Crystal Alignment of Bi–Sn Alloy by Simultaneous Imposition of a Static Magnetic Field and an Alternating Current during Solidification

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Crystal alignment of a Bi–10mass%Sn alloy solidified under different electromagnetic field imposing condition has been experimentally investigated in this study. Simultaneous imposition of a static magnetic field and an alternating current excited an electromagnetic vibration and it promoted nucleation, and resulted in decrease of undercooling, though imposition of the static magnetic field alone did not affect the undercooling. Furthermore, grain size of the solidified structure under the simultaneous imposition of the static magnetic field and the alternating current was smaller than that solidified with the magnetic field alone or solidified without the electromagnetic field imposition. XRD pattern of the sample solidified without the electromagnetic field imposition was similar to that of bismuth powder. On the contrary, only specific crystal plane peaks were observed when the electromagnetic field was imposed on the sample during the solidification. That is, crystal alignment of bismuth rich primary phase was achieved not only by the static magnetic field imposition alone but also the simultaneous imposition of the static magnetic field and the alternating current. However, degree of the crystal alignment solidified under the latter electromagnetic condition was slightly higher than that solidified under the former electromagnetic condition.

KEY WORDS: solidification; crystal alignment; electromagnetic processing of materials.

1. Introduction

A material with a crystallographically anisotropic structure shows anisotropy in its physical and chemical properties, such as electric conductivity, magnetic susceptibility, and thermal conductivity. That is, the alignment of crystals in a material enhances the anisotropy of these properties. Therefore, crystal alignment is an attractive method for fabricating functional materials. For example, grain-aligned magnetic steel with a $\{110\}\{001\}$ crystallographic structure has been developed in which the magnetically easy $\langle 001 \rangle$ axis is aligned to the rolling direction, because this structure shows a marked reduction in core losses compared with conventionally produced steel.^{1,2)} Crystal alignment is also useful tool for improving the magnetic properties of ferrite magnets, because the residual magnetic flux density is proportional to the degree of crystal alignment. Graphite is suitable as a heat-extraction material because its average thermal conductivity is about three or four times larger than that of aluminum and copper. However, as a result of the hexagonal structure of graphite, its thermal conductivity in the directions of the a -axis is about two hundreds times larger than that in the c -direction, so alignment of crystals strongly intensifies the ability of graphite to act as a heat-extraction material.

Conventional methods for crystal alignment have some problems. Mechanical methods for the alignment of crys-

tals, such as rolling, have been used industrially, although crystal alignment by such processes is limited to a specific direction. Slip casting in a magnetic field can be applied for the crystal alignment of ceramics, but this process is not suitable for large-scale mass production because of its low productivity. Epitaxial growth is used to produce thin films, but it is difficult to form bulk materials by this process. Thus, a new method for metallic crystal alignment suitable for large-scale mass production is desired.

With the development of superconducting technologies, static magnetic fields have become sufficiently powerful to permit their use in materials processing.^{3,4)} For example, a process for grain-refinement of a solidified structure⁵⁾ has been proposed in which a static magnetic field and an alternating current are locally imposed on an alloy during solidification. In this process, the dendrite tips are broken into pieces during the initial stage of solidification. This satisfies the essential condition for a crystal alignment using a static magnetic field, in that the crystals suspending in liquid can easily rotate to the magnetically stable direction, although it is generally difficult to introduce this condition during solidification because a columnar solid is usually formed from the liquid phase.⁶⁾ Therefore, this process was applied for the crystal alignment.^{7,8)} Furthermore, the simultaneous imposition of a static magnetic field and a direct current on a metallic alloy during solidification has been also utilized for the crystal alignment.⁹⁾ However, only the crystal align-

ment of a Sn–Pb alloy has been achieved until now.^{7–9)} Thus, elucidation of crystal alignment behavior of other materials in the process mentioned above is useful information for the formation of crystal aligned material.

In this paper, crystal alignment behavior of a Bi–10mass%Sn alloy under the simultaneous imposition of a static magnetic field and an alternating current during solidification has been experimentally investigated.

2. Magnetic Anisotropy

An alloy adopted in this study is a Bi–10mass%Sn alloy. Its liquidus temperature and eutectic temperature are 506 K and 412 K, respectively as shown in **Fig. 1**. Since the primary phase composition of the alloy used in this experiment is very close to pure bismuth, physical property of the primary crystal must be close to that of pure bismuth. On the other hand, tetragonal structure of tin-rich eutectic crystal is the same with that of pure tin. Both crystals are expected to have magnetic anisotropy because pure bismuth and pure tin have magnetic anisotropy as shown in **Table 1**.^{10,11)} The magnetic anisotropy of pure bismuth is about two hundreds times larger than that of pure tin. Thus, the bismuth rich primary crystal must align easily under the imposition of the strong magnetic field to reduce magnetic energy in comparison with the tin rich eutectic crystal. The *c*-axis of the bismuth rich primary crystal must be parallel to the magnetic field direction because the magnetic susceptibility in *c*-axis must be larger than that in *a*-axis.

3. Experimental Procedure

Pure bismuth (99.9% purity) and pure tin (99.9% purity) were used as starting materials for preparation of the alloy adopted in this investigation. They were mixed with mass ratio of 9 : 1 and then melted for homogenization in a furnace. Experimental apparatus is shown in **Fig. 2**. The prepared liquid alloy poured in a glass rectangular vessel of 40 mm length and 25 mm width was set in the bore of a super-conducting magnet, which can excite a magnetic field in vertical direction. A couple of copper electrodes were inserted in the vicinity of a short wall to supply an alternating current to the alloy. Thus, not only electromagnetic vibration but also convection is induced in the liquid alloy by the simultaneous imposition of the magnetic field and the alter-

nating current.⁵⁾ The copper electrodes were heated to reduce temperature disturbance caused by heat extraction from the alloy through the electrodes. The electrodes were covered by an electrical insulator except 5 mm×5 mm square tip. Temperature was measured by thermocouple located in the vicinity of the short wall of the vessel.

We solidified four samples under the different experimental conditions. The sample 1 was solidified without a static magnetic field and without an alternating current. The static magnetic field of 8 T was imposed on the sample 2 during its solidification while the alternating current was not applied. The samples 3 and 4 were solidified under the simultaneous imposition of the static magnetic field of 8 T and the alternating current of 80 A, 1 kHz. The imposing period of the static magnetic field on the both samples was the same with that on the sample 2. On the contrary, the imposing period of the alternating current on the sample 3 and that on the sample 4 were different. The alternating current was imposed on the sample 3 from the start of the solidification till the end while it was imposed on the sample 4 only in the initial stage of the solidification. Because the magnetic field direction excited by the super-conducting magnet was vertical direction and the main component of the alternating current was horizontal direction, horizontal vibration was induced in the samples 3 and 4 during the simultaneous imposition. The experimental conditions are summarized in **Table 2**. These four samples were solidified

Fig. 1. A part of Bi–Sn phase diagram.

Table 1. Magnetic susceptibility of Bi and Sn.^{10,11)}

	$\chi_{a,b}$	χ_c	$\Delta\chi$
Sn	2.48×10^{-6}	2.21×10^{-6}	2.7×10^{-7}
Bi	-1.77×10^{-4}	-1.24×10^{-4}	5.3×10^{-5}

Fig. 2. Experimental apparatus.

Table 2. Experimental condition.

	Magnetic flux density B(T)	Electric Current I(A)	Imposing Duration t(s)
sample 1	0	0	0
sample 2	8	0	0
sample 3	8	80	all
sample 4	8	80	60

Fig. 3. Observed surfaces of structure and X-ray diffraction.

and cooled in air. After the solidification, the sample was cut into pieces. Then, the horizontal surface in the vicinity of the electrodes was polished to observe solidified structure as shown in **Fig. 3**. And X-ray was irradiated on the same surface for the evaluation of crystal alignment in which the X-ray diffractometer (Rigaku Corp., cat. no. 2035G403) with a Cu K α X-ray source was used.

4. Results

4.1. Effect of Magnetic Field Imposition on Crystal Alignment

Temperature histories of the samples 1 and 2, and the imposing period of the magnetic field are shown in **Fig. 4**. Solidification started with undercooling of about 8 K in the both samples. Therefore, the magnetic field did not affect nucleation.⁵⁾ The measured temperatures recovered to about the liquidus temperature and then they decreased with time. The temperatures of the both samples were kept almost constant at the eutectic temperature of 412 K. The temperature histories of the samples 1 and 2 are quite similar. Thus, the imposition of the magnetic field on the sample did not affect the temperature history during the solidification. Solidified structures of these samples are shown in **Fig. 5**. Boundary of the bismuth rich primary phase and the eutectic phase are mainly composed of straight lines in the both samples because of facet growth of the primary phase. The XRD results are shown in **Fig. 6**. Each detected peak was specified using the powder diffraction data of bismuth and tin. Peak intensity of tin planes is very weak in the both samples while that of bismuth is clearly observed. The first, second and third main peaks in the sample 1 is Bi(012), Bi(110) and Bi(104) planes. This tendency is similar to the

X-ray diffraction pattern of bismuth powder. Thus, the bismuth rich primary crystals in this sample do not align to the specific direction but has random orientation. On the other hand, only a few peaks are detected in the sample 2. The first and second main peaks of Bi(003) and Bi(006) planes in this sample are *c*-plane, and the Bi(012) plane peak observed in the sample 1 almost disappears. That is, the bismuth rich primary crystals in this sample aligned parallel to the magnetic field direction.

4.2. Effect of Electromagnetic Vibration on Crystal Alignment

The samples 3 and 4 were solidified under the simultaneous imposition of the current and the magnetic field. Temperature histories of these samples, and the imposing periods of the current and the magnetic field are shown in **Fig. 7**. Not only the temperature histories in these samples are similar but also these are similar to those of the samples 1 and 2 except the undercooling. Undercoolings of the samples 3 and 4 were about a few Kelvin while those of the samples 1 and 2 were about 8 Kelvin. The most likely explanation is that the electromagnetic vibration excited by the simultaneous imposition of the static magnetic field and

Fig. 4. Temperature histories of samples 1 and 2. (a) Sample 1, (b) sample 2.

Fig. 5. Solidified structures of samples 1 and 2. (a) Sample 1, (b) sample 2.

Fig. 6. XRD results of samples 1 and 2. (a) Sample 1, (b) sample 2.

Fig. 7. Temperature histories of samples 3 and 4. (a) Sample 3, (b) sample 4.

Fig. 8. Solidified structures of samples 3 and 4. (a) Sample 3, (b) sample 4.

Fig. 9. XRD results of samples 3 and 4. (a) Sample 3, (b) sample 4.

the alternating current affected nucleation.⁵⁾ The solidified structures of the samples 3 and 4 are shown in Fig. 8. Grain sizes in the samples 3 and 4 are small in comparison with those of the samples 1 and 2. This is due to the grain refinement effect of the electromagnetic vibration. The XRD results obtained in the samples 3 and 4 are shown in Fig. 9. The first and second main peaks in the sample 3 are Bi(006) and Bi(003) planes, while those in the sample 4 are Bi(003) and Bi(006) planes. This means that the crystal alignment of bismuth rich primary phase was achieved by the simultaneous imposition of the static magnetic field and the alternating current on the sample during the solidification.

5. Discussion

Electromagnetic vibration is induced by the simultaneous imposition of a static magnetic field and an alternating current on the sample. Thus, a primary phase crystal moves periodically as indicated Eq. (1) if viscous force surrounding the crystal can be neglected.

$$F_0 \cos \omega t = \rho \frac{dv}{dt} \quad (1)$$

where F_0 is electromagnetic body force, t is time, v is velocity of crystal, ρ is density of crystal and ω is angular frequency, respectively.

Because not only thermal fluctuation is disturbance but also electromagnetic vibration is disturbance from the viewpoint of crystal alignment, magnetic energy caused by the magnetic anisotropy must be larger than the sum of these two disturbances. Thus, the inequality (2) should be satisfied for the crystal alignment.

Fig. 10. Ratio of magnetic energy to the sum of vibration energy and thermal fluctuation.

$$U_M > U_T + U_V \quad (2)$$

$$U_M = \frac{1}{2} \mu_0 \Delta \chi H^2 V \quad (3)$$

$$U_T = k_B T \quad (4)$$

$$U_k = \frac{1}{2} m v^2 \quad (5)$$

where H is magnetic field strength, k_B is Boltzmann constant, m is mass of crystal, T is absolute temperature, U_M is magnetic energy caused by the magnetic anisotropy of crystal, U_T is thermal fluctuation, U_V is vibration energy, V is volume of crystal, μ_0 is magnetic permeability in vacuum, $\Delta \chi$ is magnetic susceptibility difference in crystal, respectively.

The ratio of the magnetic energy to the sum of the vibration energy and thermal fluctuation was calculated using Eqs. (1) to (5) for a spherical bismuth crystal under the experimental condition adopted in this investigation, in which the electromagnetic body force and temperature were assumed to be $2 \times 10^6 \text{ N/m}^3$ and 473 K, respectively. The calculated ratio as a function of a spherical crystal radius is shown in Fig. 10. A micrometer radius is enough for the crystal alignment. Thus, the crystal alignment in the samples 2, 3 and 4 might be achieved in the initial stage of the solidification.

Degree of the crystal alignment of the bismuth rich primary phase can be quantitatively evaluated as weighted average angle, θ defined by the following equation.

$$\theta = \frac{\sum (I_{hkl} \times \theta_{hkl})}{\sum I_{hkl}} \quad (6)$$

where I_{hkl} is intensity of (hkl) plane, θ_{hkl} is angle between the (hkl) plane and the c plane and θ is the weighted average angle based on the c plane, respectively.

Decrease of the weighted average angle means that crystals whose c -axis aligns parallel to the magnetic field direction increase because the irradiated plane of the X-ray was perpendicular to the magnetic field direction. The weighted average angle was calculated for every sample and the result is listed in Table 3. The weighted average angle, θ of the samples 2, 3 and 4 solidified with the 8 T magnetic field are drastically small compared to that of the sample 1. That is, the c -axis of the primary crystals in the samples 2, 3 and 4 aligned parallel to the magnetic field direction by the magnetic field imposition. Furthermore, the weighted aver-

Table 3. Weighted average angle.

sample No.	1	2	3	4
weighted average angle/degree	56.3	11.3	8.1	7.7

age angle slightly decreases by the simultaneous imposition of the static magnetic field and the alternating current. This can be explained as follows. Floating primary particles increased by the simultaneous imposition because it promoted nucleation as mentioned in the previous section. And the particles rotated to reduce the magnetic energy and finally the solidification finished. The difference between the weighted average angles of the samples 3 and 4 solidified under different imposing period of the electromagnetic vibration might be experimental error because the electromagnetic vibration in the latter stage of the solidification might be neglected in comparison with the magnetic energy as shown in Fig. 10, although imposition of the electromagnetic vibration in the initial stage of solidification was effective for the nucleation. However, further investigation is required to reveal effect of the electromagnetic vibration imposing period on the crystal alignment of the alloy used in this investigation.

6. Conclusion

Crystal alignment of a Bi–10mass%Sn alloy solidified under different electromagnetic field imposing condition has been experimentally investigated.

The main results are as follows.

(1) Undercooling of the alloy and grain size of the solidified structure were decreased by the simultaneous imposition of the static magnetic field and the alternating current. However, decrease of the undercooling and the grain size was not observed in the sample solidified with the magnetic field alone.

(2) Crystal alignment of the bismuth rich primary phase was achieved not only under the imposition of the static magnetic field alone but also under the simultaneous imposition of the static magnetic field and the alternating current.

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