Review

Crystal orientation of non-magnetic materials by imposition of a high magnetic field

Shigeo Asai*, Ken-suke Sassa, Masahiro Tahashi

Department of Materials Processing Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya, Aichi 464-8603, Japan

Received 19 May 2003; revised 10 July 2003; accepted 11 July 2003

Abstract

From the viewpoint of learning from the nature, the controlling of crystal orientation is accounted to be a major subject for materials processing. This paper reviews the researches on the crystal orientation by use of a high magnetic field and belongs to the category of researches for mimicking structures, namely the crystal orientation, which nature or living bodies are forming. Regarding to the crystal orientation, several methods such as unidirectional solidification and epitaxial growth and so on have been developed hitherto. On the other hand the magnetization force that is familiar with the force to attract iron to a magnet, has been recognized to be effective even in non-magnetic materials when those are placed under a high magnetic field, which has become rather conveniently available by developing superconducting technologies in these days. In this paper, main results obtained when the imposition of a high magnetic field was accompanied to several materials processing such as electrodeposition, vapor-deposition, solidification, baking, slip-casting and precipitation, are reviewed from the viewpoint of crystal orientation of non-magnetic materials.

Keywords: Electromagnetic processing of materials; High magnetic field; Magnetization force; Crystal orientation; Non-magnetic materials

1. Introduction

It is well known that in hard tissues of bones and teeth, crystals of hydroxyapatite are highly aligned along strings of collagen to reveal sophisticated functions in living bodies [1]. The reason why the crystals in the hard tissues are oriented is considered that the properties of substances largely depend on crystal orientation. From the viewpoint of learning from the nature, the controlling of crystal orientation is accounted to be a major subject for materials processing. This paper reviews the researches on the crystal orientation by use of a high magnetic field and belongs to the category of researches for mimicking structures, namely the crystal orientation, which nature or living bodies are forming, i.e. crystal orientation, from the viewpoint of learning from the nature.

The recent development of superconducting magnet technologies has enabled to provide a rather large space
with a high magnetic field even in small-scale laboratories. Under such circumstance various effects of a high magnetic field have been studied in the field of materials science and engineering. As a result it has been found that these effects are tangible in not only ferromagnetic materials but also non-magnetic ones such as paramagnetic and diamagnetic, on which a magnetic field has been considered to reveal negligible effects hitherto. These effects are based on magnetization force, which is classified into two different kinds. One force is by which ferromagnetic and paramagnetic materials are pulled to a magnet and diamagnetic ones are repulsed, and the other force is by which materials are rotated to a magnetic field direction as a compass rotates to the north direction. The former force has been mainly used for magnetic separation [2], magnetic levitation [3] and measurement of the magnetic susceptibility of materials [2,4]. The latter one is used for the alignments of crystal orientations and texture structures on the basis of the magnetic susceptibility difference due to crystal magnetic anisotropy and the demagnetization factor difference due to shape anisotropy [5–13]. Especially, most of materials have different magnetic susceptibilities in each direction of their unit crystals so that such crystal cells have the possibility to align to a magnetic field direction, even if they are non-magnetic materials. Therefore, the possibility of magnetic transportation and magnetic rotation was examined under several processes such as solidification [5–8], electro-deposition [9], vapor-deposition [10–12] and solid phase reaction [13]. Now the application of a high magnetic field is expected as one of promising technologies in materials processing.

In this review paper, the control of the crystal orientation by use of a magnetic field in several materials processing such as electrodeposition, vaperdeposition, solidification, baking, slip-casting and precipitation has been reviewed mainly from author’s works.

2. Principle and evaluation of crystal orientation

There are three conditions to be indispensable for the crystal orientation by the imposition of a magnetic field. The first one is that materials have a magnetic anisotropy in their unit crystal cells. The second is that the magnetization energy should be larger than thermal energy. This condition is written as Eq. (1)

\[ |\Delta U|/V > kT \quad (1) \]

where \( V \) is volume of a particle to be rotated, \( k \) is Boltzmann’s constant, \( T \) is temperature and \( \Delta U \) is magnetization energy difference in crystal orientations [5] and defined in Eq. (2)

\[ \Delta U = U_i - U_j, \quad U_i = -\frac{x_i}{2\mu_0(1 + N\chi_i)}B^2 \quad (2) \]

where the subscript \( i \) or \( j \) indicates the crystal orientation of \( i \)- or \( j \)-direction, \( \chi \) is a magnetic susceptibility, \( \mu_0 \) is a permeability in vacuum, \( N \) is a demagnetization factor, \( B \) is an applied magnetic field. The third condition is that the materials should exist in the weak constraint medium enough to be rotated by such a feeble magnetization force. That is, in general the magnetization force induced in non-magnetic materials is so weak that this condition indicates the materials should be surrounded by a fluid.

Both zinc and bismuth have a hexagonal crystal structure, which has different magnetic anisotropies depending on each direction of their unit crystals. Magnetic susceptibilities along \( a \)- or \( b \)-axis and \( c \)-axis of zinc are \( \chi_{a,b} = -1.81 \times 10^{-5}, \chi_c = -1.33 \times 10^{-5} \) [14], and those of bismuth are \( \chi_{a,b} = -1.24 \times 10^{-4}, \chi_c = -1.76 \times 10^{-4} \) [15, 16], respectively. The magnetization energy determines the favorable crystal direction depending on the magnetic susceptibility of each crystal axis in a given magnetic field. When a crystal is set in a magnetic field, a crystal tends to align to a favorable crystal direction with the lowest magnetization energy. Substituting values of the magnetic susceptibility of zinc and bismuth into Eq. (1), we get \( U_a < U_{a,b} \) in the case of zinc and \( U_{a,b} < U_c \) in the case of bismuth. These results tell that \( c \)-axis of zinc crystal and \( a \)- or \( b \)-axis of bismuth are the favorable crystal directions in parallel to a magnetic field as shown in Fig. 1.

A new method [17] that evaluates the degree of crystalline orientation from the intensity of X-ray diffraction lines obtained by an X-ray diffraction analyzer (XRD) is proposed here as given in Eq. (3)

\[ \theta_f = \frac{\sum(I_{hkl} \times \theta_{hkl})}{\sum I_{hkl}} \quad (3) \]

where \( \theta_f \) is defined as a facial angle measured from \( c \)-plane of a crystal, and \( \theta_{hkl} \) is the facial angle between \( (hkl) \) and \( (00n) \)-planes. \( I_{hkl} \) is the intensity of \( (hkl) \)-plane in the X-ray diffraction pattern, and defined as the height of the peak intensity measured from the background level. The facial angle \( \theta_f \) is reduced to 0’ when all crystals are oriented to \( c \)-plane and to 90’ when to \( a, b \)-plane.

In the evaluation of the facial angle in following experiments, copper was used as target materials for X-ray diffraction.
3. Materials processing for crystal orientation under a magnetic field

3.1. Vapor-deposition process

A crucible filled with a target material of bismuth with 5 nine purity was put into a vacuum chamber set in the bore of a superconducting magnet generating a magnetic field of 12 T at the maximum intensity and a glass plate as a substrate was set in perpendicular to the magnetic field direction at the position with the maximum magnetic flux density in the bore. After the degree of vacuum in the chamber reached at a value of $5 \times 10^{-3}$ Pa, bismuth as the target in the crucible was heated up to 1073 K by an electric heater.

Fig. 2 shows the relation between the magnetic field intensity and the facial angle $\theta_f$, which is evaluated by using Eq. (3). The orientation toward a, b-plane is steep up to 5 T and then gradually increases with increase of a magnetic field. That is, the result that the rotation to a, b-plane increases with increase of the magnetic field intensity agrees with the theoretical prediction as given in Fig. 1.

3.2. Electro-deposition process

Fig. 3 shows the schematic view of an experimental apparatus. A copper substrate as cathode and a zinc plate as anode were set in a cubic vessel as an electrolytic cell. The magnetic field of 12 T was imposed in perpendicular to the cathode substrate plane. The detail of the experimental condition is given in Ref. [9].

Fig. 4 shows the relations between the orientation index and the imposed magnetic flux density in the electrodeposits obtained at $J = 700 \text{ A/m}^2$. The higher the magnetic field is, the more the c-plane orientation is elicited. This result agrees with the theoretical derivation based on the magnetization energy as shown in Fig. 1.

3.3. Solidification process

Bi-5mass%Sn alloy, which is an eutectic composition, was used as a specimen. Fig. 5 shows the schematic view of an experimental apparatus. The specimen was heated up at the rate of 300 °C/h, kept for 30 min at 300 °C in argon atmosphere, cooled down to 255 °C at the rate of 180 °C/h, stirred at 255 °C for 3 min and finally cooled down to
the room temperature in a furnace. The specimen was cut in the direction perpendicular to that of the magnetic field and polished to examine the crystal orientation by use of XRD.

The X-ray diffraction patterns of Bi–Sn alloy are shown in Fig. 6. Only the peak of (00n) appeared in the case of 0 T, but those of a, b-plane (hk0) and (012) increased in the case of 12 T. The facial angle of bismuth crystal evaluated Eq. (3) is shown in Fig. 7. In the case of 0 T, the bismuth crystal tilts only 15° from the c-plane and in the case of 12 T, the crystal inclines to 56°. This result agrees with the theoretical prediction shown in Fig. 1.

3.4. Baking for carbon fibers

Carbon fibers as reinforcements in composite materials had mainly been developed in 1970s from strong requirements of both performance and safety aspects in the aerospace industry [18] and have been used from 1980s in a wide variety of industries such as construction, sports, medicine and so on. Now they are considered to be one of the indispensable materials supporting crucial industries in future.

Though the tensile strength and elastic modulus of PAN (Polyacrylonitrile)-based carbon fibers produced from polyacrylonitrile as a precursor can be increased to comparatively high values by stretching them in a heat treatment process, they are still confined within several percent of their theoretically expected values. This large discrepancy from theoretical values attributes to the lack of a low-dimensional regular structure in a graphite crystal plane [19].

The relation between the tensile strength and the diameter of graphitized fibers produced in a high magnetic field of 12 T is shown in Fig. 8. The increase of the tensile strength to more than 30% has been achieved by imposing a magnetic field, particularly in a direction parallel to the fiber axis rather than perpendicular to it. However, no clear difference in the degree of crystal orientation in an X-ray diffraction analysis was detected between the samples treated with and without the magnetic field. On the basis of theoretical and experimental results, the reason why the tensile strength of carbon fibers was increased by the magnetic field has been explained as the increase of a low-dimensional regular structure in a graphite crystal plane by use of an intermolecular cross-linking reaction model under a magnetic field [20].

3.5. Slip casting of hydroxyapatite

In the fields of medicine and dentistry, various biomaterials such as giant molecules, metals and ceramics have been used these days. The biomaterials must have chemical durability and high chemical safety even if components of the biomaterials are eroded. Moreover, an adequate physical strength is also required and an organism safety that is not required in other engineering fields is indispensable. A hydroxyapatite (HAp) is a main component in bones and teeth of vertebrates and has an excellent biocompatibility. Bioactive phenomena are different on a, b-plane or c-plane of HAp crystal. Thus, the crystal orientation of HAp has strongly been desired in the biomaterial field.

The slurry of HAp with solid fraction of 40 vol% was poured into a crucible and a slip casting that is widely utilized as one of ceramics shaping methods, was carried out under the high magnetic field of 12 or 10 T. The direction of the magnetic field was in parallel to the direction of the slip casting, i.e. gravitational
direction. The dried HAp was sintered at 1423 K for 2 h in air under no magnetic field. The sintered body was cut in horizontal and vertical cross sections to the imposed magnetic field. X-ray diffraction patterns are shown in Fig. 9. The effect of the magnetic field is remarkable. With the vertical magnetic field, the diffraction intensity of c-plane is higher in the plane parallel to the magnetic field, and the diffraction intensities of a, b-plane increase in the plane perpendicular to the magnetic field. It is noticed that a, b-plane orientation appears in the cross section perpendicular to the magnetic field direction, and c-plane orientation appears in the cross section parallel to the magnetic field direction. On the basis of these results, it is found that HAp aligns in a, b-axis to the magnetic field direction, and the slip casting method under a high magnetic field produces the highly crystal orientated HAp block.

3.6. Precipitation of hydroxyapatite

The hydroxyapatite itself has low mechanical strength for usage as biomaterials. For a joint part, where a large mechanical load is imposed, a composite material made of a titanium plate coated with HAp has been used. That is, the coated HAp ensures an organism safety, and the titanium plate provides mechanical strength.

A magnetic field has been introduced into a heat substrate method proposed by Okido et al. [21, 22]. The experimental apparatus of the method is shown in Fig. 10. A titanium foil was submerged in an aqueous solution with 0.3 mM Ca(H2PO4)2 and 0.7 mM CaCl2 and heated by passing electric current through the titanium foil to precipitate HAp on the foil. The plane of the titanium foil was set in perpendicular or parallel to the magnetic field direction.

Fig. 11 shows in the morphology of HAp precipitated on the surface of the titanium foil, which was observed by SEM.
a scanning electron microscope. When the titanium foil was set in parallel to a magnetic field direction, hexagonal pillars are observed. This fact indicates that c-plane is parallel to the surface of the titanium foil. On the other hand, when the titanium foil was set in perpendicular to a magnetic field direction, the titanium foil was coated by thin hexagonal flakes with a, b-plane orientation. This experimental result indicates that a, b-axis in HAp aligns in a magnetic field direction.

4. Conclusion

From the view point of learning from the nature, the controlling of crystal orientation has been taken up as one of researches for mimicking structures which the nature and living bodies are forming. The experimental works on the crystal orientation using a high magnetic field, on vapor-deposition, electro-deposition and solidification for non-magnetic materials of Zinc and Bismuth, baking for carbon fibers, slip casting and precipitation for hydroxyapatite, have been reviewed and discussed from the theoretical view point of magnetization energy. In all of the materials processing except the baking for carbon fibers, the effect of a magnetic field on the crystal orientation has been detected as given in the theoretical prediction. In the baking process, the reason why the tensile strength of carbon fibers was intensified by imposition of a magnetic field has been discussed from the intermolecular cross-linking theory. From the experimental results and theoretical consideration, it is noticed that the crystal orientation of non-magnetic materials is available in the various processing by use of a high magnetic field.

This work was supported in part by the 21st Century COE Program ‘Nature-Guided Materials Processing’ of the Ministry of Education, Culture, Sports, Science and Technology

References

[1] N. Sasaki, Y. Sudoh, Calcif Tissue Int. 60 (1997) 361–367.
[2] N. Waki, K. Sassa, S. Asai, Tetsu-to-Hagane 86 (2000) 363–369.
[3] E. Beaugnon, R. Tournier, Nature 349 (1991) 470.
[4] F. Gaucherand, E. Beaugnon, Phys. B 294–295 (2001) 96–101.
[5] H. Morikawa, K. Saasa, S. Asai, Mater. Trans., JIM 39 (1998) 814–818.
[6] H. Yasuda, K. Tokieda, I. Ohnaka, Mater. Trans., JIM 41 (2000) 1005–1021.
[7] B.A. Legrand, D. Chateignier, R. Perrier de la Bathie, R. Tournier, J. Magn. Magn. Mater. 173 (1997) 20–28.
[8] J.O. Noudem, J. Beille, D. Bourgault, D. Chateignier, R. Tournier, Phys. C 264 (1996) 325–330.
[9] T. Taniguchi, K. Sassa, S. Asai, Mater. Trans., JIM 41 (2000) 981–984.
[10] S. Mitani, H.L. Bai, Z.J. Wang, H. Fujimori, M. Motokawa, The 3rd International Symposium on Electromagnetic Processing of Materials, Japan, ISIJ, 2000, pp. 630–634.
[11] M. Tahashi, K. Sassa, I. Hirabayashi, S. Asai, Mater. Trans., JIM 41 (2000) 985–990.
[12] S. Awaji, K. Watanabe, Y. Ma, M. Motokawa, Phys. B 294–295 (2001) 482–485.
[13] M. Ito, K. Sassa, M. Doyama, S. Yamada, S. Asai, TANSO 191 (2000) 37–41.
[14] L. Wehrli, Phys. Kondens. Mater. 8 (1968) 94–95.
[15] K.-H. Hellwege, A.M. Hellwege, Landolt-Börnstein: Eigenschaften der Materie in ihren Aggregatzuständen, 9teil, Magnetic Properties I, Springer, Berlin, 1962, pp. 1–12.
[16] K.H. Hellwege, A.M. Hellwege, Landolt-Börnstein: Eigenschaften der Materie in ihren Aggregatzuständen, 10teil, Magnetic Properties II, Springer, Berlin, 1967, pp. 2–65.
[17] M. Tahashi, M. Ishihara, K. Sassa, S. Asai, Mater. Trans., JIM 44 (2003) 285–289.
[18] A.R. Bunsell, Fibre Reinforcements for Composite Materials, Elsevier, Amsterdam, 1988, pp. 74–93.
[19] D.J. Johnson, J. Phys. D: Appl. Phys. 20 (1897) 286–291.
[20] M.G. Sung, K. Sassa, H. Ogawa, Y. Tanimoto, S. Asai, Mater. Trans. JIM 43 (2002) 2087–2091.
[21] K. Kuroda, R. Ichino, M. Okido, O. Takai, J. Biomed. Res. 59 (2) (2002) 390–397.
[22] M. Okido, R. Ichino, K. Kuroda, R. Ohsawa, O. Takai, Mater. Res. Soc. Symp. Proc. 599 (2000) 153–157.