High Magnetic Field Effect on the Growth of 3-Dimensional Silver Dendrites

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A liquid/solid redox reaction between silver ion and copper metal was investigated under high magnetic field (maximum field strength: 15 T). 3-Dimensional silver dendrites produced via the reaction were affected drastically by the magnetic field. Dense and large quantity dendrites were obtained under the magnetic field. Magnetic force will determine the shape and quantity of the silver dendrites.

Control of chemical reaction by magnetic field has been one of the interesting topics in chemistry.[1] In this paper, we studied a liquid/solid redox reaction, i.e. the reaction between silver ion and copper metal, under *vertical* high magnetic field how magnetic forces affect 3D-pattern and chemical yield of silver dendrites. It is demonstrated that the magnetic field affects significantly topology and chemical yield of silver dendrites. The results are interpreted in terms of magnetic convection of the solution which is induced by the magnetic force on paramagnetic copper ions generated in the reaction.

A superconducting magnet (JMT, JMTD-LH15T40, $\leq$15 T, ϕ 40 mm vertical bore tube) was used in our experiment. Figure 1 shows axial distributions of magnetic field, z being the distance from the center of the bore tube along the axis. Silver nitrate (Nacalai Tesque GR grade) was used as supplied. Copper wire (Nilaco, 99.99%, ϕ 6 mm) was polished just before its use. Distilled water was used. A copper wire (10 mm), fixed on a rubber stopper, was immersed in a 0.05 mol/dm^3 silver nitrate solution, full-filled in a glass vessel (54 mm high, 30 mm diameter, volume: ca. 34 mL). The vessels were placed at z to -95 mm (bottom; 9.3 T, 980 T^2/m), z to 0 mm (middle; 15 T, -160 T^2/m), and z to 95 mm (top; 5.6 T, -940 T^2/m) in the bore tube, as shown in Figure 1. One vessel was placed outside of the magnet ($<$0.005 T) as a control experiment. Hereafter, these positions shall be called bottom, middle, top, and outside, respectively. After 2 h reaction, the shapes of dendrites were recorded by a digital camera. Yields of silver dendrites were determined by gravimetry and those of copper ion were determined by absorption spectrometry (Hitachi, U-3500), where molar extinction coefficient of copper ion, Cu^{2+}, was assumed to be 11.92 cm^{-1} mol^{-1} dm^3 at 807 nm. All the experiments were carried out at room temperature.

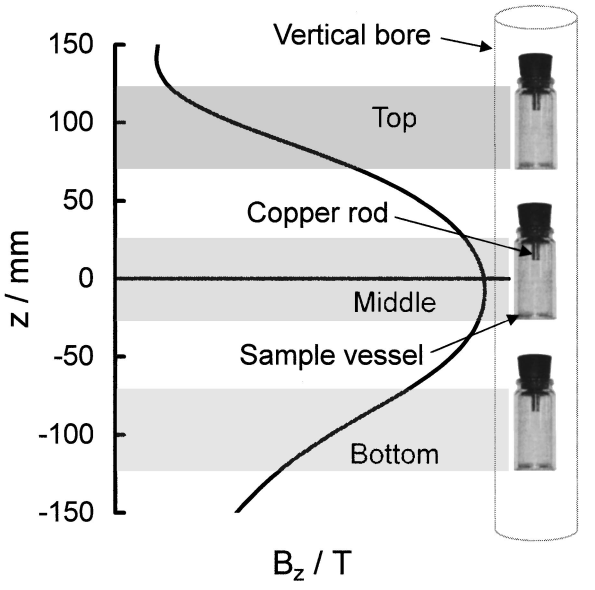

Figure 1. The distribution of the vertical magnetic field $B(z)$. z is the distance from the center of the magnetic field (15 T) along the magnetic axis. The gray parts show the area of the magnetic fields where the sample vessels were placed. These positions shall be called top, middle, and bottom from the top. The right-hand vertical bore's picture corresponds to the plot of distribution of the magnetic field.

The liquid/solid redox reaction investigated is given by the following equation:

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

The reaction progresses by the ionization tendency, and silver metal deposits around a copper wire as a dendrite.

Figure 2 shows the photographs of the silver dendrite produced under various magnetic fields. The magnetic field caused drastic changes in the color and shape of silver dendrites. At zero field, branches of metallic silver grew in dendrite with metallic color under the gray and cylindrical dendrites (Figure 2(a)). In the magnetic fields of 9.3 T and 980 T^2/m, the shape of the dendrites becomes slightly spherical, and the size of the metallic branches tree became small (Figure 3(b)). In the magnetic fields of 15 T and -160 T^2/m and 5.6 T and -940 T^2/m, dendrites are black in color and almost spherical in shape (Figure 2(c), (d)). Figure 3 shows photomicrographs of dendrites in magnetic fields. All dendrites took tree-like structure. The length of each branch is longer than at least 1 mm at zero field (a). The length became remarkably smaller under the magnetic field ((b), (c)).

Table 1 shows the relative yields of the silver dendrites and the copper ion produced through the present redox reaction. The value

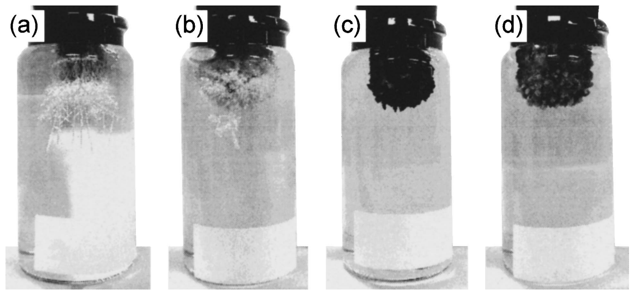

Figure 2. The photographs of silver dendrites after 2 h reaction. (a) the outside of the bore tube (control, $<$0.0005 T), (b) the bottom position (9.3 T, 980 T^2/m), (c) the middle position (15 T, -160 T^2/m), (d) the top position (5.6 T, -940 T^2/m).

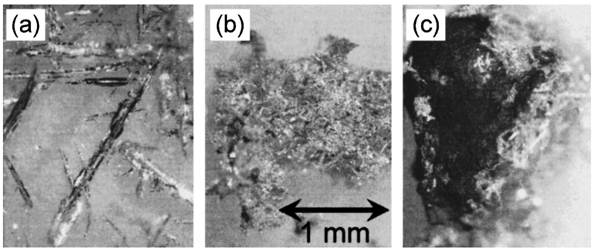

Figure 3. The photomicrographs of the silver dendrite. (a) the outside of the bore tube (control), (b) the bottom position (9.3 T, 980 T^2/m), (c) the top position (5.6 T, -940 T^2/m).

Table 1. The effects of magnetic fields on the yields of copper ion and silver dendrites

	B/T	Magnetic force $/T^2m^{-1}$	Ratio[a] Ag	$[Cu^{2+}]$
Outside	≈0	≈0	1.00	1.00
Bottom	9.3	980	1.29	1.54
Middle	15.0	−160	2.08	2.29
Top	5.6	−940	2.06	2.12

[a]The values are the ratio of the yield in magnetic field and that of control. These data contain the error of about 10%.

obtained at zero field was set to a standard. The yields of the silver metal and the copper ion at zero field were 0.078 g and 0.010 mol/dm^3, respectively. The magnetic field caused significant acceleration of the redox reaction. Yields of both silver dendrite and copper ion exhibit analogous increase in magnetic fields. The yields at the middle and top positions showed the maximum yield of ~2. But, the yield at the bottom position was smaller than that at the top position by nearly a half, though the magnetic field strength was stronger than that at the top position and the magnetic force in both the positions were almost equal except the direction of the force. These results show that the Lorentz force is minor contribution to the phenomenon.

The almost similar behavior of the yield of the silver and copper ion implied that the reaction occurs quantitatively under magnetic fields. The color of the dendrites growing under the magnetic field was black. This would result from the multiple reflection of incident light by the small-size dendrites.

In a previous paper, we have studied the effects of high *horizontal* magnetic field (8 T, ca. ±400 T^2/m) on the 2D-pattern and the yield of silver dendrite generated by the redox reaction (1).[2,3] A dendrite shape changed drastically and its yield increased by about 50% in the magnetic field. All the results have been interpreted in terms of the magnetic force on copper ion generated, which induced magnetic convection of solution, though there were several mechanisms for interpretation of observed magnetic field effects. This interpretation was further verified by the computer simulation study.[4] Therefore, the results shown in Figure 2 and 3 could be explained predominantly by the term of the magnetic force, though the Lorentz force[5] could be partly responsible for the results shown in Figure 2.

This magnetic force on a compound, of which molar magnetic susceptibility is χ, is given by the following equation.

$$F = \chi \frac{1}{\mu_0} \frac{dB(z)}{dz} B(z) \tag{2}$$

where $B(z)$ is the magnetic field at the position z and μ_0 is magnetic permeability of vacuum. Paramagnetic ions are attracted to the higher field, whereas diamagnetic ones are pushed out to the lower field. In the reaction (1), copper ion is solely a paramagnetic whereas others are diamagnetic. Molar magnetic susceptibilities of copper metal, copper ion, silver, and silver ion are $-4\pi \times 5.46 \times 10^{-12}$ m^3 mol^{-1}, $+4\pi \times 1.28 \times 10^{-9}$ m^3 mol^{-1}, $-4\pi \times 2.05 \times 10^{-11}$ m^3 mol^{-1}, and $-4\pi \times 2.4 \times 10^{-11}$ m^3 mol^{-1}, respectively. At the top and bottom positions the forces on copper ion are estimated at −12.0 N/mol and +12.5 N/mol, respectively, whereas the forces on which silver ion are estimated at +0.23 N/mol and −0.24 N/mol, respectively. The magnetic force on copper ions is strong enough to induce convection of solution, since it is about 19 times larger than gravity. The solution rich with copper ions undergoes convection as a whole in magnetic fields, since copper ions collide with their surroundings, i.e., water, and other solutes.

At the top and middle positions, the magnetic forces around a copper wire are downward. They will make the solution rich with copper ions, move out from the copper metal and dendrite surfaces and, as a natural consequence, a fresh bulk solution is supplied to the surfaces. All of the solution in the vessel undergoes magnetic convection. So, the redox reaction will be accelerated about the double at the present condition. On the other hand, at the bottom position, the magnetic force near the copper wire is upward and, therefore, the solution rich with copper ions will be restricted around the copper wire, in addition of the magnetic convection of solution. In this case, the direction of convection is reversed and localized at the upper part of the solution. This reduces the efficiency in supply of a fresh bulk solution to the reaction zone. As the result, the redox reaction there will not be enhanced very efficiently.

So far we discussed the effects of magnetic fields on the chemical yield of reaction (1). Analogously we can explain the dense structure of dendrite in magnetic fields. However, within the framework of the above-mentioned consideration, the shape of dendrite should be cylindrical in shape in magnetic fields, which is slightly different from the experimental results. The shape of dendrites depend strongly on the detailed pattern of convection of solution which will be affected by shape and size of a vessel, and copper wire, and concentration of silver ions (i.e., copper ions generated), and shape and intensities of magnetic force. Further analysis of the results will be given in the near future.

Conclusively the magnetic field affected the shape, color, density and yield of the silver dendrite remarkably. The results are explained by the magnetic convection of solution which is induced by the magnetic force on paramagnetic copper ions generated by the reaction. These findings strongly suggest that a magnetic force is a potential tool to control not only chemical yields but also topology of dendrites and crystals.

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