Article ID: 1003-6326(2003)06-1405-05

Alignment behavior of MnBi phase in Bi-Mn alloy solidified in static magnetic field①

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Abstract: During the solidification of Bi-Mn alloys from the mushy zone between 262 ℃ and 355 ℃ in a static magnetic field up to 1.0 T, the alignment behavior of the MnBi primary phase in the alloys was studied experimentally. The ferromagnetic MnBi crystals are magnetized and rotate their *c*-axes parallel to the field. Then, the oriented crystals congregate and grow up under the influence of magnetic interactions so that the alignment structure of the rod-like MnBi phase is produced. It is found that the orientation of MnBi crystals occurs immediately when the heating temperature or magnetic intensity reaches a critical value and beyond the value the orientation factor Γ of the MnBi phase is increased with increasing the heating temperature and the magnetic intensity. The critical temperature for Bi-6% Mn alloy is 275 ℃ in a 1.0 T magnetic field and increases to 290 ℃ when the magnetic field intensity decreases to 0.1 T. When the alloys are hold at 275 ℃, the critical magnetic intensity for Bi-6% Mn alloy is 0.4T and 0.05 T for Bi-3% Mn alloy. The orientation and congregation of the MnBi crystals were analyzed in terms of the magnetic anisotropy of the crystals and their magnetic interactions.

Key words: magnetic field; Bi-Mn alloy; MnBi; alignment; congregation
CLC number: TG 111.4 **Document code:** A

1 INTRODUCTION

Regular structures in materials are always prepared to improve their properties. It is well known that powdered ferromagnetic materials can be oriented in a static magnetic field. In recent years high magnetic field was applied to induce alignment of particles in some nonferromagnetic materials with anisotropic magnetic susceptibility in room temperature, such as paramagnetic $YBa_2Cu_3O_7$ ceramic[1] and diamagnetic graphite[2]. If the materials have a residual anisotropy in their magnetic susceptibility at a high temperature, they can be textured by solidification in a magnetic field, for example, $YBa_2Cu_3O_{7-\delta}$[3] and Benzophenone[4]. Now the alignment behavior of materials solidified in a magnetic field is of great interest both in theoretic studies and potential applications, especially in the preparation of in situ composite materials.

The anisotropic susceptibility in a nonferromagnetic crystal is so small that it is difficult to align it in a normal magnetic field. A ferromagnetic MnBi crystal is easy to orient in a magnetic field because of its large magnetic anisotropy ($K = 1\ MJ/m^3$)[5]. According to the phase diagram of Bi-Mn system[6], the Curie temperature of MnBi (355 ℃) lies above the eutectic transformation temperature (262 ℃) and so the orientation of the ferromagnetic crystals in the molten alloy under the influence of magnetic field is possible. Therefore, the Bi-Mn alloy appears to be a suitable system for studying the crystallization of materials in a magnetic field.

The intermetallic compound MnBi has long been of interest as a hard magnetic material and a possible material for magneto-optic memory applications[7]. The Bi-Mn alloys were also experimentally studied by directional solidification[8, 9]. During crystallization of Bi-Mn alloys in magnetic fields[2, 10, 11], preferred growth orientation of elongated MnBi crystals and their orientation along the applied field have been observed. The magnetization on the alloys crystallized in the field was found to be strongly anisotropic. But the laws and the mechanisms of the formation of the orientation structure of the MnBi phase in the alloys under the influence of magnetic field are not well understood.

In the present work, the critical conditions of the formation of the orientation structure of the MnBi phase in Bi-Mn alloys by solidification from the semi-solid zone between 262 ℃ and 355 ℃ with a magnetic field are studied experimentally and a theoretical model is investigated to explain the experimental re-

① **Foundation item:** Project(59871026, 50225416, 50234020) supported by the National Natural Science Foundation of China; Project (98SG37) supported by "Shu Guang" Education Development Foundation of Shanghai, China
Received date: 2002-12-09; **Accepted date:** 2003-04-14
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sults.

2 EXPERIMENTAL

The Bi-Mn alloys with composition of 3% Mn and 6% Mn (mass fraction) were prepared from 99.0% pure bismuth and 99.5% pure electrolytic manganese. The alloys were molten in an inductive furnace and cast with graphite molds under argon at a pressure of 50.6 kPa. The sample(9.5 mm in diameter and 25 mm in length) was sealed in a graphite tube and inserted into a resistance furnace, which was placed between poles of the electromagnet, as shown in Fig. 1. The intensity of magnetic field between poles of the electromagnet can be adjusted from 0 to 1.3 T and the temperature in the furnace chamber can be controlled automatically during the experiment. The difference between the controlled temperature and the actual one was within ±1 ℃. The furnace was specially designed so that the sample in the furnace was able to fall directly into water to quench.

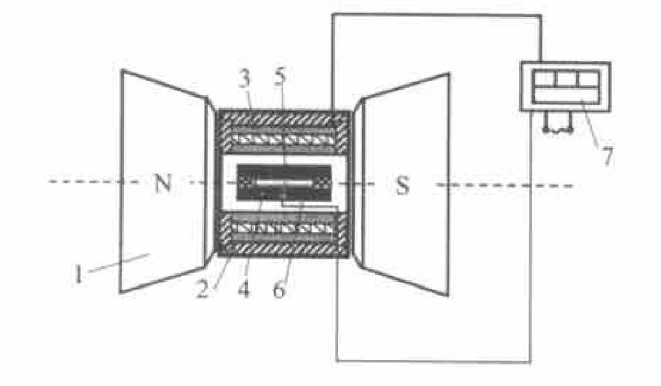

Fig. 1 Schematic diagram of experimental device for metal solidification in magnetic field
1—Electromagnet yoke; 2—Refractory; 3—Heater; 4—Graphite tube; 5—Sample; 6—Thermocouple; 7—Temperature controller

Since the liquidus temperatures of 3% and 6% Mn alloys are all above 355 ℃, the alloys are in semi-solid states between 262 ℃ and 355 ℃. The alloys were heated at a rate of 10 ℃/min to the temperature in mushy zone without the magnetic field, hold for 30 min and then cooled to the temperature below 262 ℃ with a magnetic field up to 1.0 T. The cooling rate was about 8 ℃/min. For characterizing the morphology of the MnBi phase, the samples obtained in the experiments were mechanically polished parallel and perpendicular to the applied field.

3 RESULTS

Fig. 2 shows the microstructures of Bi-6% Mn alloy heated up to 345 ℃ and cooled with and without magnetic field, respectively. The MnBi crystals (dark grey) were randomly oriented in the matrix (white) in the sample crystallized without magnetic field. In the case of solidification with the field, the elongated MnBi crystals were oriented and grew up preferentially along the applied field. The hexagonal sections of the crystals only appeared in the section perpendicular to the field. It indicates that the c-axis of hexagonal MnBi crystal (easy magnetization axis) is aligned parallel to the magnetic field. This has been confirmed by X-ray diffraction. The results will be discussed in detail in other articles.

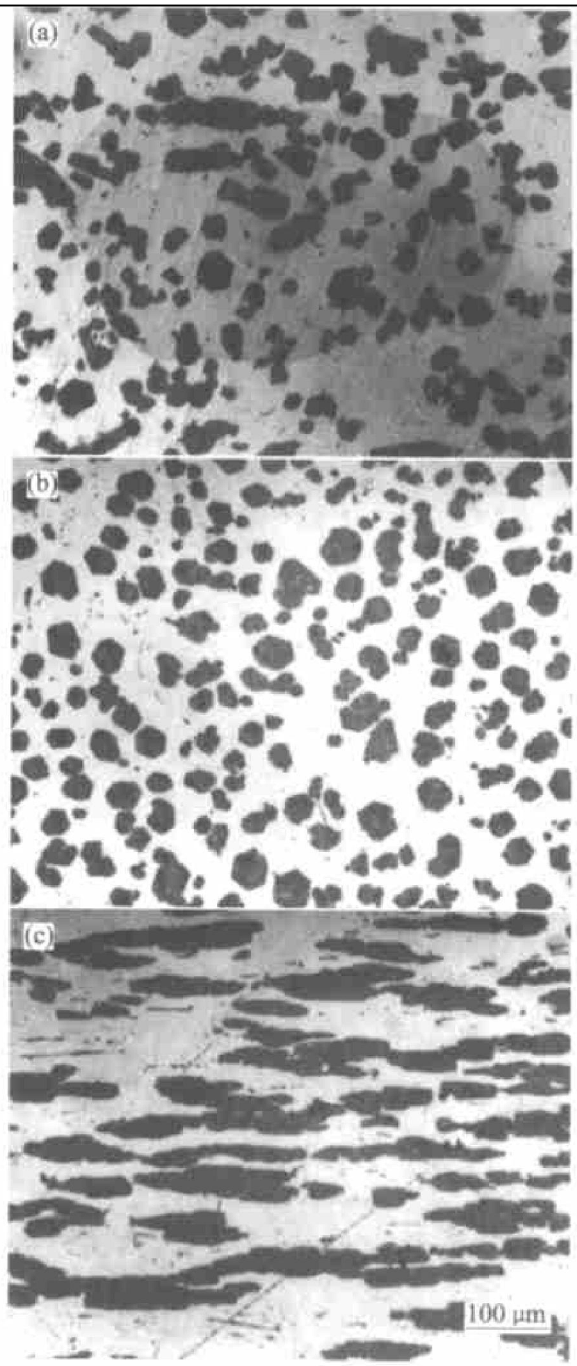

Fig. 2 Morphologies of Bi-6% Mn alloy heated up to 345 ℃ for 30 min and cooled at a rate of 8 ℃/min
(a) —0 T; (b) —1.0 T, transverse section; (c) —1.0 T, longitudinal section

A special experiment was performed to investigate the early stage of MnBi crystals orienting in magnetic fields. Bi-3% Mn alloy was heated up to 300 ℃ for 30 min, then 1.0 T magnetic field was applied for a very short time (about 30 s) and then shut down. The sample was quenched as soon as the field was switched off. The result is shown in Fig. 3. Groups of little MnBi crystals were oriented and congregated along the magnetic field. It means that the MnBi crystals in the mushy zone in Bi-3% Mn alloy can be oriented and congregated rapidly by a 1.0 T magnetic field.

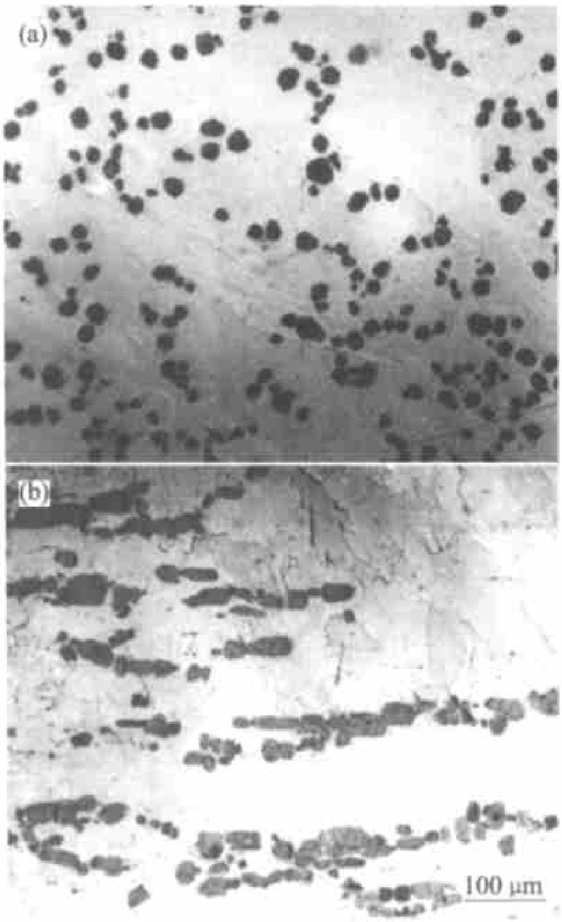

Fig. 3 Morphologies of Bi-3% Mn alloy with 1.0 T magnetic field applied for 30 s at 300 ℃ and quenched
(a) —Transverse section; (b) —Longitudinal section

For evaluating the degree of orientation of MnBi crystals, an orientation factor Γ is defined as a ratio of the volume of all oriented MnBi crystals to that of total ones. An oriented MnBi crystal is that the angle between *c*-axis of the crystal and magnetic field is within 15°. For perfectly oriented sample the parameter Γ is unit, while for unoriented sample the parameter Γ is below 0.1.

During the solidification of Bi-6% Mn alloy in a magnetic field, the dependence of orientation factor Γ on heating temperature is presented in Fig. 4. In the case of solidification in a 1.0 T magnetic field, Γ is low than 0.1 at the temperature below 275 ℃, increases suddenly to 0.9 just at 275 ℃

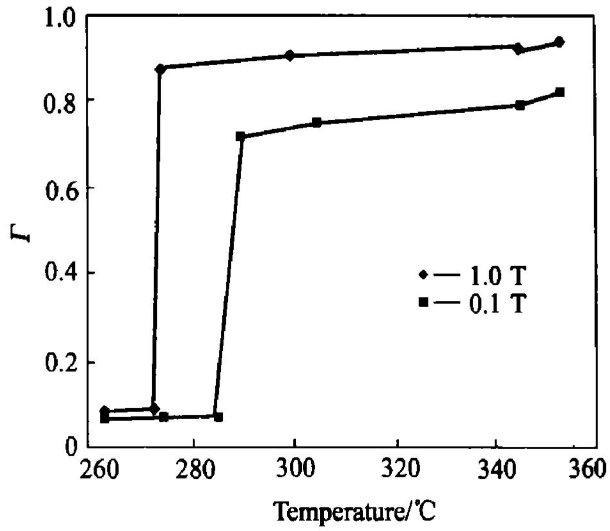

Fig. 4 Dependence of MnBi orientation factor Γ on heating temperature of Bi-6% Mn alloy solidified in magnetic field

and increases slightly with further increasing temperature. That is, the alignment structure in Bi-6% Mn alloy is induced at this temperature and above. When Bi-6% Mn alloy is solidified in a 0.1 T magnetic field, Γ is small till a sudden increase from 0.1 to 0.75 occurred at 290 ℃. It is obvious that the critical temperature for the parameter Γ transition in a 0.1 T magnetic field is higher than that in a 1.0 T field.

When the heating temperature is 275 ℃, for both the Bi-Mn alloys, the dependence of orientation factor Γ on the intensity of applied magnetic field is shown in Fig. 5. As demonstrated above, the orientation factor Γ of the Bi-6% Mn alloy is about 0.1 in the magnetic field below 0.4T, and jump to 0.7 in the 0.4 T field. Then Γ increases gradually to near 0.9 with increasing the applied field from 0.4 T to 1.0 T. For the Bi-3% Mn alloy, the critical magnetic flux density is as small as 0.01 T, significantly lower than that of the Bi-

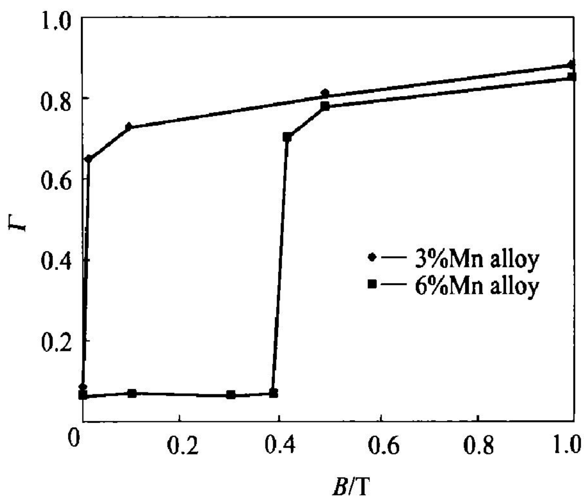

Fig. 5 Dependence of MnBi orientation factor Γ on magnetic flux density of Bi-Mn alloys held at 275 ℃ and solidified in magnetic fields

6% Mn alloy.

4 ANALYSES AND DISCUSSION

4.1 Magnetization and orientation of MnBi crystal

According to the magnetization theories, a ferromagnetic MnBi crystal is spontaneously magnetized along its c-axis (the easy magnetization axis) of the hexagonal crystal. The spontaneous magnetization in one domain is equal in quantity and opposite in direction to the other one so that the magnetization of the whole crystal is zero, as shown in Fig. 6(a). When the MnBi crystal is placed in an external magnetic field H_{ex} (Fig. 6(b)), the domain in which the direction of spontaneous magnetization is close to the direction of the applied field is stable and grows up in volume, the other domain is unstable and reduced correspondingly. As a result, the MnBi crystal is magnetized along c-axis by the mechanism of domain-wall motion and under the influence of a magnetic moment L, which can be calculated and simplified as[12]

$$L = -mlH_{ex}\sin\theta \qquad (1)$$

where m is pole strength; l is the length of crystal; θ is the angle between c-axis and magnetic field ($0° \leqslant \theta \leqslant 90°$).

$$m = VM_c, \quad M_c = \chi_c H_{ex}$$

Hence,

$$L = -Vl\chi_c H_{ex}^2 \sin\theta \qquad (2)$$

where V is the volume of the crystal; χ_c is the magnetic susceptibility and M_c is the intensity of magnetization per unit volume along c-axis. For $\theta = 0°$, the magnetic moment L is zero. It means that the MnBi crystal is stable with its c-axis parallel to the field. For $\theta \neq 0°$, the MnBi crystal is unstable and tends to rotate with its c-axis parallel to the field under the influence of magnetic moment L, as shown in Fig. 6(c).

When Bi-Mn alloy is solidified from mushy zone between 262 ℃ and 355 ℃ in a magnetic field, the orientation of MnBi crystals is affected by the magnetic moment and the resistance forces originated from the viscosity of molten alloy, collisions between the crystals and thermal disturbance. If the magnetic moment L on the crystal is larger than the resistance forces, the crystal will rotate with its c-axis parallel to the applied field.

Eqn. (2) shows that the magnetic moment is in proportion to the square of magnetic intensity. Moreover, with the increase of heating temperature, the resistance forces are decreased because of the reduction of the viscosity of molten alloy and the volume fraction of MnBi phase. Therefore, it is easy to understand that the orientation factor Γ increases with increasing magnetic intensity and heating temperature.

As shown in Fig. 4 and Fig. 5, the orientating of MnBi crystals occurs suddenly when the heating temperature or magnetic intensity reaches a critical value. This may be explained as the balance broken between the magnetic moment and the resistance forces and the crystals turn to orient immediately.

In Fig. 4, the forces on the MnBi crystals in 6% Mn alloy may reach a balance just below 275 ℃ in a 1.0T magnetic field. Hence, in the case of 0.1 T magnetic field, the magnetic moment is too weak to orient the crystals at 275 ℃ and a new balance may reach at a higher heating temperature. Consequently, the critical temperature increases with decreasing the magnetic intensity.

In Fig. 5, the critical magnetic intensity of Bi-6% Mn alloy is higher than that of Bi-3% Mn alloy. This may be caused by the difference in volume fraction of MnBi phase between them. The volume fraction of the MnBi phase in Bi-6% Mn alloy is 25.89%, nearly double of that in Bi-3% Mn alloy. Thus, the possibility of collisions between the crystals in Bi-6% Mn alloy is larger than that in Bi-3% Mn alloy. Namely, at the same temperature, the resistance forces of rotation for the MnBi crystals in Bi-6% Mn alloy is larger than that in Bi-3% Mn alloy and needs to be balanced by a stronger magnetic field.

4.2 Congregation of oriented MnBi crystals

After magnetizing and orientating in a magnetic field, there are magnetic attractive forces between the magnetized MnBi crystals along the direction of the field. If the attractive force between

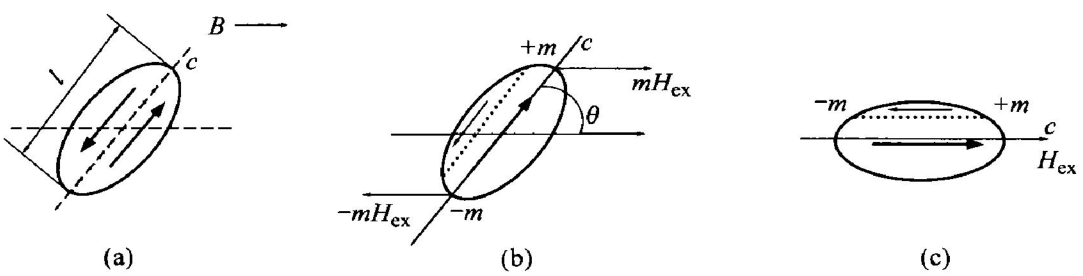

Fig. 6 Schematic diagrams of MnBi crystal
(a) —Spontaneously magnetized along c-axis; (b) —Magnetized in external magnetic field by mechanism of domain-wall motion; (c) —Oriented with c-axis parallel to direction of field

two crystals is larger than the resistance forces from the viscosity of the molten alloy, thermal disturbance and magnetic force from other crystals, the two oriented crystals will congregate along the magnetic field, just as learned from the experiments. The force between two magnetized crystals is[12]

$$F = \frac{m_1 m_2}{4\pi\mu r^2} \qquad (3)$$

where μ is the magnetic permeability of the MnBi crystals in molten alloy; r is the distance between the poles of two crystals; m_1 and m_2 are the pole strength of crystal 1 and 2.

$$m_1 = V_1 M_c,\quad m_2 = V_2 M_c,\quad M_c = \chi_c H_{ex},$$

where V_1 and V_2 are the volume of crystal 1 and 2. Therefore,

$$F = \frac{V_1 V_2}{4\pi\mu r^2}\chi_c^2 H_{ex}^2 \qquad (4)$$

It is indicated from Eqn. (4) that the increase of distance between the crystals causes a square decrease of the force. So, only the crystals in a small scope are possible to be congregated by the force. Beyond the scope, the force decreases so quickly that its influence on other crystals can be neglected.

On the basis of orientation and congregation of MnBi crystals along the magnetic field, the crystals tend to grow up preferentially along the field during the solidification of Bi-Mn alloys in the magnetic field. In this way the long rod-like structure of MnBi phase is produced.

5 CONCLUSIONS

1) The MnBi crystals in mushy zone orient, congregate and grow up preferentially along the direction of the applied magnetic field during solidification of Bi-Mn alloys. As a result, the alignment structure of rod-like MnBi phase is formed.

2) The orienting of MnBi crystals occurs immediately when the heating temperature or the magnetic intensity reaches a critical value. Beyond the value, the orientation factor Γ of MnBi phase increases with increasing the heating temperature or the magnetic intensity.

3) The critical temperature in Bi-6% Mn alloy is 275 ℃ in a 1.0 T magnetic field and increases to 290 ℃ when the magnetic field intensity decrease to 0.1 T. When the alloys are hold at 275 ℃, the critical magnetic intensity for Bi-6% Mn alloy is 0.4 T and 0.05 T for Bi-3% Mn alloy.

ACKNOWLEDGMENTS

The authors would like to express deep thanks to Profs. SHI Tai-hua and WANG Zhong-cheng for their helpful discussions in magnetism physics.

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(Edited by HE Xue-feng)