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Magnetic Field Effects on the Morphology of Bi-Mn alloy prepared by solid-phase reactive sintering

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Abstract

The scanning electron microscope (SEM) observation and powder X-ray diffraction (XRD) measurements were performed for Bi-20at.%Mn alloys prepared by solid-phase reactive sintering in magnetic fields up to 15 T. The ferromagnetic MnBi grains were elongated and aligned along the magnetic field direction in the Bi-rich matrix for 523 K under $\mu_0 H \geq 10$ T. At 513 K, MnBi phase was not formed even the application of $\mu_0 H = 15$ T. The obtained results suggested that the elongated grain of ferromagnetic MnBi was synthesized without connecting or rotating in magnetic field.

Keywords: Magnetism in Solids, MnBi, magnetic field effect, solid-state sintering

1. Introduction

MnBi is one of the Mn-based ferromagnetic alloys. Ferromagnetic MnBi (low temperature phase: LTP) has a hexagonal NiAs-type structure and a large uniaxial magnetic anisotropy along *c*-axis. The magnetic moment of LTP is 3.9 μ_B/Mn.[1)] The magnetic phase transition from a ferromagnetic state to a paramagnetic state occurs at ~ 628 K, which is accompanied with the decomposition from MnBi (LTP) to $Mn_{1.08}Bi$ (high temperature phase: HTP).[2,3)]

In-field heat treatment effect has been reported for Bi-Mn alloys. There have been many reports for the control of crystal orientation, morphology, and magnetic properties, by in-field heat treatment. The elongated MnBi grains were separated each other, and each grains aligned along the magnetic field direction.[4–6)] Magnetic properties of in-field annealed Bi-Mn alloy were anisotropic due to the crystal orientation. These magnetic field effects were explained by the rotation of the elongated ferromagnetic grain, anisotropic crystal growth, and connecting of the grains.[7)] The other magnetic field effects on Bi-Mn system are the change of phase equilibrium under the magnetic field due to gain of the Zeeman energy of ferromagnetic phase.[8–10)]

Recently, it was found that magnetic field influenced the solid-phase reactive sintering of MnBi.[11)] Magnetic field effects on reactive sintering from Mn and Bi to ferromagnetic MnBi were reported to be the enhancement of the reaction and the uniaxial crystal orientation.[11–13)] The almost completely uniaxial orientation was obtained by in-field solid- and liquid-state reactive sintering. However, magnetic field effect on the morphology obtained by reactive sintering was not investigated yet.

In this study, magnetic field effects on the microstructure of the samples annealed in solid-state reactive sintering were investigated.

2. Experimental

The pellets of ϕ10 mm and 7 mm thick were prepared by pressing under a pressure of 2×10^3 kg/cm^2 after mixing Mn (3N, grain size $d < 100$ μm) and Bi (5N, $d < 100$ μm) powders. The molar ratio of Mn to Bi was 20:80. The pellets were sealed in a quartz tube with argon gas. After that, in-field heat treatment was carried out under magnetic fields of

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$\mu_0 H$ = 0 T, 5 T, 10 T and 15 T. The annealing temperatures were 523 K and 513 K. These temperatures were below the eutectic temperature of Bi and Mn. This reaction was the solid-state reaction from Bi + Mn to MnBi.

The magnetic field direction was applied parallel to the thickness of the pellet. The annealed samples were cut for the characterization measurements. The powder X-ray diffraction (XRD) measurements at room temperature were performed for characterizing the synthesized phases. The microstructural observations were performed by scanning electron microscope (SEM). The observed plane was parallel to the applied magnetic field direction.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the samples sintered at 523 K in magnetic fields of $\mu_0 H$ = 0 T (a), 5 T (b), 10 T (c) and 15 T (d). Here, *hkl* denotes the Miller indices of MnBi. The diffraction peaks of unreacted Mn and Bi were observed for $\mu_0 H$ = 0 T and 5 T. It was found that MnBi phase was not synthesized at these conditions. As seen in Fig. 1, for $\mu_0 H$ = 10 T and 15 T, the diffraction peaks of MnBi phase were observed, indicating that the magnetic field induced the reaction.

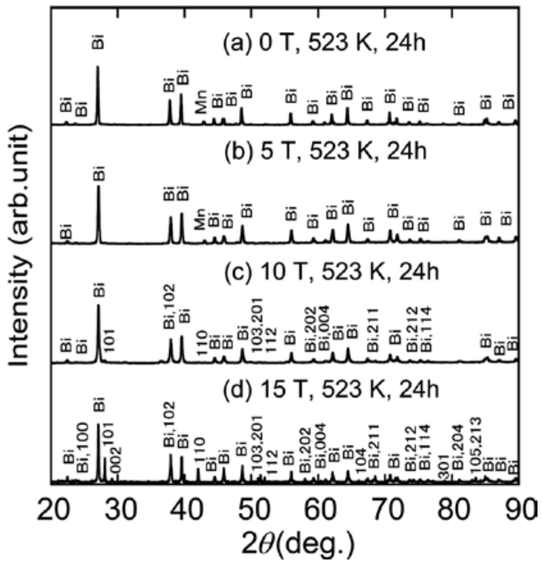

Fig. 1. The powder XRD patterns of the samples at 523 K for 24 h at magnetic fields of $\mu_0 H$ = 0 T (a), 5 T (b), 10 T (c), and 15 T (d).

Fig. 2 shows the microstructures of Bi-Mn alloys for magnetic fields of $\mu_0 H$ = 0 T (a), 5 T (b), 10 T (c) and 15 T (d). The white, gray and black areas indicate pure Bi, MnBi, and Mn phase, respectively. As seen in Fig. 2 (a) and (b), Mn grain was observed in the Bi-matrix. MnBi phase was not observed for these conditions. This suggests that the magnetic field of $\mu_0 H$ = 5 T is not enough high to enhance the reaction effectively at this annealing temperature.

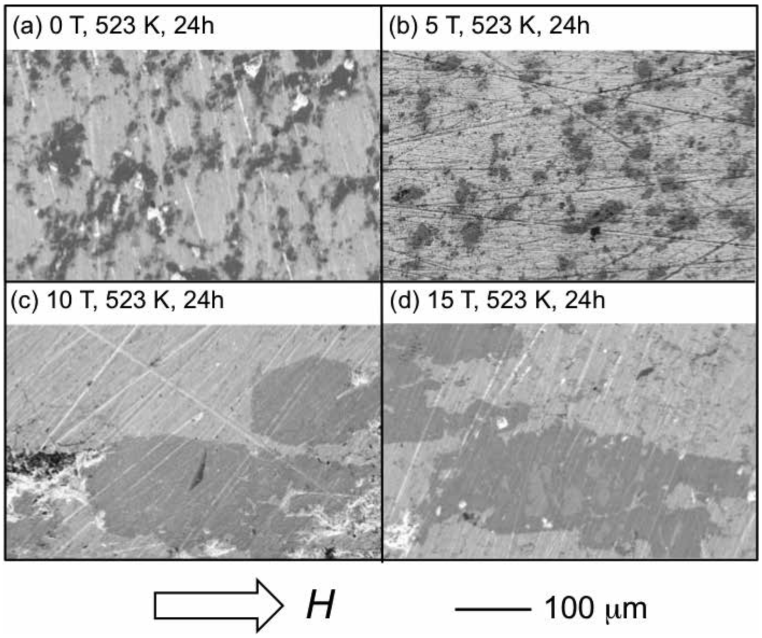

Fig. 2. The microstructure at 523 K for 24 h at magnetic fields of μ_0H = 0 T (a), 5 T (b), 10 T (c), and 15 T (d).

For the sample annealed in μ_0H = 10 T and 15 T, the synthesized MnBi grains were observed. These grains became elongated and tended to align along the parallel to the direction of magnetic field. It was observed that some MnBi grains were close each other. This morphology was similar to that prepared by semi-solid melting state under magnetic fields.[7] However, the connection of the ferromagnetic grain was not observed, which is different from that of semi-solid melting sample.

The annealing temperature effect for the reaction was evaluated. Fig. 3 shows the XRD pattern (a) and SEM image (b) of the sample sintered at 513 K for 24 h in magnetic field of μ_0H = 15 T. The obtained XRD and SEM results showed that the MnBi phase was not formed.

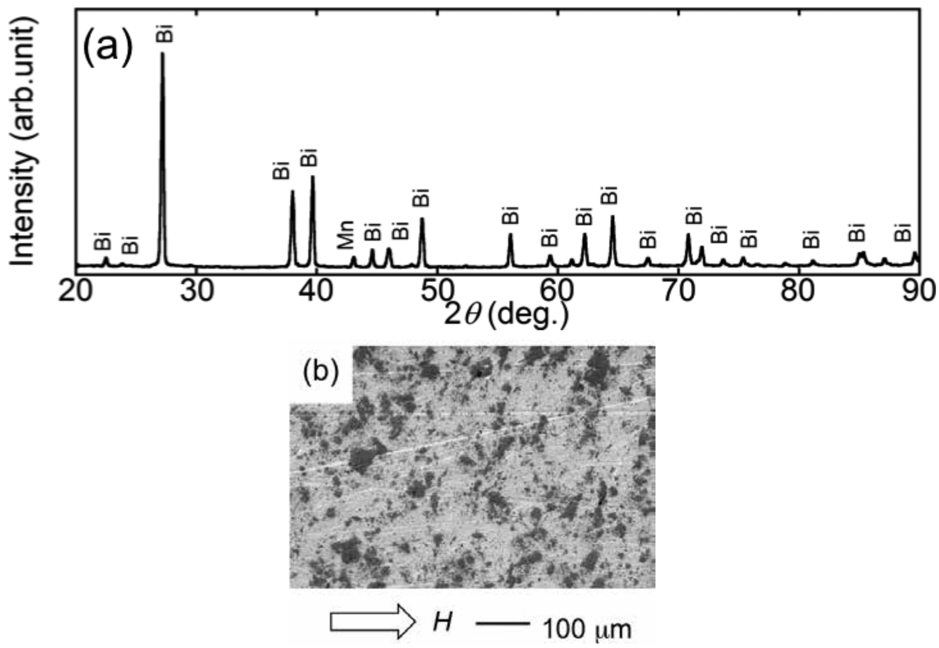

Fig. 3. (a) The powder XRD patterns of the sample at 513 K for 24 h at a magnetic field of μ_0H = 15 T (b) The microstructure at 513 K for 24 h at a magnetic field of μ_0H = 15 T.

Fig. 4 shows the schematic illustration of an in-field reaction model. Since the Bi-rich matrix was solid for the solid-state reactive sintering, it is hard for the formed MnBi phase to rotate and align parallel to magnetic field direction. However, the formed MnBi showed the similar behavior to the solidified sample from the semi-solid state under the magnetic fields. These results indicated that the anisotropic crystal growth occurred under magnetic fields without the rotation and the connecting of the ferromagnetic MnBi grain. As seen in Fig. 2 (c) and (d), some MnBi grains were close each other. For the initial stage of reaction, the grain boundary diffusion and phase formation of MnBi exhibits. The grain boundary partially was melted by reaction heat, inducing the growth of the reactant. Since there are some eutectic melting states at the boundary, this is considered to be similar to the semi-solid melting state. Although the melted area was small, the formed ferromagnetic grain can move in the melted area, resulting in the closeness of the ferromagnetic grain.

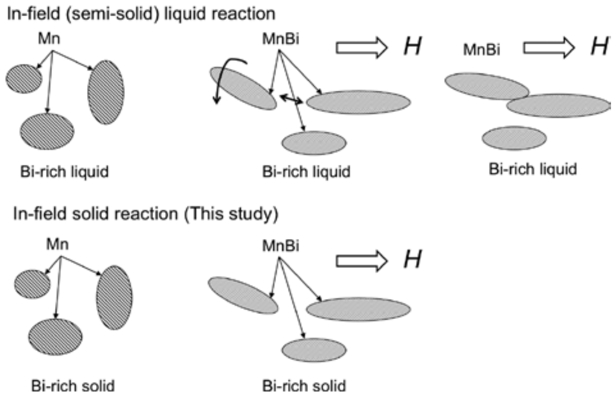

Fig. 4. The schematic model in field reaction for this experimentation.

In addition, MnBi phase was not synthesized at 513 K even applying $\mu_0 H = 15$ T. The decrease of annealing temperature of 10 K critically suppressed the reaction. This result indicated that the thermal activation of the reaction was more effective than the application of magnetic field.

4. Summary

Magnetic field effect on the morphology of solid-state reaction for Bi-20at.%Mn was investigated. It was found that the obtained MnBi grain in $\mu_0 H = 15$ T was elongated and aligned along the magnetic field direction. This behavior was similar to a magnetic field effect on the solidification from semi-solid melt. The obtained results suggested that the elongated grain of ferromagnetic MnBi was synthesized without connecting or rotating in magnetic field.

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