

Effects of Vertical MHD Flows and Cell Rotation on Surface Chirality in Magneto-electrodeposition

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Abstract

The combination of vertical MHD flows and micro-MHD vortices can produce chiral surfaces in magneto-electrodeposition (MED) of metals. Here we show two effects on the chiral surface formation in MED of copper. The first one is the effect of perturbation of vertical MHD flow using a tube wall around the electrode. The MHD flow penetrated into the tube and affected the chiral surface formation, as a result, the surface chirality depended on the height of wall. The other is the effect of rotation of electrochemical cell in magnetic fields. The rotational direction allowed the control of surface chirality.

Key words : magneto-electrodeposition, micro-MHD vortex, vertical MHD flow, chirality, rotation, amino acid

Introduction

Chiral surfaces of materials can serve as enantioselective catalysts, which are of great significance in pharmaceutical industries. Magneto-electrodeposition (MED) produces chiral surfaces on metal films, and such films exhibit chiral recognition of amino acids [1-5].

When a magnetic field is imposed perpendicularly to a working electrode surface, the Lorentz force generates two types of MHD convections around the electrode [6,7]. One is a macroscopic vertical MHD flow around the electrode edge, the other is a micro-MHD vortex around a local bump on the deposit surface. The latter affects the numbers of right- and left-handed screw dislocations, leading to chiral surfaces. We have examined the chiral surface formation in the MED of copper with various conditions. The results showed that the surface chirality depends on several parameters, such as magnetic fields, deposition currents, electrode diameters and the specific adsorption of chloride ions [2-4]. In this study, we have investigated the effects of vertical MHD flow and cell rotation on the chiral surface formation of MED copper films.

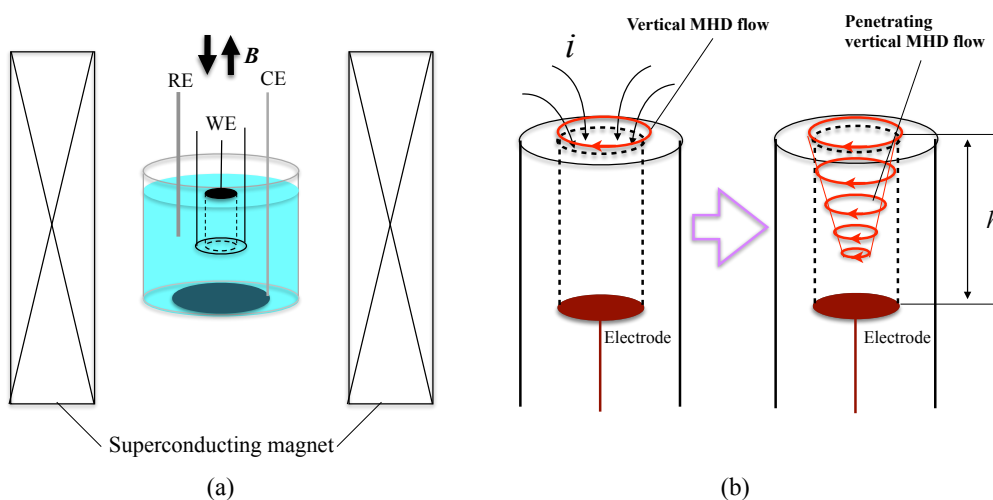


Fig. 1. (a) Schematic of magneto-electrodeposition in a superconducting magnet. WE; a Pt working electrode, CE; a Cu counter electrode, RE; a Ag/AgCl reference electrode. The WE is embedded in a Teflon tube with the wall height h of up to 12 mm. (b) Schematic of the vertical MHD flow in the tube. The MHD flow is generated around the entrance (left) and then it penetrates into the tube (right).



Effects of vertical MHD flow

The vertical MHD flows have asymmetric influence on the micro-MHD vortices [7]: The cyclonic micro-MHD vortices are stable, whereas anticyclonic ones become unstable. In order to examine the effects of vertical MHD flows, the MED of Cu films was conducted on a working electrode embedded in a Teflon tube, where the tube wall could be expected to suppress the vertical MHD flow.

The electrochemical cell was placed at the bore center in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd.), which generated a magnetic field of 5 T, as shown in Fig.1a. The applied magnetic field was parallel (+5 T) or antiparallel (−5 T) to the faradaic current i . The cell consists of conventional three electrodes: a polycrystalline Pt disc working electrode with a diameter of 3 mm (ALS Co. Ltd.), a Cu plate counter electrode, and a Ag | AgCl | 3 M (M = mol dm^{−3}) NaCl reference electrode. The working electrode was embedded in a Teflon tube, whose length was varied from 2 to 12 mm. The Cu films were electrodeposited up to the passing charge of 0.4 C cm^{−2} (the thickness of ~150 nm) on the working electrode via the potentiostatic electrodeposition at constant potentials of −0.05 – −0.45 V in a 50 mM CuSO₄ aqueous solution containing 0.5 M H₂SO₄. The films prepared in a magnetic field of +5 T or −5 T are termed the +5T-film or the −5T-film, respectively. In this configuration, the vertical MHD flow is generated around the tube entrance (Fig. 1b left), and then it could penetrate into the tube with damping (Fig. 1b right). Thereby, the influence of vertical MHD flows on the MED film surfaces depends on the height of tube wall h .

The surface chirality of MED films was examined by the measurements of voltammograms of alanine enantiomers (20 mM) on the MED film electrodes in a 0.1 M NaOH aqueous solution. To evaluate the chirality in voltammograms, an enantiomeric excess (ee) ratio can be defined as $ee = (i_p^L - i_p^D) / (i_p^L + i_p^D)$, where i_p^L and i_p^D represent the peak currents of L- and D-alanines, respectively. The positive sign of the ee ratio represents L-activity, and the negative one represents D-activity.

Figs. 2a and 2b show the ee ratio profiles of the +5T-film and −5T-film electrodes prepared without tube wall at various deposition potentials. The +5T-film exhibits D-activity in the small overpotential region around −0.1 V, and then L-activity in the larger overpotentials around −0.4 V (Fig. 2a). On the contrary, the −5T-film exhibits L-activity around −0.3 V and D-activity around −0.4 V. These results demonstrate that the chiral sign depends on both the

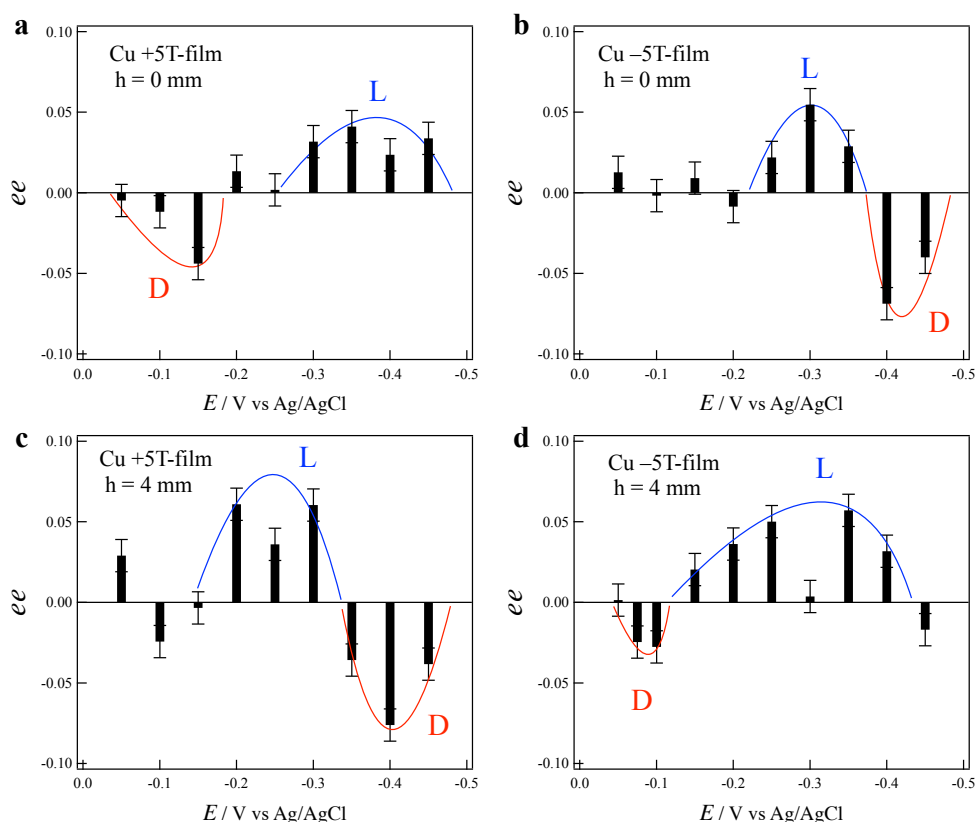


Fig. 2. The ee ratio profiles versus the deposition potentials. **a**: the +5T-film electrode without wall ($h = 0$ mm), **b**: the −5T-film electrode without wall, **c**: the +5T-film electrode prepared with wall at $h = 4$ mm and **d**: the −5T-film electrode with wall at $h = 4$ mm.

deposition potential and the polarity of magnetic field.

Our previous paper [4] showed that the surface chirality of MED Cu film depends on the deposition current in the galvanostatic MED. This current dependence of the chirality is due to the difference in the rate-determining step of the MED process. The potential dependence of the chirality in Figs. 2a and 2b can be similarly understood. The change of rate-determining step in Cu MED at 5 T occurs around -0.3 - -0.4 V [4], the electrode process is a kinetic-controlled at more positive potentials and mass-transfer-controlled at more negative potentials. Such a change in the rate-determining step corresponds to that in the chiral signs of MED films.

On the other hand, the magnetic-field-polarity dependence of chiral sign is easily understood by considering the direction of vertical MHD flow. As mentioned before, under the vertical MHD flow, the cyclonic micro-MHD vortices becomes stable, and the anticyclonic ones becomes unstable [8]. The reversal of magnetic field polarity reverses the vertical MHD flow and thus changes the chiral signs of the MED films.

Figs. 2c and 2d show the *ee* profiles of the +5T-film and -5T-film electrodes prepared with the tube wall at $h = 4$ mm. It is surprising that the *ee* profile of the +5T-film (Fig. 2c) is almost the same as that of the -5T-film without wall (Fig. 2b), and the profile of the -5T-film (Fig. 2d) is the same as that of the +5T-film without wall (Fig. 2a). These facts imply that the vertical MHD flow around the electrode surface at $h = 4$ mm is opposite to that without wall. Fig. 3 shows a possible scheme for such reversal of vertical MHD flow. When the vertical MHD flow penetrates into the tube with damping and its front would reach near the electrode surface, the reverse flows could be caused around the penetrating MHD flow such that the adjoining flows never conflict with each other. The effects of tube wall were examined with taller walls. The surface chirality almost disappeared at $h = 12$ mm, indicating that the penetrating MHD flow could not reach the electrode surface. These results demonstrate that the vertical MHD flow plays significant roles in the chiral surface formation and that the tube wall around the electrode would be useful for the control of surface chirality.

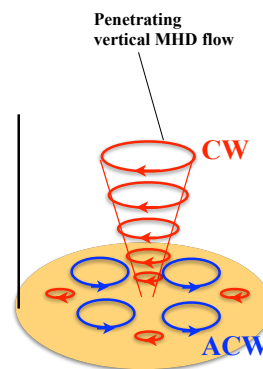


Fig. 3. Schematic of the reversal of the vertical MHD flow near the electrode surface in the tube wall.

Effects of cell rotation

The rotation of electrochemical cell in magnetic fields could break the symmetry of micro-MHD vortices through the Coriolis force, producing chiral surfaces [7,9]. We have conducted such rotational MED experiments and examined the surface chirality of the MED copper films.

The electrochemical cell was rotated in the bore of a cryocooled superconducting magnet, and the magnetic field is imposed perpendicularly to the working electrode embedded in a tube ($h = 20$ mm). Clockwise (CW) and anticlockwise (ACW) rotations were generated by a geared motor with a frequency of 4 Hz.

Figs. 4a and 4b show the voltammograms of alanine enantiomers on the +5T-film electrodes prepared in the CW and ACW rotations, respectively. The CW-film exhibits D-activity, and the ACW-film exhibits L-activity. This result indicates that the cell rotation allows control of the surface chirality of MED films.

On the other hands, the comparison between the voltammograms of the same enantiomer on CW- and ACW-film electrodes shows the influence of the rotational direction on the chiral site formation. Fig. 5a shows the voltammograms L-alanine on the -5T-film electrodes prepared with CW and ACW rotations, and Fig. 5b shows the voltammograms D-

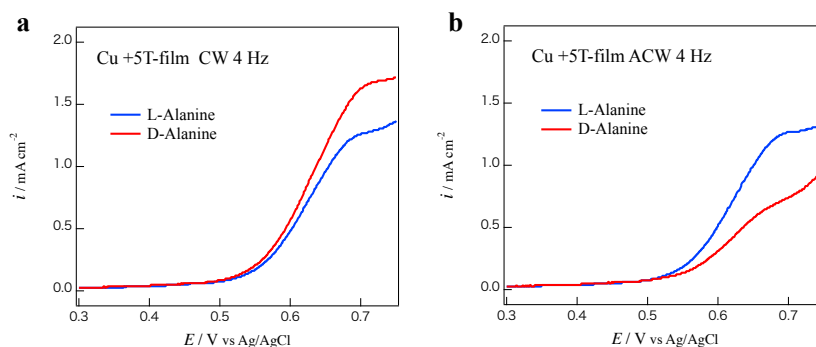


Fig. 4. Voltammograms of L- and D-alanines on the Cu +5T-film electrodes prepared in rotational MED at 4 Hz. **a**: the CW-film electrode and **b**: ACW-film electrode.

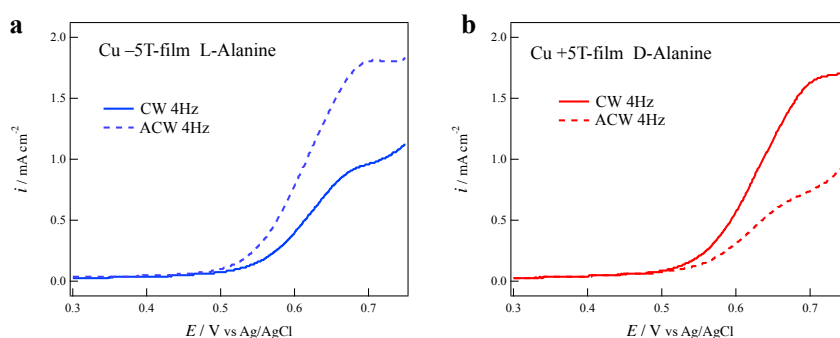


Fig. 5. Voltammograms of alanine on the CW-film and ACW-film electrodes prepared in the rotational MED at 4 Hz. **a**: L-alanine on the $-5T$ -film electrode, **b**: D-alanine on the $+5T$ -film electrode.

alanine on the $+5T$ -film electrodes with CW and ACW rotations. In Fig. 5a the ACW-film exhibits greater currents of L-alanine than the CW-film. This means that in $-5 T$ the ACW rotation increases the number of L-chiral site and the CW one decreases it. On the contrary, Fig. 5b exhibits that in $+5 T$ the CW rotation increases the number of D-chiral site and the ACW one decreases it. These results demonstrate that there exists beautiful symmetry among the magnetic field polarity, rotational direction and surface chirality. Hence, the rotational MED could be a useful tool for the control of surface chirality of metal films.

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