has occurred at the hypereutectic compositions by the rapid solidification.

DSC curves of the rapidly solidified Bi-50 at%Mn particles and the cast Bi-50%Mn alloy in a metal mold are shown in Fig. 3. In the case of the rapidly solidified particles, an exothermic reaction was realized before an endothermic reaction at 535 K due to the melting of the boundary region between Bi and BiMn, and Bi phase. After the endothermic reaction was completed, exothermic reactions were clearly observed. The exothermic reaction suggested the production of BiMn grains from the Bi-rich liquid phase and the primary Mn grains. On the other hand, no exothermic heat evolution was observed for the cast Bi-Mn alloy. Thus, the fine eutectic structure produced by the rapid solidification enhanced the production of BiMn grains.

Figure 4 shows the microstructures of the specimens solidified under a magnetic field of $3.18 \times 10^6$ A/m (4T). In the Bi-30 at%Mn alloys produced by the semi-solid processing, the BiMn grains (gray) were observed in the Bi matrix (white), as shown in Fig. 4(a). Major axes of the BiMn grains
tended to align in the magnetic field which was imposed in the horizontal direction of the figure. In contrast, coarse Mn grains (black) were surrounded by the BiMn grains (gray) in the Bi-30 at%Mn alloys produced by the peritectic solidification processing (Fig. 4(b)). When the specimen was heated up to temperatures above the peritectic temperature, the Mn grains coarsened, reducing the peritectic reaction rate. The low reaction rate of the peritectic reaction resulted in the unreacted Mn grains (black).

As seen in Fig. 4(c), the Bi-50 at%Mn alloy produced by the semi-solid processing consisted of BiMn matrix (gray) which contained the unreacted Mn grains and Bi grains (typical diameters was less than 10 μm). During the semi-solid processing, the liquid formed due to the melting of the Bi phase sufficiently reacted with the solid Mn phase to produce the BiMn grains. The exothermic reaction after the melting as seen in Fig. 3 corresponded to the BiMn grain formation. The fine structure produced by the rapid solidification promoted dissolution of the primary Mn grains and consequently growth of the BiMn grains. As seen in Fig. 4(d), in the peritectic solidification processing, the coarse Mn grains produced above the peritectic temperature were not sufficiently reacted with the liquid phase, since the reaction rate was controlled by diffusion in the BiMn phase. Consequently, the coarse Mn grains surrounded by the BiMn grains, and the Bi phases were observed in the Bi-50 at%Mn alloy produced by the peritectic solidification processing.

Comparing the semi-solid processing to the peritectic solidification processing, the peritectic reaction was enhanced by the partial remelting of the rapidly solidified structure in which the fine Mn grains were distributed in the Bi-BiMn eutectic structure. As a result, the specimens consisting of BiMn grains could be produced even for the Bi-50 at%Mn alloys.

X-ray diffraction patterns of the Bi-50 at%Mn alloys produced by the semi-solid processing are shown in Fig. 5. “Parallel” and “perpendicular” indicate planes on which X-ray diffraction was measured with respect to the magnetic field imposed during the solidification procedure.
peak of (110) reflection was observed. The X-ray diffraction patterns showed that the c-axes of the BiMn tended to align parallel to the imposed magnetic field.

Magnetization curves of the Bi-50 at%Mn alloys produced by the semi-solid processing under a magnetic field of \(2.89 \times 10^5 \text{ A/m} (0.3T)\) are shown in Fig. 6(a). "Parallel" and "perpendicular" indicate directions of the magnetic field imposed for the magnetization measurement with respect to the magnetic field imposed during the solidification. In the magnetization curves, a clear anisotropy in the parallel and the perpendicular magnetization curves was found, indicating that c-axes of BiMn grains aligned with the direction of the magnetic field. Figure 6(b) shows the magnetization curves of the Bi-50 at%Mn alloys produced by the semi-solid processing under a magnetic field of \(3.18 \times 10^6 \text{ A/m} (4T)\).

Comparing to the magnetization curves for the specimen produced under a magnetic field of \(2.89 \times 10^5 \text{ A/m} (0.3T)\), the anisotropy in the magnetization became higher for the specimen produced under a magnetic field of \(3.18 \times 10^6 \text{ A/m} (4T)\). The magnetization curves of the specimens produced by the semi-solid processing exhibited the anisotropy in the magnetization, indicating that the c-axes alignment of the BiMn was achieved. As seen in Fig. 6(c), the anisotropy in the magnetization was relatively small for the specimen produced by the peritectic solidification processing. Furthermore, the magnitude of the magnetization was also small.

The magnetic anisotropy energy of the specimens, which were subjected to the magnetic fields of \(2.89 \times 10^5 \text{ A/m} (0.3T)\) and \(3.18 \times 10^6 \text{ A/m} (4T)\), was estimated from the magnetization curves in the parallel direction and the perpendicular direction. The estimation was performed by integrating difference of the magnetization curves between the parallel direction and the perpendicular direction from 0 A/m to 1.19 \(\times 10^6\) A/m.

Figure 7(a) shows the magnetic anisotropy energy estimated by the above method for the specimens solidified under a magnetic field of \(2.89 \times 10^5 \text{ A/m} (0.3T)\). The

Fig. 6 Magnetization curves of the Bi-50 at%Mn alloys. (a) The specimen produced by the semi-solid processing under a magnetic field of \(2.89 \times 10^5 \text{ A/m} (0.3T)\), (b) the specimen produced by the semi-solid processing under a magnetic field of \(3.18 \times 10^6 \text{ A/m} (4T)\) and (c) the specimen produced by the peritectic solidification processing under a magnetic field of \(2.89 \times 10^5 \text{ A/m} (0.3T)\). “Parallel” and “perpendicular” indicate directions of the magnetic field imposed for the magnetization measurement with respect to the magnetic field imposed during the solidification.

Fig. 7 Magnetic anisotropy of the specimens solidified under a magnetic field of (a) \(2.89 \times 10^5 \text{ A/m} (0.3T)\) and (b) \(3.18 \times 10^6 \text{ A/m} (4T)\). The Semi-solid processing and the peritectic solidification processing are indicated by “573 K 2h” and “0.026 K/s from 893 K”, respectively.
magnetic anisotropy energy increased with increase in the Mn content for the specimens produced by the semi-solid processing. However, the anisotropy energy tended to saturate at higher Mn concentrations, decreasing the degree of the alignment. Comparing to the anisotropy energy induced by the semi-solid processing, the anisotropy energy induced by the peritectic solidification was small and decreased in the high Mn concentration range.

The anisotropy energy in the specimens solidified under a magnetic field of $3.18 \times 10^6$ A/m (4T) is shown in Fig. 7(b). The anisotropy energy of the specimens produced by the semi-solid processing increased linearly with increasing the Mn content. Higher values of the magnetic anisotropy energy induced by the semi-solid processing show high degree of the alignment of the BiMn grains. Although values of the anisotropy energy induced by the peritectic solidification was not as high as those induced by the semi-solid processing, the peritectic solidification processing also achieved a certain degree of the alignment.

Comparing the anisotropy energy induced at a magnetic field of $3.18 \times 10^6$ A/m (4T) to that at a magnetic field of $2.89 \times 10^5$ A/m (0.3T), The magnetic field of $3.18 \times 10^6$ A/m (4T) remarkably increased the anisotropy energy at the higher Mn concentrations for both the peritectic solidification and the semi-solid processing. Therefore, the experimental results indicate that the semi-solid processing and the rather high magnetic field of $3.18 \times 10^6$ A/m (4T) were effective to produce the alignment of the BiMn grains.

Assuming the magnetic anisotropy energy of the BiMn compound as $630$ kJ/m$^3$, the magnetic anisotropy energy for each grain is approximately order of $10^{-6}$ J for the BiMn grains with radii ranging from $10^{-6}$ to $10^{-7}$ m. The value is much higher than the thermal activation energy, $kT$, at the annealing temperature of $573$ K. The anisotropy energy is sufficiently high to align c-axes of the BiMn grains in a favorable direction if the grains can freely rotate. Recently, rotation of magnetically anisotropic particles in an electroconductive fluid was analyzed from kinetics viewpoint. The model pointed out that the inertia term in the equation of the rotational motion is negligible at very beginning of the rotation. According to the analysis, the angle between the c-axes and the external magnetic field, $\theta$, is expressed by a following equation

$$\tan \theta = \tan \theta_0 \exp \left[ -\frac{r}{\tau} \right]$$  \hspace{1cm} (1)

Here,

$$\tau = \frac{30\eta + r^2\sigma B^2}{10K_u}$$ \hspace{1cm} (2)

It should be noted that the magnetic anisotropy energy for the paramagnetic or diamagnetic materials in the normalized parameter, $\tau$, in Ref. 17) is replaced with the magnetic anisotropy energy, $K_u$, for ferromagnetic materials. The first term and the second term in the numerator correspond to resistance due to viscosity of the melt and the electromagnetic force operating the melt surrounding the particle, respectively. By substituting the typical properties for metallic systems ($\eta = 10^{-3}$ Pas, $\sigma = 10^6 \, \Omega \cdot \text{m}$, $B = 3.18 \times 10^6$ A/m (4T)) and the magnetic anisotropy energy of the BiMn compound ($r = 10^{-6}$ m, $K_u = 630$ kJ/m$^3$), the normalized parameter, $\tau$, is estimated to be the order of $10^{-6}$ s.

Thus, it is apparent that the time required for the BiMn grains with radius of $10^{-6}$ m to rotate in a typical metallic melt will be much smaller than 1 s. As seen in the DSC curve (Fig. 3), the growth of the BiMn grains in the semi-solid state takes more than in the rapidly solidified Bi-50 at%Mn alloy. Therefore, the BiMn grains have extremely sufficient time to rotate in the favorable direction if they can freely rotate in the melt. To obtain the aligned structure, it is important to achieve suspension of the BiMn grains in the melt during the solidification path under a magnetic field.

In the peritectic solidification path of the Bi-50 at%Mn alloy, the solidified structure (Fig. 4) indicated that the BiMn grains nucleate on the Mn grains. Comparing size of the BiMn grain to size of the Mn grain, it is difficult for the BiMn grains attached on the Mn grain to rotate in the favorable direction. In general, the BiMn grains produced through the peritectic reaction are not suspended in the melt during the conventional solidification path. Therefore, the alignment of the peritectic compound cannot be achieved in the conventional solidification path.

For the rapidly solidified Bi-50 at%Mn alloy (Fig. 2), the BiMn grains existed as a constituent phase of the eutectic structure (Bi-BiMn), since the coupled growth occurred even at off-eutectic compositions. According to the DSC measurement (Fig. 3), the melting of the Bi and the boundary region occurred when the rapidly solidified specimens are heated up to $355$ K, and the growth of BiMn accompanying the exothermic reaction follows the melting. The rapidly solidified structure (Fig. 2) shows that volume fraction of the liquid phase will be as large as 50% in the Bi-BiMn eutectic region. In principle, melting immediately begins at the well-defined temperatures such as eutectic temperature and solidus temperature. On the other hand, growth of the BiMn grains produced form the rapidly solidified is controlled by solute diffusion in the liquid phase. Thus, the growth mostly occurs after the melting. As a result, the BiMn grains in the melt rotate in the favorable direction and then the aligned BiMn grains grow by consuming the Bi-rich liquid phase and the Mn phase. Furthermore, the fine structure produced by the rapid solidification promoted the growth of the aligned BiMn grains. Consequently, the alignment of the BiMn grains is obtained even at the stoichiometric composition.

As mentioned above, the semi-solid processing using the rapidly solidified Bi-Mn alloys were effective to achieve the crystallographically aligned structure of the BiMn compounds. However, it is not explained that the magnetic field of $3.18 \times 10^6$ A/m (4T) remarkably improved the anisotropy energy, comparing to the magnetic field of $2.89 \times 10^5$ A/m (0.3T). There are two possible explanations as follows.

As seen in Figs. 6(a) and (b), the magnetization curve in the perpendicular direction did not saturate at a magnetic field of $2.89 \times 10^5$ A/m (0.3T). It means that the magnetic filed of $2.89 \times 10^5$ A/m (0.3T) is too small to saturate the magnetization of a BiMn compound with the large anisotropy. Here, the apparent magnetic anisotropy energy, $K_u$, is introduced by the following equation.
When a magnetic field, $H$, is sufficiently high to saturate a BiMn grain, the apparent magnetic anisotropy energy of the BiMn grain is equal to the magnetic anisotropy energy of the BiMn compound. The magnetization curves suggest that the apparent magnetic anisotropy energy at the magnetic field of $2.89 \times 10^5$ A/m (0.3T) will be smaller than the magnetic anisotropy energy, whereas the apparent magnetic anisotropy energy at the magnetic field of $3.18 \times 10^5$ A/m (4T) almost reaches the magnetic anisotropy energy. Thus, torque caused by the magnetic anisotropy energy at the magnetic field of $2.89 \times 10^5$ A/m (0.3T) will be lower than that at the magnetic field of $3.18 \times 10^5$ A/m (4T).

At rather low magnetic fields, the magnetic field at a position of the BiMn grain does not coincide with the magnetic field imposed by a magnet, because the magnetic field induced by neighboring BiMn grains cannot be negligible. Even if the BiMn grains freely rotate, the c-axes do not always align in the imposed magnetic field. Thus, it is required to impose a magnetic field of which intensity is sufficiently high, comparing to the magnetic field induced by the neighboring BiMn grains.

The present study shows that achievement of the semi-solid structure, which is favorable for the rotation of the magnetically anisotropic grains, is important for the magnetic alignment during solidification. The coupled growth, which produces the so-called eutectic structure even at the off-eutectic composition, resulted in the favorable microstructure in the Bi-Mn system. The microstructures produced by the non-equilibrium processing such as rapid solidification can be used as an initial microstructure to produce the suspension. The results also showed that rather high magnetic field such as $3.18 \times 10^5$ A/m (4T) is required to improve degree of the alignment.

4. Conclusions

Alignment of the BiMn grains during solidification under a magnetic field was examined by using two solidification procedures.

(1) In the case of the peritectic solidification processing, the BiMn grains produced through the peritectic reaction nucleated on the primary Mn phase. Since growth of the BiMn grains were limited by diffusion in the BiMn phase, the primary Mn phase did not completely react with the Bi-rich liquid. The coarse Mn and the Bi phases were observed in the solidified structure. The low magnetic anisotropy energy induced during the peritectic solidification processing under a magnetic field of $2.89 \times 10^5$ A/m (0.3T) shows that the alignment of the BiMn grains was not obtained. Even under a magnetic field of $3.18 \times 10^5$ A/m (4T), the magnetic anisotropy energy induced during the peritectic solidification processing was small, comparing to that induced the semi-solid processing.

(2) Rapid solidification produced the uniform distribution of the BiMn grains with diameters of 1-3 μm in the Bi-

matrix for the Bi-30 at%Mn alloy and the eutectic structure along with the primary Mn grains for the Bi-50 at%Mn alloy. Heating the rapidly solidified alloys resulted in the semi-solid state in which the BiMn grains are isolated from each other in the Bi-rich liquid phase. The semi-solid state enabled the BiMn grains to rotate in the favorite direction. The rotation is followed by growth of the aligned BiMn grains. Consequently, the semi-solid processing under a magnetic field successfully achieved the c-axes alignment of the BiMn grains. Degree of the alignment was improved by imposing a magnetic field of $3.18 \times 10^5$ A/m (4T).

(3) The present study shows that the semi-solid state produced from the non-equilibrium structure such as rapidly solidified structure can be useful to produce the aligned structure even for the alloy compositions in which no semi-solid state exists in equilibrium.

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