Double helical formation of cobalt silicate tubes under magnetic fields

H Yokoi1,3, Y Araki1, N Kuroda1, S Usuba2 and Y Kakudate2

1Department of Materials Science and Engineering, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan
2Research Center for Explosion Safety, National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Tsukuba, 305-8565, Japan

E-mail: yokoihr@kumamoto-u.ac.jp

Abstract. Magnetic field effect on the growth of cobalt silicate tubes in aqueous solution of sodium silicate is studied. Cobalt silicate tubes grown from CoCl₂ powders in 10wt.% sodium silicate solution under a horizontal magnetic field of 2.2 T and a field gradient of 20.3 T/m are found to tilt toward the higher field direction, which is attributed to the paramagnetic property of the Co²⁺ ion. In addition, twisted structures are recognized on the tube walls. The direction of the twist is right-handed in the case that the higher field direction is parallel to the field direction and left-handed in the anti-parallel case. Observing the growth of the tubes in situ under magnetic fields has revealed that two cusps of silicate proceed revolving around at the growing end to form a tube wall double-helically. We have proposed a model for the mechanism of the helix formation that Lorentz force exerted on anions (Cl⁻) flowing through and out of the tubes would cause vortex around the growing ends and the vortex could strand the two cusps, which explains the twist direction with respect to the field direction reasonably.

1. Introduction
Helicity is one of the most important characteristics of substances in manifesting their specific functions, as observed in deoxyribonucleic acid (DNA), sense organs, liquid crystals and so on. Magnetic control of helicity has long been one of the most attractive subjects for researchers from the viewpoint of the application of magnetic fields to materials science and engineering. In this study, we report magnetically induced double helix observed in metal silicate membrane tubes formed from metallic salt powders immersed in water glass.

The formation of silicate tubes in water glass is well-known as ‘Chemical Garden’[1]. Typical chemical reaction in the case of Cu(NO₃)₂ is as follows.

\[
\text{Cu(NO₃)₂ + Na₂SiO₃ → CuSiO₃ + 2NaNO₃}
\]  \(\text{(1)}\)

The metal silicate membrane, which covers the entire surface of each metallic salt powder when the powders are immersed in water glass, is semi-permeable. Water permeates inside through the membrane due to the osmotic pressure and the increased inner pressure breaks a part of the membrane.
Water solution of metallic salt is emitted through the hole and forms new membrane on reacting with surrounding water glass. This process is repeated upward due to buoyant force, resulting in the formation of metal silicate tubes growing upward. We have examined magnetic field effect on the growth of metal silicate tubes by applying horizontal magnetic fields to 6.7 T with field gradients to 61.0 T/m for various metallic salts including MnSO₄·5H₂O, Fe₃(PO₄)₃·xH₂O, FeCl₃·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuSO₄·5H₂O, and ZnCl₂, and have found that the growth direction of the tubes is tilted according to magnetic susceptibility of the metallic salts and also the product of the field and the field gradient. This phenomenon is thus attributed to magnetic force exerted on metallic ions that is paramagnetic around growing ends of the silicate tubes [2,3].

We have also found that the tilted metal silicate tubes growing from paramagnetic salts including FeCl₂ and CoCl₂ have twisted or helical structures while such regular structures are not observed on the tubes formed without fields. Formation of the helical structures appeared inconsistent to the electromagnetics as there seemed no apparent movement of ions that is perpendicular to the applied magnetic fields. However, the helicity was observed to be reversed when the field direction was reversed while the field gradient was unchanged. The direction of the twist was right-handed with respect to the direction of magnetic fields in the both cases. These results suggest strongly that the helical structure should be induced by Lorentz force exerted on anions moving perpendicularly to the field. We have proposed that flow of anions discharged from aqueous solution of metallic salt emitted outward at the growing ends, while metallic ions are trapped in the tube walls, could be bent by the Lorentz force and generate vortices around the growing ends, which twists silicate tubes before their solidification [2,3]. Hereafter, we refer to this model as Lorentz Force on Anion Flow (LFAF) model.

There have been also a few reports on formation of helical structures in the Chemical Garden under magnetic fields. In Ref. [4], it was reported that strips of zinc silicate membrane spiral up, creeping on the inner wall of a cylindrical vessel in vertical magnetic fields to 15 T. In Ref. [5], it was exhibited that Mg(II) or Zn(II) silicate membrane tubes growing apart from the vessel wall were twisted in a vertical magnetic field of 15 T. The latter observation is similar to our findings in horizontal fields. The authors also adopted the LFAF model to explain the formation of the twisted metal silicate tubes.

The LFAF model has to be verified by some means including the observation of vortex around the growing ends. We have developed observation systems so as to investigate flow around the growing ends during the growth of silicate tubes in situ under magnetic fields. Using the systems, we have found that the helical structure of the silicate tubes is formed double-helically. In this paper, we report the evidence of the double-helical formation of cobalt silicate tubes by the application of magnetic fields and discuss the formation mechanism.

2. Experiment

Water glass was prepared by diluting sodium silicate solution (Nacalai Tesque Inc., Kyoto, Japan) to 10wt% with ultra-purified water. A metallic salts of CoCl₂·6H₂O (>99%) was employed as received from Kojundo Chemical Laboratory Co., Ltd. (Saitama, Japan) in this study.

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. In the magnet bore, fields \( B \) were generated horizontally and the absolute value of \( B(dB/dx) \) (hereafter, referred as ‘magnetic force field’) became maximal at two positions 85 mm away from the field center, where \( x \) is corresponding to the horizontal position along the bore axis. 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 of the two positions as the magnetic force on paramagnetic materials becomes largest there. Magnetic fields of 3 T at the field center were generated in all the experiments under magnetic fields in this work, when the field and the magnetic force field at these positions were 2.2 T and 46 T/m, respectively. The glass cells were placed at the positions immediately after the metal salt powders were immersed in the water glass. Application of fields above 3 T was avoided as some instruments employed in the experiments were turned out to be weakly magnetic.
In observing the growing ends in situ, we utilized a monitoring system that consisted of a charge-coupled-device (CCD) video camera with a small cylindrical camera head of φ6.5 mm in diameter and a lens of 2.2 mm in focal length, and a light guide as shown in figure 1. A configuration where the magnetic force exerted on Co\(^{2+}\) ions was directed on the side of the CCD camera was selected, so that the growth direction of cobalt silicate tubes was tilted toward the camera [2,3]. The magnetic field was applied on the front of the camera, i.e., parallel to the magnetic force.

### 3. Results and Discussion

Figure 2 shows the typical helical structure formed on cobalt silicate tubes at \(B\) of 2.2 T and \(B(dB/dx)\) of 46 T\(^2\)/m. The directions of magnetic field and magnetic force were parallel as shown in the figure. The diameter of tubes was around 0.14 mm. The direction of the tube growth was tilted by about 60° toward the higher field direction, which is attributed to the magnetic force exerted on cobalt ions that is paramagnetic. One can recognize that the cobalt silicate tube has a right-handed twist with the pitch of about 0.6 mm along the growth direction.

In the observation of the growing ends in situ in the same field condition as above, two cusps of silicate were found to proceed revolving along the wall with a period of around 30 s, as if they are twining around each other, to form a helix as exhibited in figures 3. This means that the helical structure is formed double-helically as it is the case with DNA. It is thought that the formation of the two cusps at the growing ends itself is not related to magnetic fields as it was often recognized in the growth of metal silicate tubes without magnetic fields. The rotation of the two cusps can be explained in the framework of the LFAF model. One can also notice in figures 3 that spouts from the growing ends were bent right-handed along the direction of the magnetic field. This result is clear evidence that

![Figure 1. Schematic diagram of experimental setup with a glass cell for observing the growth of cobalt silicate tubes in situ. A: cobalt silicate powder, B: cobalt silicate tube, C: sodium silicate aqueous solution, D: lens, E: CCD camera, F: light guide. Arrows above the cell indicate the directions of the magnetic force exerted on cobalt (II) ion and the magnetic field, respectively.](image1)

![Figure 2. Typical appearance of silicate tubes growing from CoCl\(_2\) powders at 2.2 T and 46 T\(^2\)/m. The directions of the applied magnetic field and magnetic force exerted on cobalt (II) ions are shown in the left lower part of the figure. The arrow along the tube exhibits the direction of tube growth.](image2)
the Lorentz force exerted on the anions emitting from the growing ends governs the flow around there. It is assumed in the LFAF model that the same mechanism as this bent of flow could apply to the double-helical formation of the silicate tubes. Further investigation is required for the visualization of convex around the growing ends as well as the formation mechanism of two cusps at the growing ends.

4. Conclusion
Helical structure is induced on cobalt silicate tubes grown in the Chemical Garden reaction by the application of horizontal magnetic fields with gradients. The typical size of the helical tube is 0.14 mm in diameter and 0.6 mm in pitch in a field condition of 2.2 T in field and 20.3 T/m in field gradient. It has been found that two cusps of silicate are formed at growing ends of the silicate tubes, twining each other to form the helical walls with a period of about 30 s, which has revealed that the novel structure is magnetic-field-induced double helix. We have proposed a model of the helix formation in which flow of anions discharged from aqueous solution of metallic salt emitted outward at the growing ends, while metallic ions are trapped in the tube walls, could be bent by the Lorentz force and generate vortex around two cusps of silicate at the growing ends, which twines them before their solidification.

Acknowledgments
Research at Kumamoto University was supported by a Grant-in-Aid for Scientific Research of Japan 16540299-0.

References
[1] Cartwright J H E, García-Ruiz J M, Novella M L and Otálora F 2002 J. Colloid Interface Sci. 256 351
[2] Yokoi H, Usuba S and Kakudate Y 2004 Trans. Mater. Res. Soc. Jpn. 29 3391
[3] Yokoi H, Kuroda N and Kakudate Y 2005 J. Appl. Phys. 97 10R513
[4] Uechi I, Katsuki A, Dunin-Barkovskiy L and Tanimoto Y 2004 J. Phys. Chem. B 108 2527
[5] Duan W, Kitamura S, Uechi I, Katsuki A and Tanimoto Y 2005 J. Phys. Chem. B 109 13445

Figures 3. Sequential photos of growing ends of cobalt silicate tubes captured every 4 s in the configuration exhibited in figure 1 at 2.2 T and 46 T/m. The direction of the magnetic field is indicated in figure 3(a). The arrow shows the tube where the double-helical growth is more distinct.