A Morphological Study of Electroless Deposition in High Magnetic Fields*

Susumu Okubo, Iwao Mogi and Yasuaki Nakagawa

Institute for Materials Research, Tohoku University, Sendai
(Received January 22, 1993)

Synopsis

Growth morphology of a silver metal-leaf was investigated in high magnetic fields up to 8T as an experimental approach to the diffusion-limited aggregation (DLA) with the lateral drift of particles. The silver metal-leaves were grown around a square 'seed' of copper from a $AgNO_3$ aqueous solution by means of the electroless reduction of silver ions. The growth pattern of the metal-leaf had a typical DLA structure with the fractal dimension of 1.62 in the absence of magnetic field. On the other hand, it had a spiral and dense branching structure at 8T, in which the crossover in the fractal dimension from 1.69 to 2 was observed with increasing length scale. The spiral direction was reversed by the reversal of the applied field. A metal-forest pattern of silver was also investigated, which was grown around a copper ribbon. Its growth morphology changed from the DLA pattern without the field into a canting and dense pattern at 8T.

I. Introduction

A random pattern formation in nature is one of most attractive issues in non-equilibrium and irreversible phenomena. Many growth models of computer simulation were proposed to describe them. In particular, the diffusion-limited aggregation(DLA) model[1,2] was important because it is simple aggregation process and applicable to many realistic phenomena. The DLA model in a two-dimensional space produces a self-similar pattern with fractal dimension $D_f \sim 1.7$, which has open and random structures with no characteristic length scale except their whole size. A typical DLA pattern in real physical systems has been observed by Matsushita et al.[3] in two-dimensional zinc metal-leaves grown by electrodeposition. The fractal dimension D_f of the zinc metal-leaves was determined as $D_f = 1.66$ by the density-density correlation function, which is in good agreement with the theoretical result[4] of $D_f = 5/3$.

The effects of unidirectional particle drift on the DLA have been studied by Meakin[5] by a Monte Carlo method on two-dimensional square lattices. He found that the aggregation pattern with the particle drift had the crossover from a fractal structure on short length scales to a uniform structure on long length scales. Nagatani and

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* The 1942th report of Institute for Materials Research

Sagués[6] dealt with the effects of a rotating and radial flow on DLA in two-dimensional square lattices. They found that the DLA pattern changes into a single-arm structure in a rotating flow and a multiarm structure in the presence of both radial and rotating flows. On the other hand, aggregation growth from a lattice gas of finite density in two dimension has been simulated by Uwaha and Saito[7]. According to them, the aggregation pattern changes from DLA to a compact pattern with increasing the gas density.

The purpose of the paper is to investigate the effect of a lateral particle drift on DLA in a real physical system. We have observed the growth patterns of two-dimensional silver metal-leaves in high magnetic fields up to 8T, where the Lorentz force induces the lateral drift on the diffusive motion of ions. In our previous paper[8], we reported dense radial growth of a silver metal-leaf at 8T. In this paper, we will show the dependence of the growth pattern on both Ag^+ concentration and magnetic field.

II. Experimental

Two-dimensional silver metal-leaves were grown for 120 minutes by sandwiching a piece of copper metal ($3x3x0.02mm^3$ or $3x50x0.02mm^3$) in a silver nitrate

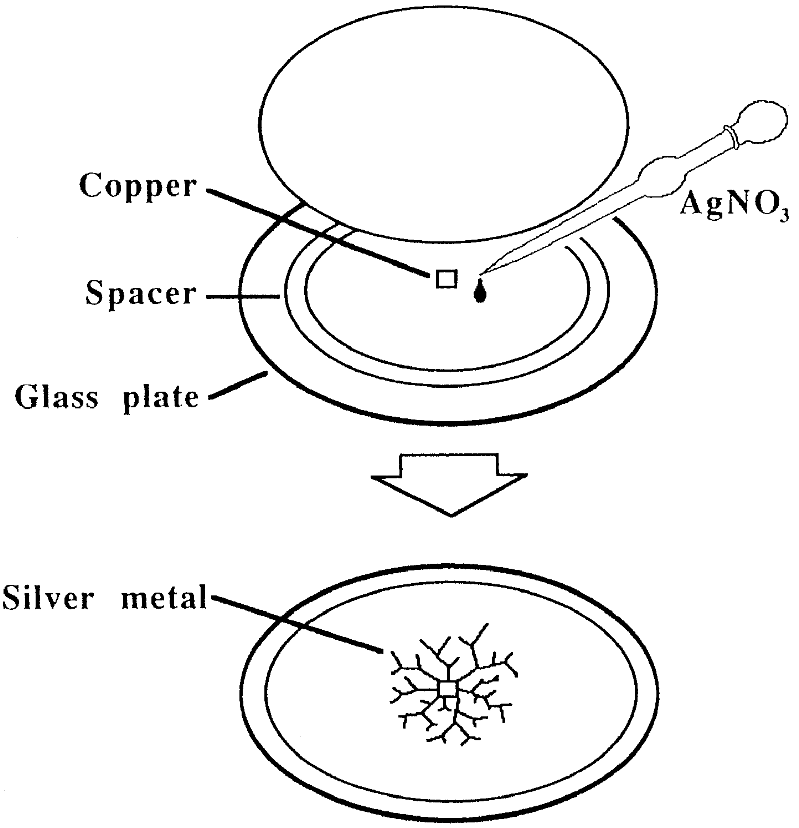

Fig. 1 Scheme of experiment to grow the silver metal-leaf.

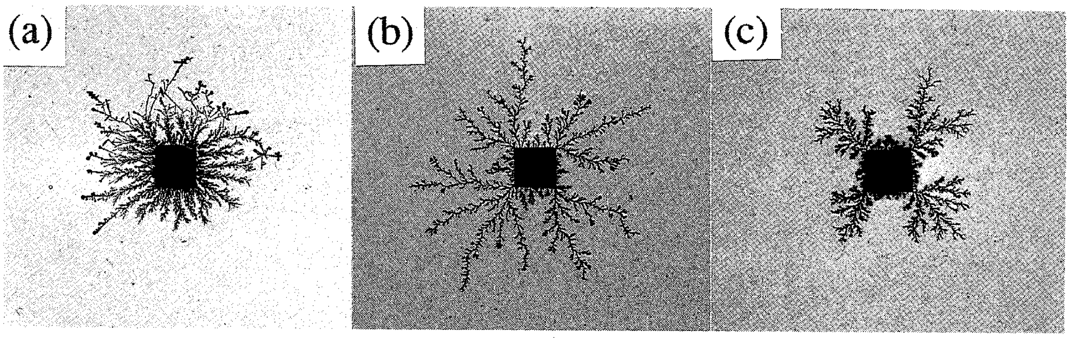

Fig. 2. Growth pattern of silver metal leaves from a $AgNO_3$ aqueous solutions of (a) 0.2M, (b)0.05M and (c) 0.025M

aqueous solution between two glass plates(Fig1). The distance between the two plates was adjusted to approximately 0.06mm by inserting a polymer film as a spacer.

The experiments with high magnetic fields were carried out using a superconducting magnetic SM-3 in the High Field Laboratory of Tohoku University. This magnet produced fields of up to 8T in a large bore of 220 mm at room temperature. Magnetic fields were applied perpendicularly to the glass plates which were placed on a bakelite holder within the magnet. Temperature within the magnet was controlled at 25±0.2°C by a water-circulating system. Silver metal-leaves were photographed and analyzed digitally with an image-scanner and a personal computer. A fractal dimension of the metal-leaf was estimated by means of the box-counting method.

III. Results and Discussion

Silver metal-leaves were grown from a $AgNO_3$ aqueous solution by the electroless reduction of Ag^+ ions. The growth pattern depends on the Ag^+ concentration, as shown in Fig. 2, in which all metal-leaves were grown for 120 minutes in the absence of magnetic fields; a square at the center of the leaf is a piece of copper ($3x3x0.02mm^3$) metal 'seed'. The metal-leaf (a) grown from a 0.20 M ($M = mol{\bullet}dm^{-3}$) $AgNO_3$ solution has a dense and mossy structure. The metal-leaf (b) from a 0.050 M solution shows a typical DLA pattern, in which some short branches cease to grow owing to the growth of longer branches. Such a screening effect is a prominent feature in DLA. In the growth pattern (c) of a 0.025 M solution, which also shows a DLA feature, there appears the dependence of pattern on the shape of the copper metal seed; the main four branches develop at the four corners of the square seed.

The chemical reaction to form a silver metal-leaf is simple redox (reduction-oxidation) reaction of

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

The difference of the redox potentials between Cu/Cu^{2+} and Ag/Ag^+ causes this reaction to proceed. Silver ions are brought to a copper piece by diffusion. They are reduced by the copper metal and deposit around it. The electron transfer process is, generally, faster than the diffusive mass-transfer process, so that DLA is realized.

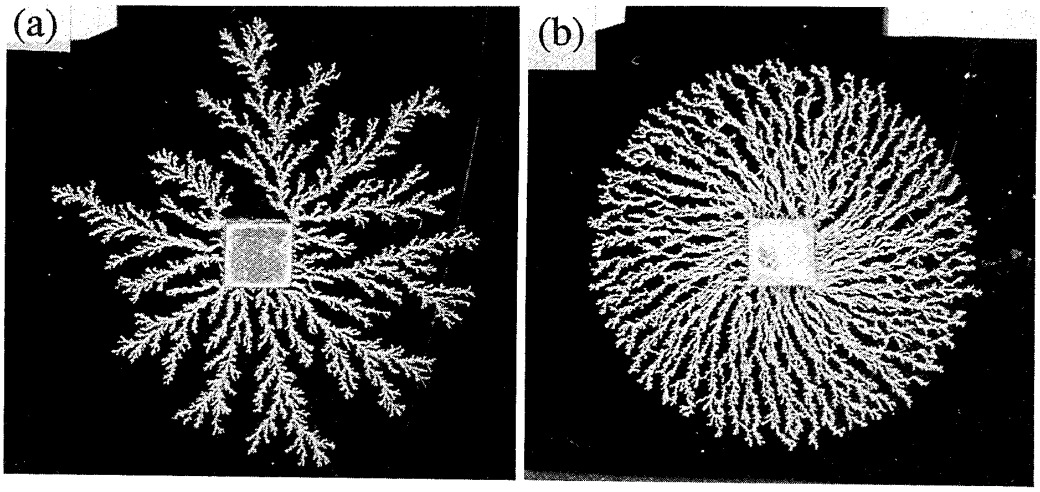

Fig. 3. Growth pattern of silver metal leaves in (a) H=0T and (b) H=8T. Both metal leaves were grown for 120 minutes at 25°C. The magnetic field was applied perpendicularly to the plates.

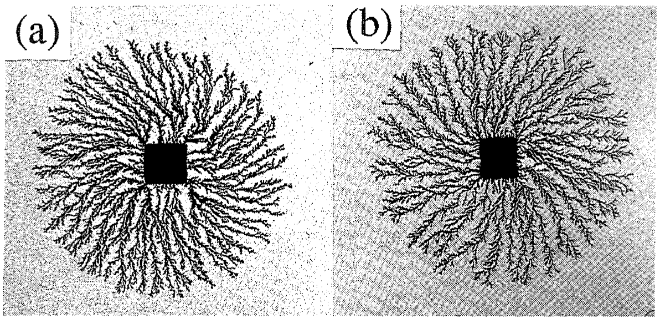

Fig. 4. Growth pattern of silver metal leaves from 0.075M a $AgNO_3$ aqueous solution in magnetic fields (a) 4T⊙,(b) 4T⊗.

Uwaha and Saito simulated aggregation patterns from lattice gases with various densities and reproduced the pattern change from a DLA fractal to compact structure with increasing the gas density. A similar pattern change is observed in Fig. 2. The aggregation pattern depends on a diffusion length which corresponds to the distance between main branches. The diffusion length decreases with increasing Ag^+ concentration, hence, the growth pattern becomes compact.

Figures 3 and 4 show the magnetic field dependence of the growth pattern of the silver metal-leaves from a 0.075 M $AgNO_3$ solution. A typical DLA pattern is observed in the absence of a magnetic field (Fig. 3(a)). In magnetic fields the growth pattern becomes dense and spiral. The metal-leaf at 8T drastically changes to dense-branching morphology with a circular periphery, as shown in Fig. 3(b). When the applied field is reversed, the spiral growth is in the opposite direction (Fig. 4). This fact indicates that the pattern change is caused by the Lorentz force acting on the motion of silver ions.

When a magnetic field is applied to an electrolytic solution, the Lorentz force

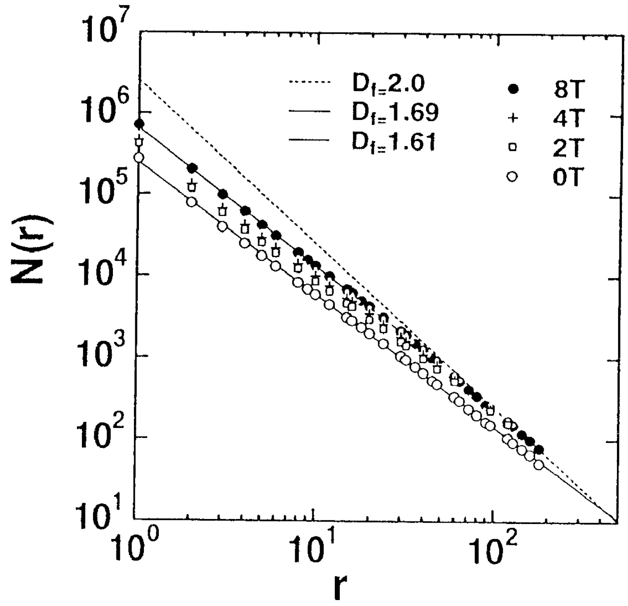

Fig. 5. The log-log plots of the number of boxes supporting the metal-leaf N(r) vs. the box size r. The unit length of the box size (r=1) is approximately 0.01 mm. The fractal dimension D_f was estimated from the slope of the linear solid lines. The dotted line represents D_f =2.

induces lateral drifts on the diffusion of ions. This is well known as the magneto-hydrodynamic (MHD) effect. According to the DLA simulation with a rotating flow by Nagatani and Sagués, a tangential drift causes a spiral DLA pattern, which changes into a single-arm structure with increasing tangential-drift probability. However, a dense branching morphology has not emerged in their simulations. This is probably because the DLA simulation does not include the term of the particle concentration, so that the dependence of the diffusion length on the tangential drift has not been considered.

In electrochemistry the MHD effect has been intensively studied; it has been found that the MHD convection makes a diffusion layer thinner in electrode reactions and increases a current. The decrease in the diffusion-layer thickness or the diffusion length is also observed in the metal-leaf growth in high magnetic fields, even though the reaction is electroless. The distance between main branches decreases with increasing fields, as can be seen in Fig. 3.

In order to estimate the fractal dimension D_f by the box-counting method, the number of boxes including parts of the metal-leaf N(r) is plotted as a function of the box size r in Fig. 5, where the copper seed was excluded from the counting. The plots at zero field show a self-similar pattern with D_f = 1.62, which is in good agreement with that of the two-dimensional DLA model D_f = 5/3. In the plots at 8T a dimension crossover is seen with increasing the box size; D_f = 1.69 at short scales and $D_f \sim 2$ at long scales.

The crossover in the fractal dimension was reported by Meakin in Monte Carlo

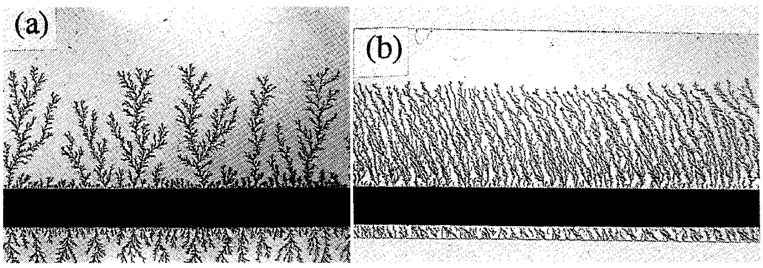

Fig. 6. Growth pattern of the silver metal forest from a 0.075M $AgNO_3$ aqueous solution in magnetic fields (a) 0T, (b) 8T. The width of ribbon is 3mm.

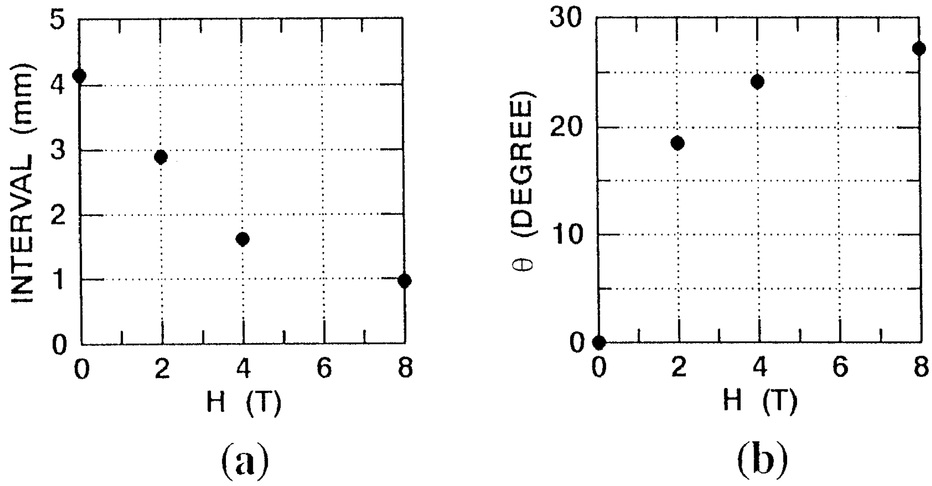

Fig. 7. The plots of (a) the averaged interval of main branches and (b) the averaged tilt angle θ of main branches vs. the magnetic field; θ is defined as the averaged tilt angle of the main branches from the vertical.

simulations of DLA with unidirectional particle drifts. He showed that the fractal structure with $D_f = 5/3$ remains on short scales in dense pattern grown with particle drifts. A similar result was observed in the metal-leaf at 8T. The log-log plots of N(r) vs. r on short scales are on a straight line with the descending slope of 1.69, as can be seen in Fig. 5. This indicates that the DLA-like fractal structure is present on short scales even in the dense branching pattern.

To demonstrate the magnetic field dependence of the distance between main branches, a silver metal-forest was grown around a copper ribbon ($3x50x0.02mm^3$) from a 0.075M $AgNO_3$ solution for 120 minutes, as shown in Fig. 6. A typical DLA pattern, which has an open and random structure, is observed in the absence of magnetic field(Fig. 6(a)). The growth pattern of the metal-forest in the magnetic field becomes dense and leaning, and the growing interface of the metal-forest is smooth(Fig. 6(b)). The fractal dimension D_f was estimated by the box-counting method; $D_f = 1.62$ at 0T, $D_f = 1.70$ at 8T. In the case of 8T, the crossover in the fractal dimension was observed at approximately 1mm from $D_f = 1.70$ on short scales to $D_f \sim 2.0$ on long scales. The interval and tilt angle of main branches depend on the magnetic field, as shown in Fig. 7. The interval of the main branches decreases with increasing magnetic field(Fig. 7(a)). The averaged tilt angle of the main branches from the vertical becomes large as the field is higher(Fig. 7(b)).

Saito and Uwaha[9] simulated the effect of a unidirectional lateral flow on aggregation growth from a lattice gas, and found that the lateral flow leads to canting branches. However, the dense pattern does not appear, because the diffusion length of particles can not be changed by the lateral flow. Thus, the dense and canting pattern at 8T suggests the MHD drift is not a simple lateral drift but it has the effect reducing the diffusion length. This probably arises from the Lorentz force that acts on the elementary movement of each ion, so that the MHD drift is not unidirectional. From the analysis of the fractal dimension we found that the interval length of the main branches at 8T corresponded to the crossover length of the fractal dimension. This fact indicates that the growth pattern is regarded as a uniform structure on scales longer than the interval length.

In conclusion, the drastic change in the growth morphology of the electroless deposition in magnetic fields is ascribed to the MHD effects. The spiral or canting branches are caused by the lateral drifts of the Lorentz force acting on the diffusion of silver ions. On the other hand, the MHD drifts make the diffusion length shorter and reduces the screening effect. As a result, the metal-leaf grows into a dense branching morphology. The analysis of the fractal dimension indicates that the DLA-like fractal structure remains on short scales even in the dense branching structure.

Acknowledgments

The authors wish to thank Dr. Uwaha of Nagoya University for valuable discussion. They are also indebted to the members of the High Field Laboratory and the Cryogenic Center of Tohoku University for operating the superconducting magnet. This work was supported in part by Grant-in-Aid for Scientific Research of Ministry of Education, Science and Culture, and the Asahi Glass Foundation.

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