

The Magnetic Orientation of 2-Dimensional Silver Dendrites

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A liquid/solid redox reaction between silver ion and zinc metal was investigated under a *vertical* and *inhomogeneous* magnetic field. 2-Dimensional silver dendrites produced via the reaction were drastically affected by the magnetic field. Oriented and tilted dendrites were observed under the magnetic field. A similar phenomenon was observed at a silver ion–copper metal system under a *horizontal* and *homogeneous* magnetic field. The mechanism of the phenomenon is discussed in detail.

Control of various chemical reaction paths, yield, process, and so on, is a very useful and important technique. A magnetic field has been proposed as one of the promising control methods.[1,2] High magnetic field condition provides not only the detailed research of spin dynamics of reaction intermediates but also the development of the other or new magnetic field effects in various reactions. Our group has already observed interesting results, e.g. the magnetic orientation of diamagnetic crystals,[3–7] drastic changes of metal dendrites due to magnetic force,[8–12] and so on, by using a superconducting magnet for some years. It is found that unequilibrium states on reaction paths are very sensitive to the perturbations due to the magnetic field. These reports show that the imposition of a magnetic field is a very useful technique to control reactions.

Chemical reactions at the interface between a solid state and a liquid state are popular ones. The metal deposition at an interface by redox reactions shows a tree-like shape, which is called a “metal dendrite”. The growth rate and shape of the metal dendrite depend on the reaction conditions such as ion concentration and temperature. Especially, the dendrite patterns are sensitive to the diffusion and the convection of a solution. That is, the dendrite pattern is a good probe for the observation of the convection.

In previous papers, we have reported the magnetic field effects on the reaction between silver ion and copper metal in the plane *parallel* to the magnetic field direction under a *vertical* and *inhomogeneous* magnetic field, and we have observed the growth of silver metal two dimensional (2D) dendrites.[13] The shape of the dendrites depended on the magnetic condition remarkably. The distribution and yield of the dendrites was affected by magnetic force on copper ions under a gradient magnetic field.

Mogi et al. reported 2D patterns of silver dendrites in the plane *perpendicular* to a magnetic field direction under a *vertical* and *homogeneous* magnetic field.[14] The significant change induced by the magnetic field was interpreted in terms of the magnetohydrodynamics (MHD) mechanism, where Lorentz forces affect motions of ions in a magnetic field. However, no orientation of dendrites was observed.

In this paper we report some magnetic field effects on the reaction between silver ion and zinc metal. The growth of silver metal 2D-dendrites was observed in the plane *parallel* to the magnetic field direction under the *vertical* and *inhomogeneous* magnetic field. This system contains only diamagnetic species, therefore, magnetic forces will be ineffective. Furthermore, the influence of the Lorentz force will be expected to decrease in this 2D reaction system. But, it is demonstrated that the magnetic field significantly affects the morphology of silver dendrites. Moreover, we investigated one other system, a silver ion and copper metal system, in a *horizontal* and *homogeneous* magnetic field for comparison.

Experimental

Two types of superconducting magnets were used in our experiment. One was provided with a vertical bore and the other was provided with a horizontal bore. The former was JMTD-LH15T40 produced by Japan Superconductor Technology, which had a room temperature vertical bore tube of 40 mm in diameter. Its maximum field and gradient field were 15 T and 1500 T^2/m, respectively. The details are described in previous papers.[12,13,15] The latter was a Spectromag-1000 produced by Oxford Instrument, which had a room temperature horizontal bore tube of 50 mm in diameter. Its maximum field and gradient field were 8 T and ± 410 T^2/m, respectively. Figure 1 shows the distribution of the magnetic field, where z is the distance from the center of the bore tube along the bore axis.

Silver nitrate (Nacalai Tesque GR grade) was used as received. Distilled water was used. A zinc metal sheet (Nilaco, thickness: 0.025–1.0 mm, 99.9%+) and a copper metal sheet (Kyuho Kinzoku, thickness: 0.1 mm, $\geq$99.9%) were polished just before the experiment. A silver nitrate solution (0.05 mol/L) was poured into a cylindrical vessel. A thin metal plate (5 mm $\times$ 19 mm) was clipped with two acrylic plates (53 mm $\times$ 20 mm) and immersed in a silver nitrate aqueous solution (30 mL) in a cylindrical glass vessel (30 ϕ $\times$ 54 mm). The vessel was then placed in a bore tube of the magnet. The redox reaction occurs at only the section of a metal sheet. Therefore, the dendrites grew two-dimensionally from the upper and lower surfaces of the sheet; the dendrites grew parallel to the magnetic field. The dendrites grew at the narrow space between the acryl plates. Though the dendrites touched

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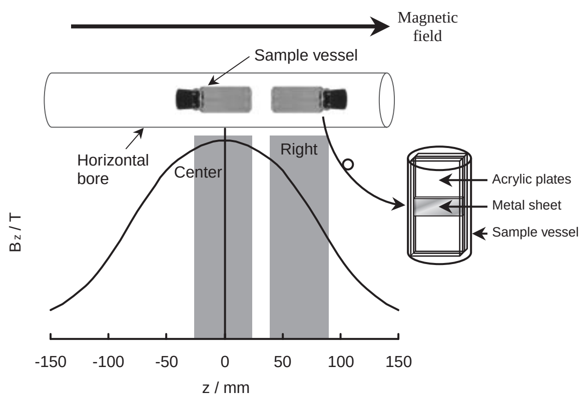

Fig. 1. The distribution of the horizontal magnetic field $B(z)$. z is the distance from the center of the magnetic field (8 T) along the magnetic field axis. The gray parts show the area of the magnetic fields where the sample vessels were placed. These positions shall be called "center" and "right" from the center. The upper horizontal bore's picture corresponds to the plot of the distribution of the magnetic field.

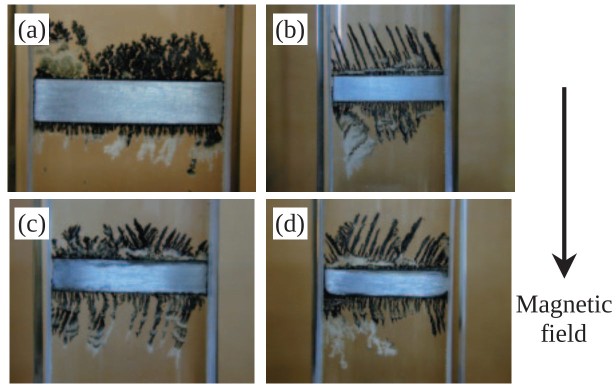

Fig. 2. The photographs of the silver dendrites which were produced from Zn–Ag^+ system after 30 min reaction in the vertical bore. The size of the zinc metal sheet is 5 mm (height) × 19 mm (width) × 0.4 mm (thickness). (a) the outside of the bore tube (control < 0.0005 T), (b) the bottom position (9.8 T, +1070 T^2/m), (c) the middle position (15.0 T, +50 T^2/m), (d) the top position (5.6 T, −940 T^2/m).

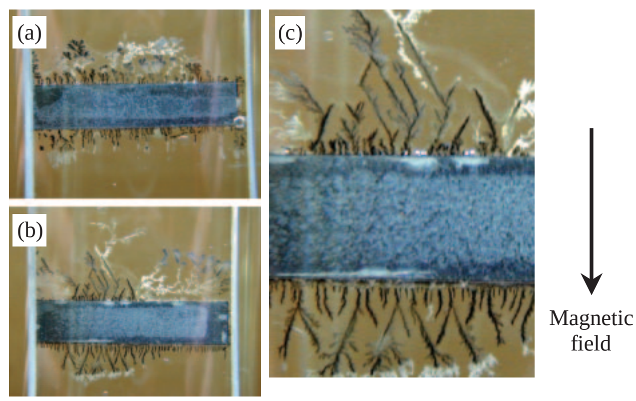

Fig. 3. The photographs of the silver dendrites which were produced from Zn–Ag^+ system after 60 min reaction in the vertical bore. The size of the zinc metal sheet is 5 mm (height) × 19 mm (width) × 0.025 mm (thickness). (a) the outside of the bore tube (control < 0.0005 T), (b) the top position (5.6 T, −940 T^2/m), (c) the enlargement of (b) (×3).

the acryl plates in places, they stood without supports. The thickness of the metal sheet determined that of the reaction solution, or reaction volume. The thickness of the reaction solution is equal to that of the metal sheet in our experiment. If the thickness of the reaction solution was larger than that of the metal sheet, the reaction and convection condition would approach three-dimensional conditions, and the dendrite growth condition would become complicated. The vessel was capped with a rubber stopper. Three sample vessels were placed at the positions in the vertical bore tube, of which the magnetic conditions are 5.6 T and −940 T^2/m, 15.0 T and +50 T^2/m, 9.8 T and +1070 T^2/m, as shown in Fig. 1 of the previous papers,[12,13] and one was placed at the outside of the tube (leak field ca. 0.5 mT). Hereafter, we shall call these positions: top, middle, bottom, and outside. On the other hand, two vessels were placed at the positions in the *horizontal* bore tube, of which magnetic conditions are 8.0 T and 0 T^2/m, 6.0 T and −410 T^2/m, as shown in Fig. 1, and one was placed at the outside of the tube (leak field ca. 0.5 mT). We shall call these positions: center, right, and outside. All reactions were carried out at room temperature. The vessels were taken out from the bore tube after 30 or 60 min reaction, and the patterns of the dendrites were recorded with a digital camera.

X-ray diffraction (XRD) patterns of the dendrites were measured using RIGAKU RINT 2200V/PC-SV. SEM images were observed with HITACHI S-4100 and JEOL JSM-5510.

Results

The liquid/solid redox reactions investigated are given by the following equations:

$$2Ag^+ + Zn \rightarrow 2Ag\downarrow + Zn^{2+}, \quad (1)$$

$$2Ag^+ + Cu \rightarrow 2Ag\downarrow + Cu^{2+}. \quad (2)$$

The reactions occur by the ionization tendency, and silver metals deposit at the top and bottom sides of each metal sheet as dendrites.

Figure 2 shows the result of the silver dendrites, which were produced from zinc metal (thickness: 0.4 mm)–silver ion system with and without the vertical magnetic field. Though the reaction system contains only diamagnetic species, a drastic magnetic effect was observed. The dendrite in the upside grew more than that in the downside at the outside. This pattern was similar to that of a copper metal–silver ion system reported previously.[13] In contrast, the dendrites under the magnetic field showed unbranched shapes, and were oriented toward about ±30 degrees for the magnetic field axis.

It is well known that the shape of dendrites is affected by convection of reaction solutions. Thus, the volume of a reaction solution is an important factor for the growth of dendrites. The thickness of a zinc sheet corresponds to the volume in our experiment, because the reaction volume is proportionate to the thickness of the zinc metal sheet. Figure 3 shows the results of the reaction at 0.025 mm thickness. The dendrites grew equally from both sides at the outside (Fig. 3a). The dendrites show the orientation of about 30 degrees at both sides under the magnetic field (Figs. 3b and c).

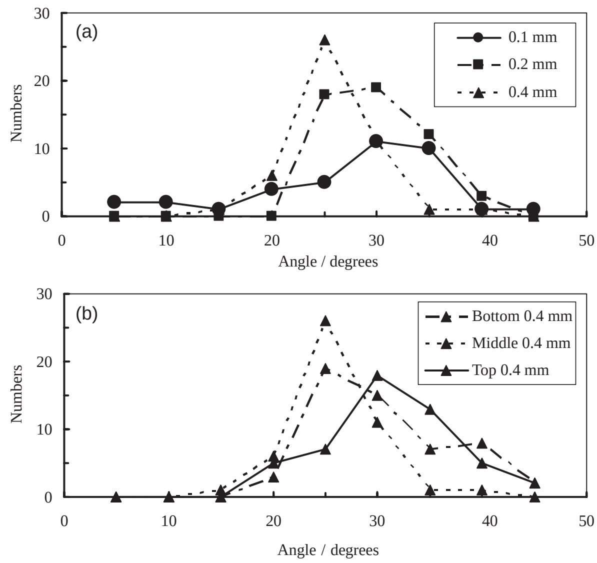

Fig. 4. The angle distribution of the dendrites (a) the dependence on the thickness of the solution, the magnetic field condition: 15 T, +50 T^2/m, (b) the dependence on the position (the magnetic field intensity).

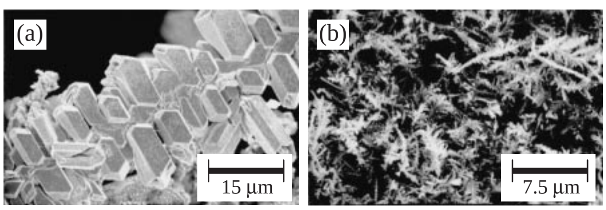

Fig. 5. The SEM images of the silver dendrites produced from Zn–Ag^+ system after 30 min reaction. The thickness of the zinc metal sheet is 0.4 mm. (a) the outside of the bore tube (control), (b) the middle position.

To consider the orientation mechanism, we investigated the angle distribution of the dendrites in detail. Figure 4 shows the dependence on the thickness of the solution (Fig. 4a), and that on the magnetic field intensity (Fig. 4b). Zero degrees means that the dendrite is in parallel with the magnetic field direction. As the thickness of the solution increased, the peak angle of the dendrites gradually shifted to the small angle, and the angle distribution became sharp. Moreover, as the magnetic field intensity increased, the peak angle gradually shifted to the smaller angles, and the angle distribution became sharp, too.

We observed SEM and XRD in order to check the differences of the microstructure between the dendrites with the magnetic field and those without the magnetic field. The SEM images of the silver dendrites, which grew at 0.4 mm thickness, are shown in Fig. 5. The dendrites of the outside showed large crystal faces. The size of these faces was a few micrometers. By contrast, the dendrites of the middle position were many micrometers in size, and crystal faces were not observed clearly. The result indicates that the dendrites grow in the magnetic field much faster than at the outside.

Figure 6 shows the XRD pattern of the silver dendrites with and without the magnetic field. Unexpectedly, the two patterns were almost identical. The pattern of diffraction angles (2θ)

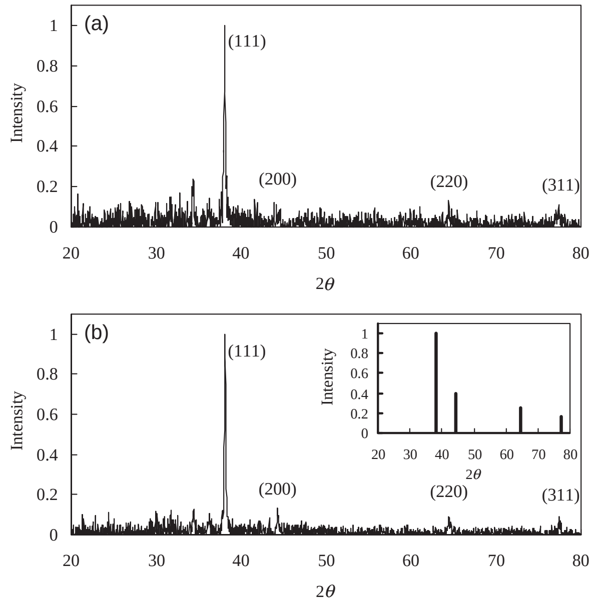

Fig. 6. The X-ray diffraction patterns of the silver dendrites produced from Zn–Ag^+ system after 30 min reaction. The thickness of the zinc metal sheet is 0.4 mm. (a) the outside of the bore tube (control), (b) the middle position. The numbers inserted represent indices of plane of silver crystal. The inset in (b) is an X-ray diffraction pattern of silver metal powder.

was the same as that of pure silver metal, but the ratio of the peak intensities was different from that of a powder pattern (the inset in Fig. 6b). A nearly single peak was observed. The peak was assigned to the face (111). That means the hexagonal faces appeared in Fig. 5a are (111) ones.

We observed a similar phenomenon in the other reaction system. Figure 7 shows the result of the silver dendrites, which were generated from copper metal–silver ion system with and without the *horizontal* magnetic field. We observed different results from those in the *vertical* field. Neglecting the force of gravity, the dendrites appeared almost equally at both sides in the outside (Fig. 7a). The distribution of the dendrites deviated from equality at the maximum gradient position (Fig. 7b). The result is almost the same as that in the *vertical* field.[13] At the center position, where no magnetic force works theoretically, the dendrites were oriented toward ca. 30 degrees (Fig. 7c).

Discussion

It is well known that the growth of dendrites is sensitive to perturbations. In Fig. 2a the upside of the dendrites at the outside becomes dense due to a gravity force. That is similar to the result of copper metal–silver ion system.[13] Sawada et al. reported that the diffusion field near dendrites was sensitive to a gravity force, and that therefore the distribution of the silver dendrites deviates from equality due to a gravity force.[16,17]

But the dendrites leaned toward about 30 degrees from the magnetic field axis in zinc metal–silver ion system under the magnetic field (Figs. 2b, c, and d). All species are diamagnetic in the zinc metal–silver ion reaction system. Hence, the magnetic force on the ions will be ineffective.

Moreover, even though the reaction region is the thin layer

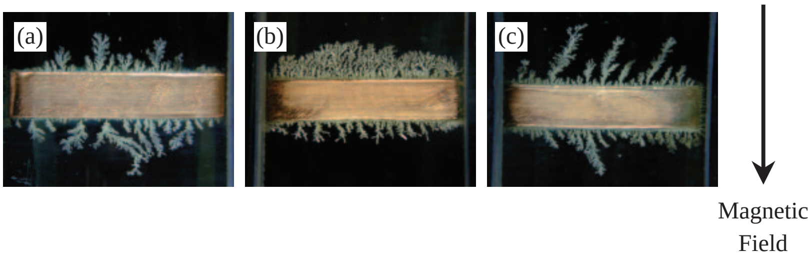

Fig. 7. The photographs of the silver dendrites which were produced from $Cu–Ag^+$ system after 60 min reaction in the horizontal bore. The size of the copper metal sheet is 5 mm (height) $\times$ 19 mm (width) $\times$ 0.1 mm (thickness). (a) the outside of the bore tube (control < 0.0005 T), (b) the right position (6.0 T, $+410$ T^2/m), (c) the center position (8.0 T, 0 T^2/m).

of 0.025 mm, the dendrites show the orientation of about 30 degrees (Figs. 3b and c) at both sides. According to the dendrites at the outside, the gravity force can practically be neglected, because of the equal growth at both sides. The convection caused by Lorentz force will hardly be effective in such a thin solution. These results imply that this phenomenon is due to a kind of the character of silver crystal itself.

The distributions of the dendrites depend on the thickness and the magnetic field intensity clearly, though the degree of the change is small relatively. The tendency of the shift reflects the occurrence of the convection in the thin solution. As the thickness of the solution, that is, the volume increases, the convection occurs easily. According to the dependence of the magnetic field, as the magnetic field intensity increases, the convection due to the magnetic field becomes stronger. We will discuss the problem of the convection in our next paper.

The SEM pictures (Fig. 5) indicate fast growth under the magnetic field. A similar result is reported for the copper metal–silver ion system, which was posed by a magnetic force.[13] This system, however, involves only diamagnetic species. The fast convection in this system will be caused by Lorentz forces at local areas.

The XRD results (Fig. 6) indicate that the hexagonal faces in Fig. 5a are (111) ones. Moreover, the dendrites that grew under the magnetic field have almost the same face distribution, though many small dendrites look scattered. This indicates that the dendrites grow anisotropically regardless of the magnetic field.

For copper metal–silver ion system in three or two-dimensional condition under *vertical* magnetic field, the shape and distribution of dendrites intensively changed due to magnetic forces on copper ions mainly.[11–13] Because only copper(II) ions are paramagnetic species in this reaction system, convection is effectively caused by the magnetic force. The magnetic susceptibility of copper(II) ions is larger than those of the others by two orders. So, the magnetic force on the copper(II) ions is more effective. However, because the magnetic force depends on the magnetic gradient, the magnetic force is ineffective under *homogeneous* magnetic field condition. Moreover, the gravity force, which affects the shape of the dendrites, is neglected under *horizontal* magnetic field condition. Therefore, the dendrites leaned toward about 30 degrees due to the magnetic field at both sides.[13]

Generally the orientation of crystals under magnetic fields is caused by their magnetic anisotropic characters. The anisotropic characters arise from three kinds of mechanisms, as follows: 1) a component molecule, complex, or cluster, 2) a crystal (magnetocrystalline anisotropy),[18–20] and 3) an anisotropic shape (shape magnetic anisotropy).[2,18] Many observations have been reported according to the above mechanisms. In our case, a silver crystal is reported as a face-centered cubic lattice (fcc), which is an isotropic crystal. Therefore, the shape magnetic anisotropy of the dendrites is the most possible mechanism. Usually, when a magnetic field is applied to a material, a certain demagnetizing field emerges in the material. The direction of the demagnetizing field depends on the shape of the material.[2,18] In our case, the shape of the silver dendrites appears anisotropic according to the SEM pictures (Fig. 5). The demagnetizing field in the silver dendrites will determine the direction of the dendrites. It is well known that a non-equilibrium state such as the growth of the dendrites is very sensitive to the perturbations due to the magnetic field. Although the anisotropic growth will contribute the orientation, the reason why the dendrites lean toward a certain angle is not clear yet. The angle will be determined by the angle of the silver crystal. Furthermore, fragments of dendrites, which are prepared at 0 T and 8 T, are floated in a magnetic field. The fragment prepared at 8 T is oriented at the angle of about 45 degrees from the magnetic field direction, whereas that at 0 T is oriented parallel to the field direction. This result indicates that the orientation is caused by the shape magnetic anisotropy of silver microcrystals.

Theoretical estimation of shape magnetic anisotropy for diamagnetic materials is in progress and will be reported in the near future.

A MHD mechanism due to a Lorentz force affects the growth of the dendrites. The fast convection will occur by a Lorentz force according to the SEM image (Fig. 5b). Though the dendrites grew in two-dimensions parallel to the magnetic field, micro-MHD mechanism[21] could work on the reaction. Intuitively since a Lorentz force depends on a magnetic field intensity, the angle of the dendrites will vary with the magnetic field intensity. That will reflect the changes in the angle distribution (Fig. 4).

Conclusion

The magnetic field affects the shape and the distribution of the silver dendrite remarkably, even though the system contains only diamagnetic species. The magnetic field will cause the orientation of the dendrites. The phenomenon will be due to the shape magnetic anisotropy of the dendrites, but the detailed mechanism is unknown. These results, however, suggest that the magnetic field still has much potential for the control of general redox reactions.

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References

1 "Dynamic Spin Chemistry," ed by S. Nagakura, H. Hayashi, and T. Azumi, Kodansha, Tokyo (1998).

2 "Jikikagaku," ed by K. Kitazawa, S. Ozeki, Y. Tanimoto, and M. Yamaguchi, IPC, Tokyo (2002).

3 A. Katsuki, R. Tokunaga, S. Watanabe, and Y. Tanimoto, *Chem. Lett.*, **1996**, 607.

4 M. Fujiwara, T. Chidiwa, R. Tokunaga, and Y. Tanimoto, *J. Phys. Chem. B*, **102**, 3417 (1998).

5 M. Fujiwara, R. Tokunaga, and Y. Tanimoto, *J. Phys. Chem. B*, **102**, 5996 (1998).

6 M. Fujiwara, M. Fukui, and Y. Tanimoto, *J. Phys. Chem. B*, **103**, 2627 (1999).

7 Y. Tanimoto, R. Yamaguchi, Y. Kanazawa, and M. Fujiwara, *Bull. Chem. Soc. Jpn.*, **75**, 1133 (2002).

8 A. Katsuki, S. Watanabe, R. Tokunaga, and Y. Tanimoto, *Chem. Lett.*, **1996**, 219.

9 Y. Tanimoto, A. Katsuki, H. Yano, and S. Watanabe, *J. Phys. Chem. A*, **101**, 7359 (1997).

10 W. Duan, M. Fujiwara, and Y. Tanimoto, *Bull. Chem. Soc. Jpn.*, **73**, 2461 (2000).

11 A. Katsuki, I. Uechi, M. Fujiwara, and Y. Tanimoto, *Chem. Lett.*, **2002**, 1186.

12 A. Katsuki, I. Uechi, and Y. Tanimoto, *Bull. Chem. Soc. Jpn.*, **77**, 275 (2004).

13 A. Katsuki, I. Uechi, and Y. Tanimoto, submitted.

14 I. Mogi, S. Okubo, and Y. Nakagawa, *J. Phys. Soc. Jpn.*, **60**, 3200 (1991).

15 R. Hirose, K. Saito, Y. Watanabe, and Y. Tanimoto, Proceeding of the 6th Meeting of Symposium on New Magneto-Science 2002, November 6–8, 2002, Tsukuba, Japan, Abstr. No. 198.

16 T. Sawada, K. Takemura, K. Shigematsu, S. Yoda, and K. Kawasaki, *J. Cryst. Growth*, **191**, 225 (1998).

17 T. Sawada, K. Takemura, K. Shigematsu, S. Yoda, and K. Kawasaki, *Phys. Rev. E*, **51**, R3834 (1995).

18 S. Chikazumi, "Kyoujiseitai no butsuri," Shokabo, Tokyo (1984).

19 T. Sugiyama, M. Tahashi, K. Sassa, and S. Asai, *ISIJ Int.*, **43**, 855 (2003).

20 J. Torbet, J.-M. Freyssinet, and G. Hudry-Clergeon, *Nature*, **289**, 91 (1981).

21 R. Aogaki and A. Sugiyama, Proceeding of the 6th Meeting of Symposium on New Magneto-Science 2002, November 6–8, 2002, Tsukuba, Japan, Abstr. No. 136.