Crystal Alignment of Sn–Pb Alloy by a Simultaneous Imposition of a DC Current and a Static Magnetic Field during Solidification

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A new crystal-alignment process in which both a static magnetic field and a direct current are imposed on an alloy during solidification was proposed and tested experimentally on Sn–10mass%Pb alloy. Various intensities of a static magnetic field and a direct current were imposed on the sample during solidification. After solidification, cross-sections of the samples were polished and the crystal alignment was evaluated by means of X-ray diffraction (XRD). As predicted theoretically, the peaks corresponding to the (200) and (220) planes were intensified in the XRD analysis when a static magnetic field larger of 3 T or more was imposed, whereas no crystal alignment was observed with a 0.1 T magnetic field. Therefore, crystal alignment was achieved by this process, and the critical intensity for crystal alignment is between 0.1 T and 3 T under the experimental conditions studied.

KEY WORDS: solidification; crystal alignment; electromagnetic processing of materials; magnetic field; electric current.

1. Introduction

A material with a crystallographically anisotropic structure shows anisotropy in its physical properties, such as electric conductivity, magnetic susceptibility, and thermal conductivity. That is, the alignment of crystals in a material enhances the anisotropy of these physical properties. Therefore, crystal alignment is an attractive process for fabricating functional materials. For example, grain-aligned magnetic steel with a {110}/H20855001/H20856001 crystallographic structure has been developed in which the magnetically easy (001) 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 for improving the magnetic properties of ferrite magnets, because the residual magnetic flux density is proportional to the degree of crystal alignment.3) Graphite is suitable as a heat-extraction material because its average thermal conductivity is about three or four times that of aluminum and copper.4) However, as a result of the hexagonal structure of graphite, its thermal conductivity in the directions of the a- and b-axes 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 crystals, such as rolling, have been used industrially,5) although crystal alignment by such processes is limited to a specific direction. Slip casting in a magnetic field6) can be applied for the crystal alignment of ceramics, but this process is unsuitable for large-scale mass production because of its low productivity. Epitaxial growth7) is used to produce thin films, but it is difficult to form bulk materials by this process.

With the development of superconducting technologies, static magnetic fields have become sufficiently powerful to permit their use in materials processing.8,9) For example, a process for refining a solidified structure 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 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.10) Crystal alignment has been achieved by simultaneous imposition of a static magnetic field and an alternating current during the solidification process.11) On the other hand, the simultaneous imposition of a static magnetic field and a direct current during the solidification12) can refine the structure during solidification. Such a process might generate the necessary environment for crystal alignment.

We propose a new crystal-alignment process in which both a static magnetic field and a direct current are imposed on an alloy during solidification, and we confirmed that crystals were aligned under these conditions.
2. Experimental Setup

The experimental apparatus is illustrated in Fig. 1. A molten Sn–10mass%Pb alloy weighing 0.3 kg was poured into a rectangular glass vessel measuring 40 mm long by 25 mm wide and located in the bore of a superconducting magnet. To control the temperature distribution in the sample, one of the short walls of the vessel was heated while the other was cooled. The direction of the static magnetic field imposed on the sample was vertical. A couple of copper electrodes were inserted near the short wall of the vessel to supply a direct current to the sample. The electrodes were covered by an electrical insulator except for the 5×5 mm square tip, as shown in Fig. 1. Furthermore, the upper portion of the copper electrodes was heated to reduce any temperature perturbations caused by extraction of heat through the electrodes from the sample.

We solidified four samples under different experimental conditions. A static magnetic field and a direct current were imposed simultaneously on all samples during solidification. The intensities of the static magnetic field and the strength of the direct current were changed in each sample as listed in Table 1. The direct current was switched on when the temperature reached 250°C, which is 31°C above the liquidus temperature of the sample; it was turned off when the sample temperature fell to 170°C, which is 13°C below the eutectic temperature.

We expected that the physical properties of the primary phase would be quite similar to those of pure tin because the composition of the primary phase in these experiments was very close to pure tin. Since tin has a tetragonal crystal structure and its magnetic susceptibility in the direction of the \( a \)-axis is \( 2.476 \times 10^{-6}(\cdot) \) and that in the direction of the \( c \)-axis is \( 2.212 \times 10^{-6}(\cdot) \), the \( c \)-axis should be oriented in the direction perpendicular to that of the magnetic field if the crystals are aligned by the magnetic field.

3. Experimental Results

3.1. Macrostructures

After solidification, each sample was cut into two pieces along a vertical plane, as shown in Fig. 2, and the cut surfaces were polished by emery paper of grade #2000 and polished by a buffing compound containing 0.05-μm alumina particles. Each surface was then chemically etched by a mixture of distilled water, hydrochloric acid, and iron(III) chloride to permit observation of its macrostructure. The remaining half of the sample was cut just below the electrodes and its upper surface was polished for X-ray diffraction analysis.

The macrostructures of the vertically cut surfaces solidified under the various experimental conditions are shown in Fig. 3. All the observed areas for each of samples I, II, and

![Fig. 1. Schematic view of experimental apparatus.](image)

**Table 1.** Experimental condition.

| Sample No. | Electric Current, I(A) | Magnetic Flux Density, B(T) | Relative Intensity of Electromagnetic Force (A-T) |
|------------|------------------------|-----------------------------|---------------------------------------------------|
| I          | 80                     | 0.1                         | 8                                                 |
| II         | 5                      | 3                           | 15                                                |
| III        | 3                      | 5                           | 15                                                |
| IV         | 5                      | 7.5                         | 37.5                                              |

![Fig. 2. Examined surfaces of macrostructure and XRD analysis.](image)

![Fig. 3. Macrostructure solidified under different experimental condition.](image)
III are refined. On the other hand, a region of refined structure and a region of coarse structure were both observed in the case of sample IV. The former region may correspond to the region of circulating flow, whereas melt flow in the latter region may have been weak.

3.2. Temperature History

The sample temperature was measured at the center of the long wall of the sample at a position 20 mm above the bottom, as shown in Fig. 1; the results are shown in Fig. 4. The refining mechanism for sample IV was nucleation excited by the electromagnetic force while the refining mechanism for samples I, II, and III was different, because recrystallization was observed in samples I, II, and III, but not in sample IV. And since the intensity of the electromagnetic force for sample IV was larger than that for samples I, II, and III, the critical intensity for exciting nucleation could lie between these two intensities. One of the refining mechanisms for samples I, II, and III might be breaking dendrites into pieces by the melt flow induced by the electromagnetic force. The other possibility is promotion of nucleation everywhere in the melt since the melt flow makes the temperature distribution uniform. Both mechanisms might be the reason why the structure was refined.

3.3. Evaluation of Crystal Alignment

X-ray diffraction analysis was used to evaluate the crystal alignment, and the results are shown in Fig. 5. The area irradiated by X-rays was about 10 mm square. In the case of sample I (magnetic field 0.1 T, direct current 80 A), the first and second main peaks correspond to the (211) and (101) planes, although the magnetically preferred peaks are planes parallel to the c-axis, such as the (200) and (220) planes. In other words, no crystal alignment is observed in this sample. In the case of samples II (magnetic field 3 T, direct current 5 A), III (magnetic field 5 T, direct current 3 A), and IV (magnetic field 7.5 T, direct current 5 A), the peak corresponding to the magnetically preferred (200) plane is intensified and other peaks, such as those corresponding to the (211) and (101) planes, are suppressed in comparison with sample I. Therefore, the crystals in these samples are aligned in the magnetically preferred direction.

For quantitative evaluation of the crystal alignment, we calculated the ratio of the intensity of the peak corresponding to the (200) plane to that of the peak corresponding to the (211) plane. Here, we chose the (200) plane peak as the representative peak for aligned crystals to the magnetically preferred direction and chose the (211) plane peak as the representative peak for non-aligned crystals, because both the peaks were observed in the XRD results as shown in Fig. 5. This ratio is index of the crystal alignment in the sample, and the crystals aligned to the magnetically preferred direction increases as the ratio increases. The results are shown in Fig. 6. The calculated ratio for sample I is smaller than the corresponding values for samples II, III, and IV in which crystal alignment was observed. The intensity ratio for sample IV is relatively small with that for samples II and III. This can be explained as follows. Alignment of solid crystals suspended in the liquid phase finishes during the initial stage of the solidification. And then it may be perturbed by the electromagnetic force.

The electromagnetic force for sample IV is larger than that for samples II and III. Therefore, degree of crystal alignment decreases with increasing the disturbance in the liquid.

A crystal that is subjected to a magnetic field rotates to decrease its magnetization energy. However, some crystals fail to align in the specific direction of the field as a result of the thermal disturbance. The probability, \( P \), of a crystal
whose magnetically hard axis and the direction of the magnetic field are oriented at an angle $\theta$ is expressed as follows:

$$P \sin \theta d\theta = \frac{\exp(-U/kT) \sin \theta d\theta}{\int_0^\pi \exp(-U/kT) \sin \theta d\theta} \quad \text{(1)}$$

where $U$ is the magnetization energy due to the anisotropy of the magnetic susceptibility, $k$ is the Boltzmann constant, and $T$ is absolute temperature.

The degree of order, $S$, as an index of crystal alignment is defined as follows:

$$S = \int_0^\pi \frac{1}{2} (3 \cos^2 \theta - 1)P \sin \theta d\theta \quad \text{(2)}$$

When the degree of order is zero, the crystals are oriented randomly, whereas all the crystals are aligned in the magnetically preferred direction when the degree of order is $-1/2$.

The theoretically calculated degrees of order for single crystals of tin with various radii are shown in Fig. 7. The intensity of the magnetic field was set to 0.1 T or 3 T in the calculation. Tin crystals with a radius larger than a few micrometers suspended in an easily rotatable environment can, in theory, be aligned by a magnetic field of 0.1 T or 3 T. On the other hand, in a 0.1 T magnetic field, the crystals orient in random directions when their radius is less than 1 $\mu$m, and they orient in random directions in the 3 T magnetic field when their radius is less than 0.1 $\mu$m. Therefore, crystals with a radius between these two radii can rotate in the 3 T magnetic field but not in the 0.1 T magnetic field. This suggests that size of the solid particles suspended in the liquid phase during the initial stage of solidification is between 0.1 and 1 $\mu$m in this experiment, because the critical magnetic field intensity for crystal alignment is between 0.1 and 3 T in this experiment.

4. Conclusion

A new crystal-alignment process in which both a static magnetic field and a direct current are imposed on an alloy during solidification was proposed and investigated experimentally by using a Sn–10mass%Pb alloy. The theoretically predicted plane peaks in the XRD analysis, such as those corresponding to (200) and (220), were intensified in the presence of a static magnetic field of 3 T or more whereas no crystal alignment was observed in the presence of a 0.1 T magnetic field. Therefore, crystal alignment was achieved by this process, and the critical intensity for crystal alignment is between 0.1 and 3 T under these experimental conditions.

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REFERENCES

1) Y. Ushigami: Bull. Iron Steel Inst. Jpn., 4 (1999), 363.
2) N. P. Goss: U.S. Patent No. 1965559, (1934).
3) K. Masuzawa: Electron. Mon., (1998), 11.
4) H. O. Pierson: Handbook of Carbon, Graphite, Diamond, and Fullerenes, Noyes Publications, Park Ridge, N.J., (1993), 43.
5) K. K. Jee, W. Y. Jangl and Y. H. Chung: J. Phys., IV France, 112 (2003), 365.
6) J. Akoyama, M. Hashimoto, H. Takadama, F. Nagata, Y. Yokogawa, K. Sassa, K. Iwai and S. Asai: Mater. Trans., 46 (2005), 203.
7) T. Watanabe, H. Funakubo, K. Saito, T. Suzuki, M. Fujimoto, M. Osada, Y. Noguchi and M. Miyayama: Appl. Phys. Lett., 81 (2002), 1660.
8) Y. Sakka and T. Suzuki: J. Ceram. Soc. Jpn., 113 (2005), No. 1, 22.
9) T. K. Jee, W. Y. Jangl and Y. H. Chung: J. Phys., IV France, 112 (2003), 365.
10) H. Yasuda: Bull. Iron Steel Inst. Jpn., 9 (2004), 789.
11) M. Usui, K. Iwai and S. Asai: ISIJ Int., 46 (2006), 859.
12) M. Usui, S. Asai and K. Iwai: ISIJ Int., 48 (2008), No. 3, 330.
13) M. Usui, K. Iwai and S. Asai: ISIJ Int., 47 (2007), 1613.