Communication—Visualization of Magnetohydrodynamic Micro-Vortices with Guanine Micro-Crystals

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Aogaki proposed the concept of micro-MHD vortices in the MED processes and observed micro-circle structures on the MED film surfaces,[7] which strongly suggested the existence of micro-MHD vortices. However, the direct observation of micro-vortices has never been conducted, even though they could play significant roles for the chiral surface formation and catalytic properties. Thus, we have tried the visualization of micro-MHD vortices by using guanine micro-crystals as a tracer, which have highly light-reflective platelet forms.[8] Here we report the trace of micro-MHD vortex motion in the silver MED processes.

Experimental

The MED of silver was conducted in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd.), which can generate magnetic fields of up to 5 T in a room-temperature vertical bore with a diameter of 220 mm. The configuration of the electrochemical cell in the magnet is schemed in Figure 1. The cell was composed of conventional three electrodes; a working electrode (WE) of a Pt disc with a diameter of 3 mm (ALS-Japan Co. Ltd.), a counter electrode (CE) of a Pt wire ring with a diameter of 10 mm and a reference electrode (RE) of a Ag wire. The WE was placed at the center of the magnet bore, and the magnetic fields were imposed perpendicularly to the WE surface. The distance between WE and CE was 10 mm, where the inhomogeneity of magnetic field is less than 1%. In the case of metal electrodeposition, the configuration with downward WE surface could suppress gravitational convections arising from the concentration gradient around the electrode. Temperature within the magnet bore was controlled at 25°C by the circulation of thermoregulated water.

The electrolytic solution was a 50 mM (M = mol dm⁻³) AgNO₃ aqueous solution containing 0.1 M NaClO₄ as a supporting electrolyte. Guanine micro-crystals were employed as a fluid tracer, and its amount was approximately 600 cm⁻³. The guanine micro-crystals were prepared from scales of a goldfish, Carassius auratus, and the preparation details were described elsewhere.[9] The micro-crystals were platelets, the average dimension was 5 × 15 × 0.07 μm². The platelet face is the (102) crystal face, which exhibits high reflectivity for visible light.[10] Moreover, the platelet form prevents the crystals from sedimentation, resulting in sufficient dispersion in the electrolytic solutions during the MED processes. Owing to such specific features, guanine crystals could serve as a good tracer for fluid observation.

The fluid motion was observed by means of a digital microscope (AnMo Electronics, Dino-Lite Premier 2SLWD) with a zoom lens and a LED light source, which was placed just below the electrochemical cell within the magnet bore. The focus depth of zoom lens is at most 2 mm, thereby the observation of guanine particles was limited to the layer with 2 mm-thickness from the electrode surface. The movie data were transferred to a personal computer and converted to a negative film form in order to display the guanine particles clearly. To follow the trace of a certain particle, the still images were captured at every 207.241.231.83

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Using guanine micro-crystals with light-reflective surfaces as a fluid tracer, magnetohydrodynamic (MHD) flows were visualized in silver electrodeposition under a magnetic field of 2 T. The trace of a guanine particle showed macroscopic MHD laminar flows at a low deposition current of 50 μA. On the contrary, at a high current of 200 μA, the trace exhibited a zigzag walk and vortex motion with the sizes of 100 ~ 500 μm. This behavior demonstrates the existence of micro-MHD vortices that play a crucial role in chiral surface formation.

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Figure 2. Trace of a guanine particle (yellow dot) in the Ag MED under the magnetic field of 2 T; (a) at every 0.2 s with the deposition current of 50 μA; (b,c) at every 0.1 s with the deposition current of 200 μA: (b) micro-circular motion in the whole electrode image: (c) a zigzag walk before the micro-circular motion. Arrows represent the moving direction of particle.

Results and Discussion

The electrodeposition was conducted with a galvanostatic mode under magnetic fields. Appropriate conditions for the flow observation were explored by varying deposition current and magnetic field. Figure 2a shows trace of a particle at the deposition current of 50 μA under the magnetic field of 2 T, where the particle is marked at every 0.2 s by yellow dots. In this MED condition, a macroscopic rotating flow was observed over the whole electrode. The rotation center almost corresponded to the electrode center, and the rotating motion was a laminar flow. The guanine particle was carried on this rotating flow with a frequency of 0.1–0.2 Hz. Such a macroscopic flow is the vertical MHD flow arising from the Lorentz force at the electrode edge. Figure 2a shows that the vertical MHD flow is dominant in this MED condition.

On the other hand, a larger deposition current caused complicated motions of guanine particles. Figure 2b shows the trace of a particle at the current of 200 μA under the magnetic field of 2 T, where the particle was captured at every 0.1 s. The particle moves on small circles with the diameters of approximately 200 μm, and then it is carried on the macroscopic MHD flow. Similar micro-circular motion with the sizes of 100 – 500 μm was observed in a lot of guanine particles. In the MED process, such micro-circular motion must be the micro-MHD vortex. The micro-MHD vortices were observed in the higher current range of 200–400 μA. This fact suggests that the increase of flow velocity causes instability in the vertical MHD flow and such instability promotes the non-equilibrium fluctuation on the deposit surface, leading to the micro-MHD vortices.

More precise motion of the guanine particle around the micro-circle is depicted in Figure 2c, where arrows represent the moving direction of particle. It is surprising that the guanine particle exhibits a zigzag walk before reaching to the micro-circle. Such a zigzag walk was observed in the movement of almost all guanine particles. Figure 3 shows the most feasible scheme for the zigzag walk: A lot of micro-MHD vortices with sizes less than 100 μm are excited around bumps on the deposit surface. The guanine particle could be trapped or bounced back by the micro-MHD vortices, resulting in the zigzag walk.
Figure 4. Inhomogeneous pattern formation of guanine fine particles with the sizes of approximately 1 μm. The MED condition is the same as that in Figure 2b. Yellow circles represent guanine “holes” and red ones represent “clouds”.

zigzag walk. Hence, the zigzag walk strongly suggests the existence of the micro-MHD vortices with μm scales. Such micro-size vortices could affect the formation of screw dislocations and cause the surface chirality of the MED films. The results in Figures 2b and 2c indicate that the multi-size micro-MHD vortices exist simultaneously under the macroscopic vertical MHD flow. A higher resolution microscope and a high-speed video camera would be necessary for the direct observation of μm-size MHD vortices.

The MED using fine guanine crystals with the size of approximately 1 μm was also conducted under the same condition as that in Figure 2b, where the movement of each particle was not detected and the fine particles looked like “fog”. The fog was homogeneous before the start of MED. In the elapse of time, the fog became inhomogeneous, several holes emerged, and several parts became cloudier. Figure 4 shows inhomogeneous distribution of the fine particles at the elapse time of 50 s, where yellow circles represent guanine holes and red ones represent clouds. This inhomogeneous pattern disappeared after the stop of MED.

Inhomogeneous pattern formation in convections is well known in the Rayleigh-Benard convection, where small vortex cells form self-organized states. Similarly, the inhomogeneous pattern in Figure 4 implies the self-organized state of the micro-MHD vortices, some of which possess upward flow components and others of which possess downward ones. The presence of such vortex cells strongly support the zigzag-walk scheme in Figure 3.

**Summary**

We have demonstrated the visualization of micro-MHD vortices in the MED of Ag films using guanine micro-crystals as a tracer. At the deposition current of 200 μA, the trace of a certain guanine particle exhibits zigzag walk and then vortex motion with the sizes of 100 ~ 500 μm. This indicates the coexistence of multi-scale micro-MHD vortices with the sizes from less than 100 μm to 500 μm. The MED with fine guanine particles exhibits inhomogeneous pattern formation, which implies the self-organized state of the micro-MHD vortices, leading to the zigzag walk of guanine particles. These results are of great significance for the elucidation of chiral surface formation and the preparation of chiral catalysts. We have also demonstrated that the guanine micro-crystals collected from fish scales serve as a powerful tracer for fluid observations.

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