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Magnetic field induced helical structure in freestanding metal silicate tubes

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Helical structure on freestanding metal silicate membrane tubes induced by a magnetic field is reported. The phenomenon is observed for iron silicate tubes and cobalt silicate tubes grown under a horizontal field of 2.2 T and a field gradient of 20.5 T/m at the room temperature in contrast to nonregular structure observed at the zero field. Direction control of helicity is achieved by changing the field gradient direction with respect to the field direction. The results are explained in terms of the magnetohydrodynamics effect on the flow of anion discharged from a metal salt solution at the growing end of the silicate tube. © 2005 American Institute of Physics. [DOI: 10.1063/1.1861394]

I. INTRODUCTION

Magnetic field effects on growth morphology have attracted both scientific and industrial interest. Application of magnetic fields to conventional material processing procedures gives rise to unexpected effects on the material morphology or texture in some cases, including magnetic alignment of liquid crystals,¹ polymers,² carbon nanotubes in composite materials,³ control of material texture,⁴ electrochemical deposits,⁵ crystal growth of proteins,⁶ and so on. In the previous paper, we have reported several magnetic field effects on the growth of metal silicate tubes from paramagnetic metal salts.⁷ We have found that the silicate tubes grow in the direction of the magnetic field center and the growth is promoted by magnetic field gradient. These results can be understood in terms of the exertion of magnetic force on paramagnetic salt solutions inside the silicate tubes. In addition to this result, we have found that the tubes have twisted or helical structure like ropes. This phenomenon is very interesting from the viewpoint of magnetic control of helicity. The aim of the current work is to clarify the mechanisms causing this magnetic field effect. Recently, Uechi *et al.* reported that zinc silicate membrane tubes grow helically along vessel walls.⁸ The difference between their observation and ours is that they observed the helicity in the growth direction of the membrane tubes while we observed it in a twist on the tube itself. They claimed that the helical structure should be induced by magnetic field-induced convection along the walls. Our findings are inexplicable by this model as the helically twisted tubes are freestanding. It will be clarified in this article that our model can be applied to the helical growth along the vessel wall as well as the helical twist on freestanding tubes.

The growth of metal silicate tubes from metal salts immersed in water solution of sodium silicate (water glass) is

well known as the Chemical Garden. The following chemical reaction (1) occurs on the surface of powders of the metal salts in the growth of metal silicate tubes.



The metal silicate forms a semipermeable membrane around the salt powder and water permeates into the inside through the membrane, which increases the internal pressure. When the membrane is broken by the internal pressure, a new membrane is formed at the touching point of the internal metal salt solution and the external water glass. This process is repeated and tubes of the metal silicate grow. By the application of a magnetic field gradient, the paramagnetic metal salt solutions are dragged toward the higher field direction with a force depending on their magnetic susceptibility. Consequently, the growth direction of the metal silicate tubes is inclined to the direction of the magnetic force.

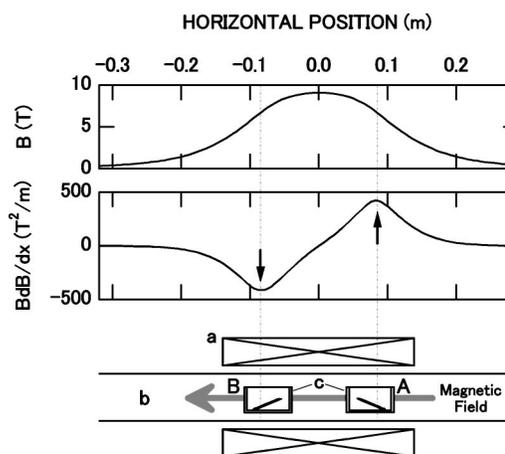


FIG. 1. Schematic diagram of the experimental setup for the growth of metal silicate tubes under magnetic fields. (a) Magnet coil, (b) magnet bore, and (c) glass cells. The positions A and B (see text) are exhibited. The figure is not to scale. Profile of a magnetic field generated by the magnet is also shown. The arrows indicate the points where the magnetic force field is maximal.

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In the formation of the helical structure on the inclined tubes, magnetohydrodynamics (MHD) should play an important role on the motion of ions involved in the reaction. We will examine what ion is most responsible for the formation of helical structure and describe its detailed process.

II. EXPERIMENT

Water glass was prepared by diluting sodium silicate solution (Nacalai Tesque Inc., Kyoto, Japan) to 10 wt % with ultra-purified water. Metal salts of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99.9%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (>99%) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.9%) were employed in this study. All of them were used as received from Kojundo Chemical Laboratory Co., Ltd. (Saitama, Japan).

Experiments with magnetic field gradients were conducted using a 17 T superconducting magnet (Oxford Instruments Inc., Oxon, UK) with a horizontal room temperature bore of 40 mm in diameter. Magnetic force F derived from magnetic field B and field gradient dB/dx is as described in Eq. (2)

$$F = (1/\mu)\chi_v B(dB/dx), \quad (2)$$

where μ and χ_v are absolute permeability and volume susceptibility, respectively. The multiplication of magnetic field and field gradient is proportional to magnetic force. We name the quantity as “magnetic force field” hereafter. The magnetic force field became maximal at two positions 85 mm away from the field center. We label the position where the direction of the magnetic field and that of the magnetic force field are the same as “*position A*” and the other as “*position B*.” The growth of metal silicate tubes was performed in glass cells with an inner size of 47 mm in length, 8 mm in width, and 24 mm in height, placed at either *position A* or *position B* as shown in Fig. 1 together with the field profile. When the center field of 3 T was generated, the field and the magnetic force field at these positions were 2.2 T and $46 \text{ T}^2/\text{m}$, respectively. The glass cells were placed at the positions immediately after the metal salt powders were immersed in the water glass and removed about 1 h later, when the growth of the tube had ceased.

III. RESULTS AND DISCUSSION

At the zero field, the tubes from all of the metal salts were observed to grow zigzag upward without any regular structure. At 2.2 T and $46 \text{ T}^2/\text{m}$, inclined and aligned growth of silicate tubes toward the field center was observed in the cases of FeCl_2 and CoCl_2 . The directions of the growth in the glass cells placed at *positions A* and *B* were opposite each other as shown in Fig. 2, which is corresponding to the direction of the magnetic force field at each position. In the case of CuSO_4 , the inclination angle of silicate tubes toward the field center was much less than those in FeCl_2 and CoCl_2 . This difference clearly reflects the fact that the Bohr magneton of Cu^{2+} ion is twice to three times smaller than that of Co^{2+} or Fe^{2+} ion. However, it was found that the tubes from CuSO_4 were bent clockwise with respect to the field direction as shown in Fig. 3, which was not observed at the zero field.

In addition to the inclined growth of the tubes from FeCl_2 and CoCl_2 , it was found that the tubes were regularly

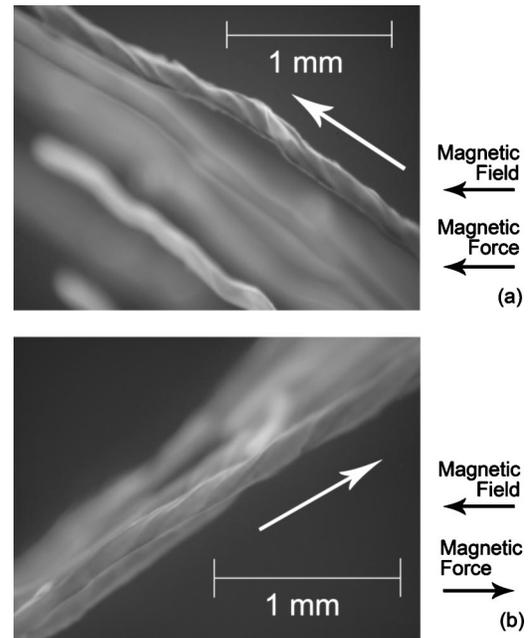


FIG. 2. Typical appearances of silicate tubes growing from CoCl_2 powders at 2.2 T and $46 \text{ T}^2/\text{m}$. (a) The cell was placed at *position A*. (b) The cell was placed at *position B*. Growth directions are indicated with arrows in white.

twisted as one would notice in Fig. 2. The direction of the twist was recognized to be clockwise for the tubes grown at *position A* and counterclockwise at *position B*. Similar results were also obtained for FeCl_2 .

It is possible to understand the bent in copper silicate tubes and the twist of cobalt or iron silicate tubes in the same framework of MHD effect on the flow of anions discharged from the growing end of the silicate tube. While the flow of metal ions is interrupted due to the formation of metal silicate tube walls with surrounding silicate ions immediately after emitted from the growing ends, the flow of chloride ions or sulfate ions is not interrupted and discharged into the surrounding medium. In the case of CuSO_4 , the direction of the anion emission is almost perpendicular to the magnetic field. Therefore the flow of the anions is bent clockwise with respect to the field direction due to Lorentz force as illustrated in Fig. 4. In the case of FeCl_2 and CoCl_2 , anions that are not used for the formation of the silicate tubes should be

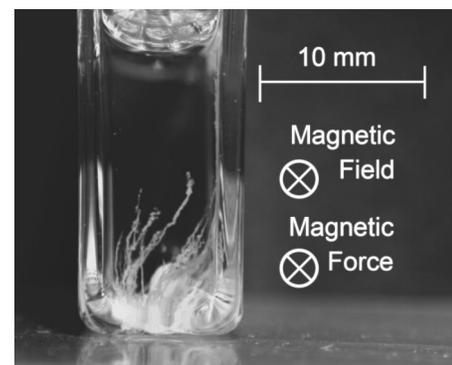


FIG. 3. Typical appearance of silicate tubes growing from CuSO_4 powders at 2.2 T and $46 \text{ T}^2/\text{m}$. The cell was placed at *position A*. Note that the view direction is different from that in Fig. 2.

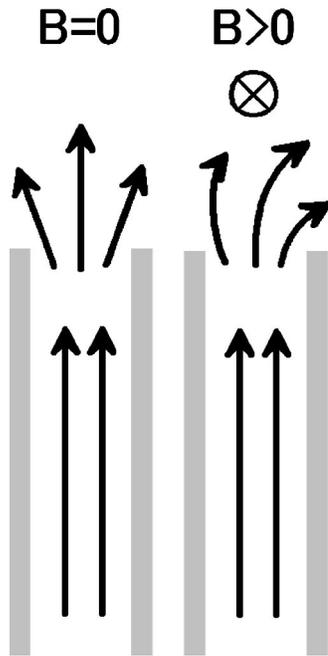


FIG. 4. Schematic side view of anion flow at the growing end of a silicate tube without (left) and with magnetic fields (right). Silicate tube walls are indicated with gray bars.

discharged outward. This flow of anions is perpendicular to the magnetic field and bent clockwise with respect to the field direction as described in Fig. 5. The Lorentz force exerted on the anion flow has been estimated as follows. Judging from the growth rate of the silicate tubes, we have assumed the flow rate of the anions to be of the order of 0.1 mm/s. Then the magnitude of the Lorentz force exerted on one mole of anions at 2.2 T would be calculated at 21 N. The anion flow bent due to this Lorentz force could control the form of the tube wall during the solidification. As the growth direction of the silicate tubes and the field direction is opposite at *position B*, it is reasonable to observe the counterclockwise twist for the tubes grown there.

Uechi *et al.* has proposed boundary-assisted MHD mechanism in order to explain the helical growth along a vessel wall or on a rod.⁸ They assumed Lorentz force exerted on the Brownian motion of ion around a wall to be unidirectional and to induce convection around the wall. This model is hard to accept as it implies that macroscopic motion could be induced without applying any energy, which contradicts

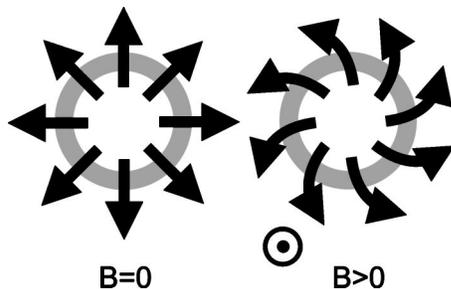


FIG. 5. Schematic top view of anion flow at the growing end of a silicate tube without (left) and with magnetic fields (right). Silicate tube walls are indicated with gray rings.

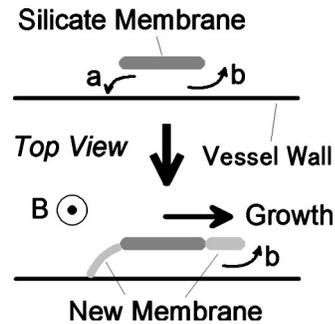


FIG. 6. Schematic diagram of silicate membrane growth on a wall under magnetic fields. The magnetic field bends anion flows clockwise with respect to the field direction. The anion flow *a* is scattered at the wall and the growing end on this side would be blocked. As a result, membrane growth on the side of the anion flow *b* is enhanced.

the first law of thermodynamics. In contrast, the phenomena that they observed can be explained consistently in the framework of our model as follows. Silicate membrane growth on a wall is schematically exhibited in Fig. 6. In this situation, the growing ends of metal silicate membranes are edges of the membrane. Anions emitted from the growing ends are bent due to Lorentz force. Viewing from the top, anion flows on one end is bent toward the water glass. This flow would keep the growing end open and enhance the growth of silicate membrane. Anion flows on the other end is bent toward the wall and scattered at it, which would suppress the membrane growth and lead to the blockage of the growing end. As a result, unidirectional growth is induced. The direction should be clockwise with respect to the magnetic field for a wall with negative curvature and counterclockwise for one with positive curvature, which agrees with the results observed by Uechi *et al.*

IV. CONCLUSION

In the growth of metal silicate tubes from FeCl_2 and CoCl_2 powders immersed in water glass under gradient magnetic fields, formation of helical structure is observed. The twist direction is clockwise or counterclockwise in the case that magnetic field direction is the same as or opposite to the growth direction, respectively. These phenomena can be explained in terms of the MHD effect on the flow of anions discharged from the metal salt solution at the growing ends of the silicate tubes. The bent flow of the anion could generate vortex around the growing ends and cause the helical structure.

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