Crystal Alignment of Primary Phase during Solidification

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Abstract. In this study, a crystal alignment method, in which imposing duration of a static magnetic field and an alternating current on a material during the solidification is controlled has been experimentally confirmed using a Sn-10% Pb metallic alloy. In the initial stage of the solidification both the magnetic and the alternating current are imposed on the alloy to break dendrites into pieces and to spread them to all the region in the sample. In the next stage, the static magnetic field is continuously imposed on the sample while the alternating current is turned off. The function of the static magnetic field in this stage is not only the rotation of the crystals to magnetically stable direction but also the suppression of the disturbance such as liquid motion. In the x-ray diffraction pattern of the sample solidified with the controlled imposition of the electromagnetic fields, peaks corresponding to theoretically predicted planes are mainly observed.

1. Introduction

A material with an anisotropic crystallographic structure shows anisotropy in physical properties such as electric conductivity, magnetic susceptibility, thermal conductivity and so on. That is, alignment of the crystals in the material enhances the anisotropy of these physical properties. Therefore, the crystal alignment is an attractive method for fabricating functional materials.

However, conventional methods for the crystal alignment have some problems. A mechanical method for the alignment of crystals such as a rolling has been industrially used [1], though the crystal alignment in this process is limited to a specific direction. Slip casting in a magnetic field [2] can be applied for the crystal alignment of ceramics. But this process is not suitable for large mass production because of low productivity. Epitaxial growth [3] is used as a thin film production process though formation of a bulk material is very difficult.

On the other hand, a static magnetic field has become a powerful tool for the crystal alignment under the development of the superconducting technology [4,5]. For the crystal alignment using a static magnetic field, environment in which crystals can easily rotate to magnetically stable direction is required. However, it is difficult to introduce this condition during solidification because a columnar solid usually forms from liquid phase [6]. Then, a new process for crystal alignment combining a rapid
cooling and re-heating is proposed to introduce semi-liquid condition suitable for crystal rotation and the magnetic property of Bi-Mn alloy produced by this method was improved [7-9].

In this study, a crystal alignment method, in which imposing duration of a static magnetic field and an alternating current on a material during solidification is controlled has been experimentally confirmed using Sn-10% Pb metallic alloy.

2. Principle of Crystal Alignment

For crystal alignment using a magnetic field, anisotropy in magnetic susceptibility or that in a material shape is required. When a material with magnetic susceptibility, \( \chi \) shape factor, \( N \) is submerged in a magnetic field, \( H \), Magnetization energy, \( U \) is expressed as

\[
U = -\frac{\mu_0 \chi}{2(1 + \chi N)} H^2
\]

where \( \mu_0 \) is magnetic susceptibility in vacuum.

In this equation, the term, \( \chi N \) is usually neglected because the magnetic susceptibility, \( \chi \) is extremely smaller than unity and the shape factor is between 0 and 1. In this condition, the magnetization energy can be expressed as

\[
U \approx -\frac{\mu_0 \chi}{2} H^2
\]

Therefore, a material with anisotropy in magnetic susceptibility should be chosen as a magnetic alignment material.

A Sn-10mass\%Pb alloy has been adopted as a model alloy in this investigation. Because a primary phase at the liquidus temperature includes only 0.38atomic % of lead in mother tin as shown in Fig.1 and magnetic susceptibility of tin in a,b axis is larger than that in c axis [10], the primary phase might have the anisotropy in magnetic susceptibility. Under the imposition of a strong magnetic field, crystal planes perpendicular to the a-axis are expected to be perpendicular to the magnetic field direction.

For crystal alignment in a solidification process, not only the anisotropy in magnetic susceptibility but also other conditions are required. One is rotatable environment for primary phase particles to reduce the magnetization energy. Furthermore, the aligned particles must keep their direction against disturbances. In this investigation, the former can be achieved by imposing an alternating current and a static magnetic field in the initial stage of solidification. And the latter can be achieved by imposing a strong magnetic field.

![Figure 1. Phase diagram of Sn-Pb alloy](image1)

![Figure 2. Experimental apparatus](image2)
3. Experiment

3.1. Experimental Setup
Experimental setup is shown in Fig. 2. A molten sample of 300g was poured into a glass vessel with 25mm length and 40mm depth. One end of the vessel was cooled while the other end was heated to control the temperature distribution in the sample. A couple of copper electrodes was inserted into the molten sample in the vicinity of the heater to apply an alternating current to the sample. Temperatures in the sample were measured at three points by thermocouples. These points were located between the cooler and the heater along the long wall of the vessel as shown in Fig. 2 (c : in the vicinity of cooler, h : in the vicinity of heater, m : middle position between them). This glass vessel was set in the bore of a super conducting magnet which generates a static magnetic field in the vertical direction. The Lorentz force is induced around the copper electrodes when the alternating current and the static magnetic field are simultaneously imposed on the sample.

We can introduce solid particles with the anisotropy in magnetic susceptibility by breaking dendrites around the electrodes where the Lorentz force is excited. These solid particles should exist not only around the electrodes but also in the other region for formation of the crystal aligned material.

3.2. Induction of convection by simultaneous imposition of alternating current and magnetic field
Convection is useful for spreading broken dendrites to the whole region in the sample. To confirm whether the convection is induced or not by the simultaneous imposition of the static magnetic field and the alternating current, we measured the temperature distribution in the molten sample during its cooling at the three points mentioned above. The measured temperature distribution in the sample is shown in Fig. 3. Only the static magnetic field of 1tesla was imposed on the sample until the temperature in the vicinity of the cooler (c) decreased to 210C. The temperature difference in the sample was about 12K in this duration. When the temperature became 210C, the alternating current of 60A with frequency of 2kHz was turned on. Then, the temperature in the vicinity of the heater (h) decreased while that in the vicinity of the cooler (c) increased. And the temperature difference in the sample reduced to less than 4K. The measured temperatures in the sample oscillated with time. This was because that hot liquid lumps and cool liquid lumps circulated in the sample with slow thermal diffusion time. From this result, we can conclude that convection is induced by the simultaneous imposition of the static magnetic field and the alternating current on the sample.

3.3. Suppression of natural convection by magnetic field
Natural convection is induced by the temperature difference in the molten sample caused by the heater and cooler. This is disturbance from the viewpoint of the crystal alignment. Therefore, to confirm the effect of the magnetic field on the convection, we also measured the temperature distribution in the sample during its cooling with and without the imposition of the magnetic field. In the both cases, the electric current was not applied to the sample. The measured temperature distribution in the sample is shown in Fig. 4. When the magnetic field was not imposed on the sample, the temperature difference in the sample was only about 1K. On the other hand, the temperature difference was larger than 10K
under the imposition of the 7.5T magnetic field. This means that imposition of the 7.5T magnetic field has a function to suppress the natural convection in this experimental setup.

![Diagram of Thermocouples and Magnetic Field](image)

**Figure 4.** Effect of static magnetic field on temperature distribution in sample

3.4. Solidification experiment for crystal alignment

We solidified two samples. For the sample I, both the magnetic field of 7.5T and the alternating current of 80A, 2kHz were simultaneously imposed on the alloy to break dendrites into pieces and to spread them to the whole area of the sample in the initial stage of the solidification. In the next stage, only the static magnetic field was continuously imposed on the sample. The function of the static magnetic field in this stage was not only the rotation of the crystals to magnetically stable direction but also the suppression of the disturbance such as liquid motion. On the other hand, only the 6.5T magnetic field was imposed on the sample II during its solidification. After the solidification, the horizontal plane of the samples were cut and polished. Then, XRD analysis was done for these samples for the evaluation of the crystal alignment.

In the X-ray diffraction pattern of the sample solidified without the imposition of the alternating current, the first and second highest peaks were (220)-plane and (211)-plane of primary tin phase as shown in Fig.5 (a). Since the heat flow in this experiment was from the heater to the cooler under the suppression of convection, the preferable growing <110> direction of the primary phase must be parallel to this thermal flow direction [11]. This is the reason why the (220)-plane peak was the highest peak in the sample II. However, the number of grains in the XRD irradiated area might not be enough to deduce the result mentioned above since the thermal condition in this experiment satisfied columnar dendrite growing condition. On the other hand, the peaks corresponding to a,b-plane were mainly observed in the sample solidified under the imposition of the controlled electromagnetic field as shown in Fig.5 (b). In this sample the (211)-plane was suppressed in comparison with the sample II and the mainly observed peak of (200)-plane well agrees with the theoretical prediction. From these results, it is understood that the crystal alignment of the primary phase is achieved.

![X-ray Diffraction Pattern](image)

**Figure 5.** X-ray diffraction pattern
4. Conclusion
A crystal alignment method, in which imposing duration of a static magnetic field and an alternating current on a sample during the solidification is controlled has been experimentally confirmed using Sn-10% Pb metallic alloy.

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