Effects of Gravitational Level & Magnetic Field Flux on Electrochemical Processing

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ABSTRACT : Silver was electrodeposited in AgNO$_3$ aqueous solution confined in a quasi-two-dimensional electrolytic cell. Ag$^+$ ion concentration profile in the electrolyte solution layer was visualized by a holographic interferometer The measured surface concentration of Ag$^+$ ion decreased much slower than the expected value based on the transient diffusion model. Then, the numerical analysis was conducted in order to quantitatively analyze the ionic mass transfer rate enhanced by a kind of natural convection induced even in such a shallow electrolyte layer. The effect of electrolytic cell height on the induction of natural convection was also analyzed. Furthermore, silver nucleation phenomena onto HOPG substrate were examined. The effect of gravitational level on nucleation phenomena was quantitatively analyzed. The aim of this work is to clarify the effect of gravitational strength both on ionic mass transfer rate in the electrolyte and the metal crystallization process. Based on these data, the research to utilize different gravitational level and magnetic field to the electrochemical processing is proposed.

1. Introduction

Electrodeposition is focused in the fields of electrocatalysis , microelectronics and recently in producing nanostructured and dispersed materials. Ii is indispensable to understand the coupling behavior between ionic mass transfer rate and morphological variation of the electrodeposited film in order to design a highly tailored interface or nanostructured devices.

Industrial electrochemical science and technology have made a great progress with the development of the study of the ionic mass transfer phenomena. Wagner [1] analyzed that the natural convection along the vertical plane cathode installed in unstirred electrolyte solution. Since then, numerous works have been carried out both theoretically and experimentally with laser interferometry technique, to obtain qualitative and quantitative information [2, 3, 4].

Based on the *in-situ* measurements, the importance of natural convection during electrodeposition and its effects on the morphological variations of electrodeposits has been recognized. We have investigated the coupling behavior between the ionic mass transfer rate and the morphological variation accompanying the electrodeposition of metal with holographic interferometer. The concentration profile of ions and the natural convection velocity of the electrolyte solution were *in-situ* measured.

Because it is impossible to avoid the natural convection in normal gravity environment, we have carried out the experiments in microgravity environment with a drop tower in order to phenomenologically understand the electrodeposition and electrodissolution processes under microgravity [5, 6, 7]. The effect of gravitational acceleration level to the ionic mass transfer rate was analyzed. Furthermore, Fukunaka et al. [6] confirmed the effect of gravitational level to the morphology of electrodeposits. They proposed that the gravitational level may influence the electrochemical nucleation related phenomena.

In this paper, the experiments and numerical analysis on the silver electrocrystallization and nucleation phenomena in AgNO$_3$ aqueous solution are reviewed. The coupling behavior between ionic mass transfer rate and morphological variation of the electrodeposited Ag film is focused.

2. Silver Electrodeposition in Quasi Two-D Cell -- Coupling Phenomena between Ionic Mass Transfer Rate and Morphological Variations [8]

Silver was electrodeposited in 250 μm thick AgNO$_3$ solution layer confined in a horizontally installed quasi-two-dimensional electrolytic cell. Ag$^+$ ion concentration profile around silver dendrite arms

electrodeposit ed on a periphery of circular disc cathode with 3 mm in diameter and 90 μm thick was visualized by a holographic interferometer (Figure 1). Ag was uniformly precipitated around a circular cathode during the initial stage of electrodeposition. SEM pictures showed that these precipitated grains appeared to form a coagulated layer with the critical thickness. Then, several dendrites started to preferentially grow on some precipitates at the surface of coagulated layer after a certain incubation time. The ionic mass transfer rate associated with the electrodeposition in stagnant electrolyte has been described by the transient diffusion equation incorporated with the migration effect. The numerical solution of surface concentration of Ag^+ ion is shown by the dotted lines in Figure 2 with measured surface Ag^+ ion concentration. It is noted that the surface Ag^+ ion concentration apparently decreased with time much slower than the transient diffusion model. The ionic mass transfer rate must be enhanced by a kind of natural convection layer.
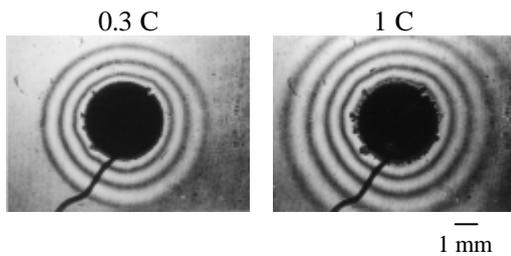
Figure 1. Effect of amount of electricity on interference fringe pattern and morphological variation of silver films. (3 M AgNO3, 1.5 A cm^{-2})
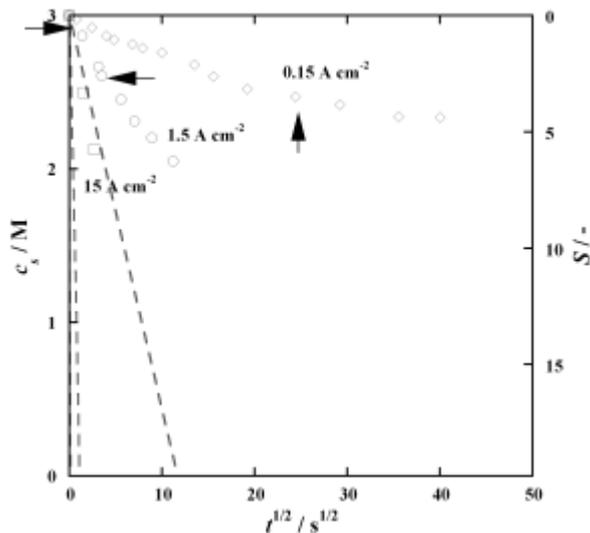
Figure 2. Time variation of surface concentration of Ag+ ion and transient behavior of interference fringe numbers appearing around a cathode surface.
(3 M AgNO3, dotted line = Calculated surface concentration)

3. Numerical Analysis of the Rate of Ionic Mass Transfer of Ag^+ Ion [9]

The ionic mass transfer rate was numerically analyzed in the axi-symmetric cylindrical coordinate system. The transient behaviors of the convective flow pattern as well as the concentration profile in the cell were simulated. The calculated radial expanding rate of the interference fringe pattern was reasonably compared with the observed one (Figure 3). Based on the present numerical analysis, the concentration of Ag^+ ion at the cathode surface, when the dendrite precursors started to significantly grow, was converted to the critical concentration overpotential.
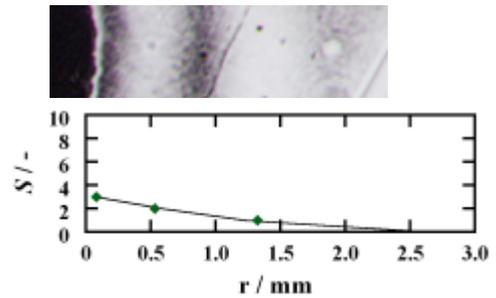
Figure 3. Comparison of observed interference fringe pattern with calculated one at 0.3 C. (3 M AgNO3, 0.15 A cm^{-2})

4. Effect of the Cell Height on the Induction of Natural Convection and the Ionic Mass Transfer Rate [10]

As described above, it is quite difficult to restrict the induction of natural convection in the normal gravity environment even in the cell with 250 μm high. A kind of natural convection is inevitably induced even in such a thin electrolyte layer, as long as the present design of electrolytic cell is employed in the normal gravitational field.

Natural convection is governed by the Rayleigh number (*Ra*), a product of Grashof number (*Gr*) and Schmidt number (*Sc*). The *Gr* number is a function of x^n, where n depends on the electrolytic conditions of limiting current density (*n* = 3) and uniform current density (*n* = 4). Thus, a shorter electrode may provide a less possibility for natural convection to be induced inside an electrolytic cell.

In this section, the numerical analysis of the ionic mass transfer rate in a quasi-two-dimensional electrolytic cell with shorter electrode and cell height. The effect of electrolyte height on the induction of natural convection and ionic mass transfer rate was examined.

Figure 4 shows the time dependence of Ag^+ ion concentration profile with different electrolytic cell height, where the both an electrode and a cell height are the same. After starting electrodeposition, the surface concentration of

Ag$^+$ ion decreases and the concentration boundary layer propagates into the bulk electrolyte. A symmetrical distribution of concentration profile of Ag$^+$ ion along the x – direction is confirmed for 25 µm cell height, while a kind of tongue shape profile near the upper edge of the cathode is seen and diluted electrolyte starts to flow along the upper slide glass at 4 seconds for 250 µm height. Ag$^+$ ion concentration around the lower edge of the cathode is still very close to the bulk solution, since the fresh electrolyte eddy circulates toward the lower part of electrode surface. The calculated velocity profile shows a stagnant zone existing inside a convection loop with an ellipsoid shape.
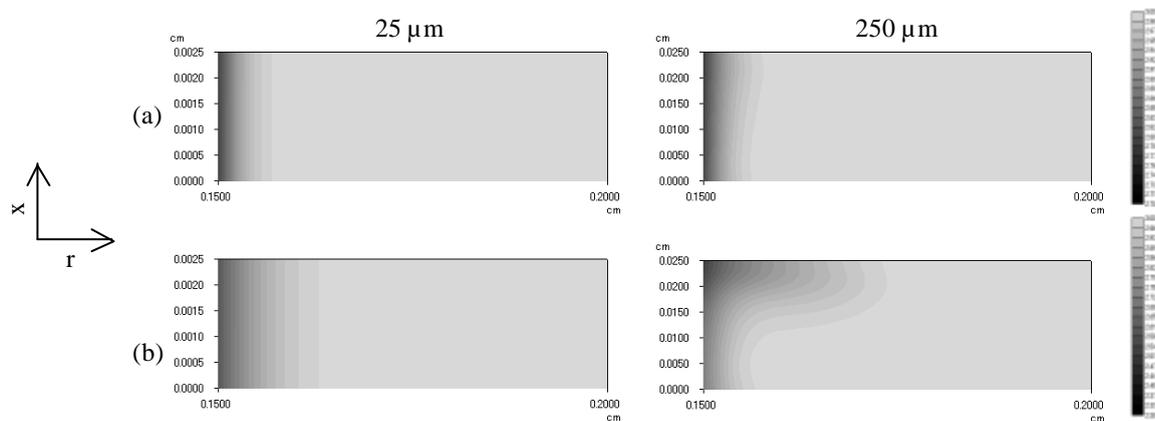
Figure 4. Time dependence of Ag+ ion concentration profile with different electrolytic cell height, (a) 1 second, (b) 4 seconds. (3 M AgNO$_3$, 0.15 A cm^{-2})

5. Effect of Gravitational Level on the Nucleation Phenomena of Electrodeposited Silver [11]

Fukunaka et al. [6] proposed that the gravitational level might affect the electrochemical nucleation related phenomena. Morisue et al. [l2] examined the effect of gravitational level to copper nucleation phenomena on TiN substrate. The nucleus number density decreased with decreasing the gravitational level.

In the present study, silver electrodeposition onto HOPG substrate was carried out. The aim is to clarify the effect of gravitational strength on nucleation phenomena in 1-G terrestrial as well as high gravity environment.

Silver was potentiostatically electrodeposited on HOPG substrate at various applied potential *vs.* Ag reference electrode from 0.05 M AgNO$_3$ solution. HOPG substrate was installed in a cavity-type electrolytic cell, which has been already illustrated in [12]. The electrolysis was conducted in cathode over anode (C/A) and anode over cathode (C/A) configurations. The amount of electricity was restricted at 15.9 mC cm^{-2}.
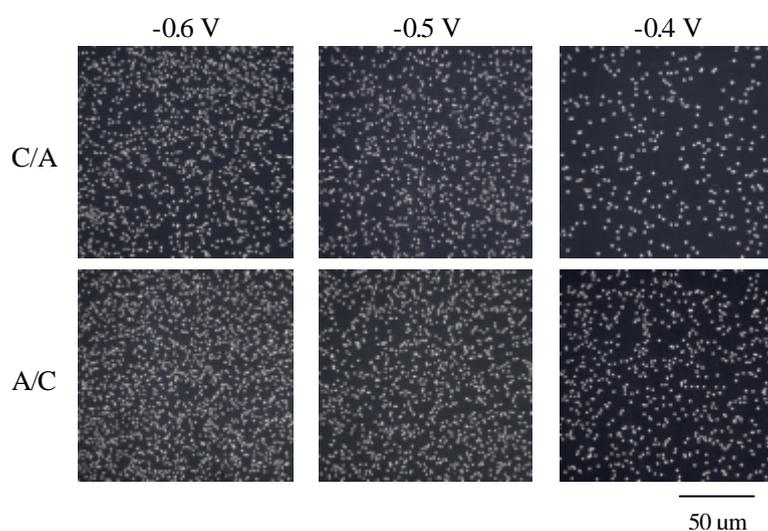
Figure 5. SEM images of silver nuclei on HOPG substrate and the applied potential dependence of the nucleus density.
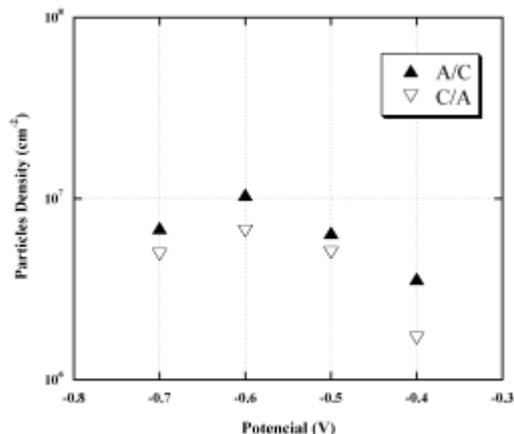
Figure 5 shows SEM images of silver nuclei electrodeposited on HOPG substrate and the applied potential dependence of the nucleus density calculated in 140 μm x 140 μm SEM images. The images in the upper row are the samples electrodeposited in C/A configuration and those in the lower are for A/C configuration. Apparently, silver nuclei are randomly distributed on HOPG surface and the nucleus densities are in the range of 10^6 to 10^7 cm^{-2}. An exponential dependence of the nucleus densities on the applied potential are recognized from -0.4 to -0.6 V, however, in the case of -0.7 V the smaller nucleus density was noticed than in the case of lower applied potential. The reproducibility must be further examined. A higher nucleus density was obtained in A/C than in C/A configuration, which was similar to the previous study with TiN substrate. Spatial distribution of the nuclei was also quantitatively analyzed [13].

The effects of high gravity environment using a centrifugal machine were also examined, although detailed results are not demonstrated here. Higher number density was noticed at higher gravitational level.

6. Summary

The effects of gravitational strength and magnetic field both on the coupling phenomena between the ionic mass transfer rate and the metal crystallization process are focused.

By applying different gravitational level and high magnetic field to the electrochemical processing, we can fabricate the shape-controlled nano-sized morphology or functional thin films. The different cell configuration, the gravitational level realized with a centrifugal machine and a high magnetic field influenced the nucleation number density of Cu or Ag.

In order to obtain the deeper understanding of the effect of gravitation strength on the electrochemical processing, the systematical experiments is necessary both in microgravity environment using a drop tower or an aircraft and high gravity environment using a centrifugal machine.

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