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Formation of Helical Structure in Silicate under Gradient Magnetic Fields

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The magnetic field effect on the growth of silicate tubes from metallic salt powders immersed in a water solution of sodium silicate was studied for $MnSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, $CoCl_2$, $CuSO_4$, and $ZnCl_2$ up to 9 T using a superconducting magnet with a horizontal room temperature bore. In horizontal field gradients, the silicate tubes growing from paramagnetic metallic salts were aligned and inclined toward the field center. Simultaneously, they were found to have twisted or helical structures like ropes. In $CuSO_4$, two kinds of growth were recognized. One was freestanding growth, which was inclined toward the opposite direction of the field center, and the other was on-wall growth, which showed a slight inclination toward the field center. On-wall growth was also observed in $ZnCl_2$, but without any inclination toward the field center. This on-wall growth took place as a result of the upward growth of the silicate tubes being bent to the right when viewed in the field direction. These magnetic field effects can be attributed to the exertion of a magnetic force on the paramagnetic metallic salt solutions, and a Lorenz force acting on anions that have a component of motion perpendicular to the field direction.
Key words: magnetic field effect, silicate membrane tube, helical structure, magnetic field gradient, chemical garden

1. INTRODUCTION

Application of magnetic fields to material processing has become a more attractive subject than it previously has been because of a recent improvement in magnet technology. Magnetic force on paramagnetic or diamagnetic materials, which used to be regarded as non-magnetic materials, is no longer considered negligible under magnetic fields of several teslas. Indeed, the surface of water has been observed to be depressed by 39 mm at 10 T, the so-called 'Moses effect'[1]. In addition, many magnetic field effects have been intensively studied, including magnetic levitation[2], magnetic alignment of liquid crystals[3], polymers[4], carbon nanotubes in composite materials[5], control of material texture[6], crystal growth of proteins[7] and so on. These magnetic field effects are classified as the competition between the magnetic field and either gravitation or thermal agitation. In this study, we are introducing a newly classified competition of the magnetic field with hydrostatic pressure and osmotic pressure, observed in the growth of silicates from metallic salts in a water glass, a so-called 'Chemical Garden'. It should be noted that the hydrostatic pressure originates from gravity. However, the hydrostatic pressure is different from gravity in that the hydrostatic pressure is isotropic whereas gravity is one-directional.

In a Chemical Garden, the following chemical reaction (1) occurs on the surface of the powders of metallic salts (copper nitrate, for example) immersed in a water solution of sodium silicate.

$$Cu(NO_3)_2 + Na_2SiO_3 \rightarrow CuSiO_3 + 2NaNO_3 \quad (1)$$

The metallic 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 point of contact between the metallic salt solution and the water glass. This process is repeated, and tubes of the metallic silicate grow. The reason for the upward growth is thought to be the following. The membrane is under osmotic pressure from the inside and hydrostatic pressure from the outside. As the hydrostatic pressure is weakest at the top of the membrane, the top shell is broken outwards.

By the application of a magnetic field gradient, the metallic salt solutions, which are paramagnetic in most cases, are supposed to be dragged toward the higher field direction with a force depending on their magnetic susceptibility. In this case, the magnetic force in addition to the osmotic pressure competes with the outside hydrostatic pressure. Consequently, the metallic silicate tubes are expected to grow in the resultant direction of the three forces or pressures. While the above conception is what motivated us to initiate this work, we have also found several interesting effects of magnetic fields, including growth enhancement and the formation of a helical structure. In this paper, we report on these phenomena and discuss the mechanisms that cause them.

2. EXPERIMENTAL

The water glass was prepared by diluting sodium silicate solution (Nacalai Tesque Inc.) to 10 wt.% with ultra-purified water. The following metallic salts were employed in this study. $MnSO_4 \cdot 5H_2O$ (purity 99.9%), $Fe_2(SO_4)_3 \cdot xH_2O$ (>99%), $FeCl_2 \cdot 4H_2O$ (99.9%), $CoCl_2 \cdot 6H_2O$ (>99%), $NiCl_2 \cdot 6H_2O$ (>99.9%), $CuSO_4 \cdot 5H_2O$ (99.9%), and $ZnCl_2$ (99.9%). All of them were used as received from Kojundo Chemical Laboratory Co., Ltd.

First of all, the growth of metallic silicate tubes was examined without any magnetic field at room temperature. Immediately after powders of these metallic salts were immersed in the water glass, metallic silicate tubes started to grow upwards. The growth ceased in twenty to thirty minutes. The growth height and form of the tubes are listed in Table I. The growths of silicate tubes from $MnSO_4{\cdot}5H_2O$, $Fe_2(SO_4)_3{\cdot}xH_2O$, and $NiCl_2{\cdot}6H_2O$ powders were remarkably small.

Table I Growth height and main appearance of silicate tubes without magnetic fields. The growth height was measured for the highest tubes. The values with a sign of inequality show that the tallest tube reached the surface of the water glass in the test tubes.

Material	Height (mm)	Appearance
$MnSO_4$	14	Thin, straight
$Fe_2(SO_4)_3$	14	Thick, knotty
$FeCl_2$	>42	Zigzag
$CoCl_2$	41	Zigzag
$NiCl_2$	4	Thin, straight
$CuSO_4$	>42	Straight, tousled end
$ZnCl_2$	15	Straight

Experiments with magnetic field gradients were conducted using a 17 T superconducting magnet (Oxford Instruments Inc.) with a horizontal room temperature bore 40 mm in diameter. Figure 1 exhibits the field profile of the magnet. The magnetic force F derived from magnetic field B and field gradient dB/dx is as described in Eq. (2).

$$F = (1/\mu)\chi_v B(dB/dx), \tag{2}$$

where μ and χ_v are absolute permeability and volume susceptibility, respectively. The product of the magnetic field and field gradient is proportional to magnetic force. We refer to the product as the 'magnetic force field' hereafter. The magnetic force field became maximal at 90 mm away from the field center. The growth of metallic silicate tubes occurred in glass cells with an inner size of 47 mm in length, 8 mm in width and 24 mm in height. An arrangement diagram of the experimental setup in the magnet bore is shown in Fig. 2.

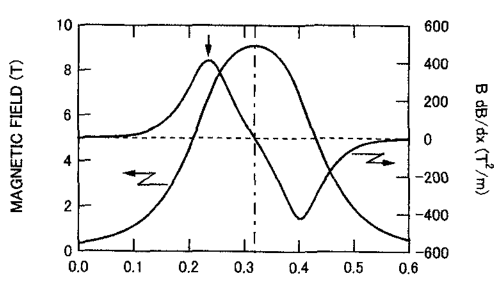

Fig. 1 Magnetic field and magnetic force field vs. depth from the bore edge in a superconducting magnet employed in this work. A magnetic field of 9 T was generated at the field center in this measurement. An arrow indicates a point where the magnetic force field was at a maximum and a reaction cell was located in all the experiments.

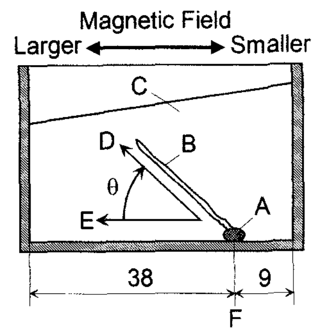

Fig. 2 Arrangement diagram of the experimental setup with a glass cell. A: metallic salt powder, B: metallic silicate tube, C: sodium silicate aqueous solution, D: tube growth direction, E: magnetic field direction, F: maximal magnetic force field point, θ: angle between the tube growth direction and the magnetic field direction. Typical lengths are shown in the unit of mm.

In all of the experiments, the cells were placed at the point where the metallic salt powders were exposed to the maximal magnetic force field as described in Fig. 2. The magnetic force field was adjusted in a range between 5 and 410 T^2/m by changing the center fields from 1 to 9 T. The fields had the same direction (left in Fig. 2) in all of the experiments.

3. RESULTS

We first examined the magnetic force field effect on the silicate tube growth in $CoCl_2$. After exposing the samples to various magnetic force fields for 1 hour, we examined the appearance of the synthesized tubes. Well-aligned and inclined growth toward the field center was observed above 46 T^2/m (3 T at the magnet center). The angles between the tube growth direction and the field direction in the range from 5 T^2/m (1 T) to 410 T^2/m (9 T) are listed in Table II. The tendency for the growth direction of the tubes to be closer to the field direction with increasing the magnetic force field is recognized clearly.

Table II Distribution of angles between the tube growth direction and the field direction at various magnetic force fields (MFFs) in $CoCl_2$. The definition of the angle is described in Fig. 2.

MFF (T^2/m)	5	46	182	410
Angle (°)	77~102	29~32	3~5	-3

Second, we compared the magnetic force field effect on the silicate tube growth among $MnSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, $CoCl_2$, $CuSO_4$, and $ZnCl_2$. After exposing the samples to a magnetic force field of 46 T^2/m (3 T) for 1 hour, we examined the appearance of the synthesized tubes (Fig. 3). In the $MnSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, and $CoCl_2$ samples, aligned and inclined growth toward the field center was observed. In the $MnSO_4$, and $Fe_2(SO_4)_3$ samples, tube growth was enhanced under gradient fields. In $CuSO_4$, two kinds of growth were recognized. One was inclined growth toward the field center, which was similar to the growth observed in the other paramagnetic samples. The growth was observed for the

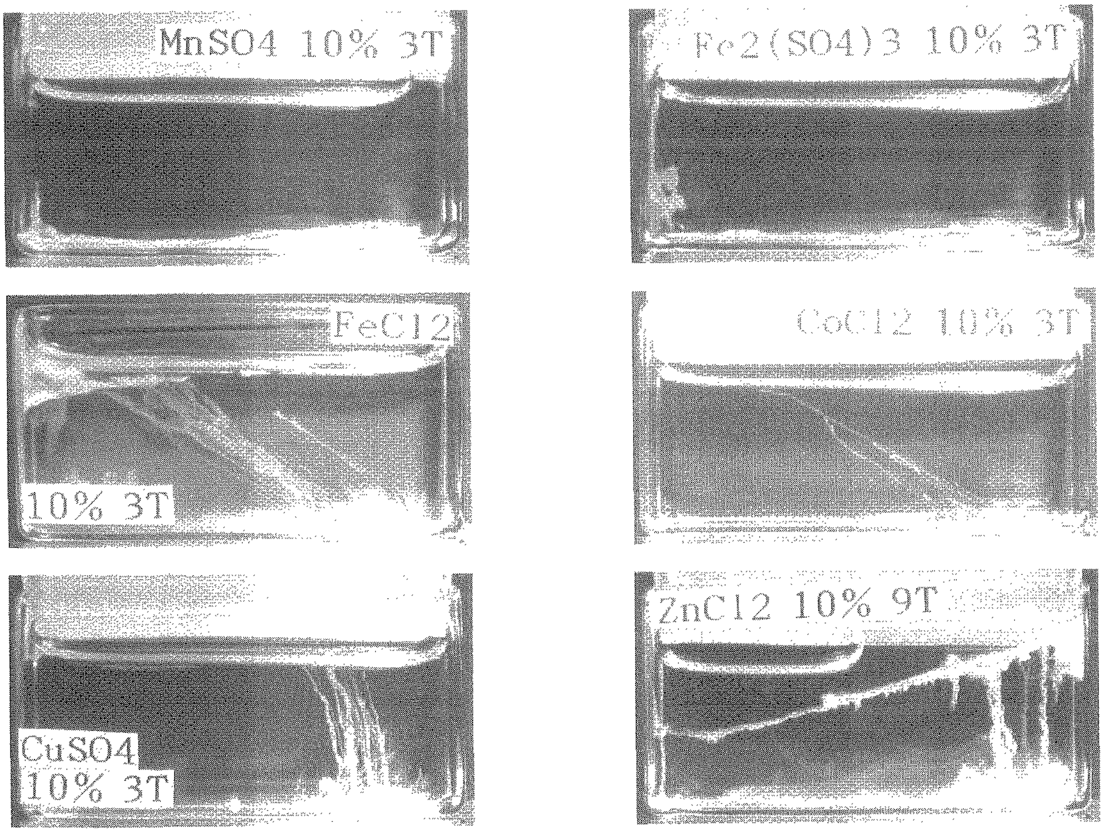

Fig. 3 Growth appearance of metallic silicate tubes for $MnSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, $CoCl_2$, and $CuSO_4$ at 46 T^2/m (3 T at the magnet center) and for $ZnCl_2$ at 410 T^2/m (9 T). In all of the experiments, the concentration of the sodium silicate aqueous solution was 10 wt.%. Experimental configurations are as shown in Fig. 2.

tubes growing on the wall of the glass cell. The other was also inclined growth, but in the direction opposite the field center. This type of growth was observed for freestanding tubes. In Table III, the angles between the growth direction and the field direction for these samples are listed together with the theoretical values of the effective Bohr magnetons of the metallic ions. In $ZnCl_2$, though no inclined growth along the field direction was observed even at 410 T^2/m (9 T), most tubes were observed to bend to one of the side walls (the opposite sidewall in Fig. 2) only. This phenomenon is also recognized in silicate tubes growing on the wall in $CuSO_4$.

In addition to these effects, we observed that a helical structure formed in the experiments using $MnSO_4$, $FeCl_2$, $CoCl_2$, and $CuSO_4$ under gradient magnetic fields. Figure 4 shows the result in the case of $FeCl_2$. At 0 T, random and zigzag growth of iron silicate tubes was observed. In the growth at 46 T^2/m (3 T), it was recognized that the tubes have a clockwise helical structure (Fig. 4). A similar structure was also observed in $MnSO_4$, $CoCl_2$, and $CuSO_4$.

Table III Distribution of angles between the tube growth direction and the field direction at a magnetic force field 46 T^2/m in $MnSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, $CoCl_2$, $CuSO_4$, and $ZnCl_2$. Theoretical values of the effective Bohr magneton for the metallic ions are also listed.

Material	Angle (°)	Bohr magneton
$MnSO_4$	-12~2	5.92
$Fe_2(SO_4)_3$	0	5.92
$FeCl_2$	30~33	4.90
$CoCl_2$	29~32	3.87
$CuSO_4$ (wall)	69~76	1.73
$CuSO_4$ (free)	137~142	1.73
$ZnCl_2$	86~90	-

3. DISCUSSION

3.1 Magnetic force field effect in $CoCl_2$

The growth direction of the silicate tubes can be

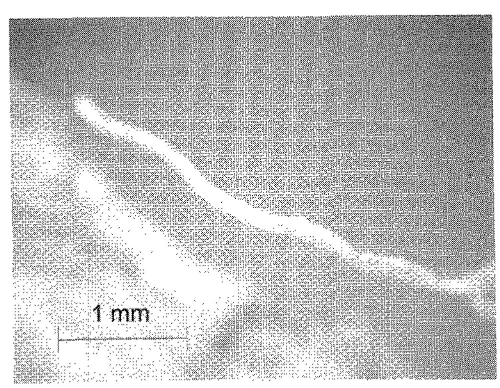

Fig. 4 Magnified view of silicate tubes growing from $FeCl_2$ powders at 46 T^2/m. The field center is in the left direction.

explained on the basis of the assumption that the magnetic force is exerted on the $CoCl_2$ solution in the silicate tubes as the tangent of the growth angle was found to be approximately in inverse proportion to the magnetic force field. Though no apparent inclination of the silicate tubes toward the field center was observed in the experiment at 5 T^2/m (1 T), this finding is reasonable as described in the following. If we calculate the growth angle at 5 T^2/m on the basis of the inversely proportional relationship mentioned above in comparison with the average growth angle 30.5° observed at 46 T^2/m (3 T), a value of 79.5° is obtained. Growth at this angle would be very difficult to distinguish from the natural growth of silicate tubes. At 182 T^2/m (6 T) and 410 T^2/m (9 T), the angles estimated as described above are 8.5° and 3.8°, respectively. The declination of the observed angles from the estimated angles can be understood if one takes into account the fact that the magnetic field at a position becomes larger and its gradient also increases as the position deviates from the center axis of the magnet bore in the radius direction, which is a common feature of conventional solenoid magnets.

3.2 Metallic ion dependence

The degree of inclination of the silicate tubes induced by the magnetic force field effect quantitatively corresponded to the magnetic susceptibility of the metallic salt solution, as expected. We interpret the growth enhancement observed in $MnSO_4$ and $Fe_2(SO_4)_3$ as follows. In addition to the drag force generated by the magnetic force field at the growth end, metallic salt solutions inside silicate tubes are always replaced by more concentrated solutions supplied from the back side.

The peculiar growth observed for the freestanding tubes in $CuSO_4$ can be interpreted in the following manner. The paramagnetic susceptibility of $CuSO_4$ is the weakest among the employed metallic salts. In silicate tubes standing almost upright, more concentrated $CuSO_4$ solutions are supposed to be distributed on the field center side. This distribution could result in the formation of a thicker membrane on the side at the growing ends. Subsequently, a thinner or weaker membrane on the opposite side would be broken by the osmotic pressure to form a new silicate membrane in the direction opposite the field center. This process should be unfavorable from the viewpoint of supplying concentrated metallic salt solution to the growing ends. One can also explain the reason that the growth height of the freestanding tubes at 46 T^2/m was only one-fourth of that at the zero field, from the same viewpoint.

In the case of growth on the wall, the formation rate of the silicate membrane is supposed to be slower in the region between the wall and silicate tubes, compared with the freestanding tubes, as the supply of sodium silicate is limited in the region. This situation might allow $CuSO_4$ solutions emitted from the broken holes to move toward the field center before forming a silicate membrane.

The bending of the silicate tubes toward one of the side walls, which was the right wall when it is viewed in the direction of the magnetic field, was a common feature observed in silicate tubes growing upward in the case of $CuSO_4$ and $ZnCl_2$. This means that the tubes were bent clockwise in the direction perpendicular to the field direction. Taking into account this common feature, this bending is thought to originate from the Lorenz force that is exerted on anions moving in a direction perpendicular to the field direction.

3.3 Formation of helical structure

This phenomenon is very interesting because helical tube structures are produced and may be controlled by the application of magnetic fields. We currently believe the origin of this phenomenon to also be the Lorenz force. The twist of the helical structure occurs in the same direction as the bending observed for $CuSO_4$ and $ZnCl_2$. Around the growing ends of the silicate tubes, anions of the metallic salt solution are evacuated outward in the process of membrane formation. This flow of anions would be bent clockwise, as it has a component perpendicular to the field direction for silicate tubes leaning toward the field direction. We tentatively propose that this flow makes a vortex around the growing end and that the tube wall is twisted during the solidification.

4 Conclusions

The following magnetic field effects on the growth of metallic silicate tubes are recognized.

4.1 Magnetic force field effect

The following effects are thought to originate from the magnetic force that is exerted on metallic salt solutions via paramagnetism. Metallic silicate tubes synthesized from paramagnetic metallic salt solutions are aligned and inclined toward the field center. The growth length of the tubes is also enhanced. If the magnetic force is relatively small, the inclination of the silicate tubes away from the field center is recognized. This result is attributed to the non-uniform distribution of the metallic salt solution toward the field center inside the tubes, which is followed by the formation of a thicker membrane on the field center side and a breach of the membrane on the other side.

4.2 Lorenz force effect

The following effects are interpreted in the framework of the Lorenz force on anions moving in a direction perpendicular to the magnetic field direction. Silicate tubes growing upward without inclining toward the field direction are bent toward the right when the viewer is looking in the field direction. Silicate tubes inclining toward the field direction have helical structures whose twist runs clockwise with respect to the growing direction. This magnetically induced helical structure has been newly found and is very interesting from the viewpoint of the magnetic control of helicity.

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