Journal of Electroanalytical Chemistry 744 (2015) 25–31

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Deposit structure and kinetic behavior of metal electrodeposition under enhanced gravity-induced convection

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ARTICLE INFO

Article history:
Received 21 November 2014
Received in revised form 28 February 2015
Accepted 3 March 2015
Available online 5 March 2015

Keywords:
Metal electrodeposition
Convection
Gravity
Limiting current density
Diffusion layer thickness

ABSTRACT

Gravity-induced convection has significant effect on mass transport during metal electrodeposition. The effects of gravity-induced convection on deposit structure and kinetic behavior of metal electrodeposition were studied. It was found that copper powders and copper foils were easily electrodeposited by inhibiting and enhancing gravity-induced convection, respectively. Current efficiency was also increased from 31.5% to 92.7% due to enhancing gravity-induced convection. Double logarithm relationships between limiting current density (i_d) and gravity coefficient (G) for both copper and nickel electrodeposition were obtained at various metal ion concentrations. It was confirmed that diffusion coefficient was about 2.25–3.47 $\times$ 10^{-6} $cm^2\ s^{-1}$ and almost independent on gravity acceleration. However, diffusion layer thickness of copper electrodeposition in 0.01 M $CuSO_4$ solution was only 0.82 $\times$ 10^{-2} cm under G value of 354 due to larger flow velocity, and was much lower than that under normal gravity condition (3.41 $\times$ 10^{-2} cm). Therefore, mass transport of metal electrodeposition was promoted and limiting current density was enlarged by enhancing gravity-induced convection.

1. Introduction

Metal electrodeposition is basic reaction in electrochemical industries such as functional material preparation, electroplating, electrometallurgy and wastewater treatment [1]. Generally, electrochemical reduction of metal ions is carried out on two-dimensional planar electrode. Therefore, concentration gradient of metal ions is formed from electrode surface to bulk solution due to the consumption of metal ions, which leads to density difference for solution in the vicinity of electrode. As a result, the rate and efficiency of metal electrodeposition are decreased. The structure and properties of deposits are also changed.

It is well known that convection and diffusion are the series processes for mass transport. Forced convection by hydrodynamic agitation is a common method to enhance mass transport and has been studied widely. On the other hand, solution in the vicinity of cathode is light phase with low density due to low metal ion concentration, while bulk solution is considered as heavy phase with high density. Gravity-induced convection happens due to density difference to balance concentration gradient of metal ions [2]. That is, heavy phase moves along gravity direction, and light phase moves along the counter direction. However, few works were focused on the effect of gravity-induced convection on mass transport during metal electrodeposition.

Gravity-induced convection is controlled by interphase separation term, $\Delta\rho g$ [3]. Therefore, gravity acceleration (g) is an important factor to adjust mass transport and concentration difference during metal electrodeposition. Under earth gravity condition (g: 9.8 m s^{-2}), mass transport by gravity-induced convection in thin electrolyte layer of electrode surface is usually neglected due to low gravity acceleration. Recently, super gravity field attracted more and more attentions and has great effects on electrochemical reactions [3–8]. Under super gravity field, $\Delta\rho g$ is enlarged inevitably due to high gravity acceleration. Therefore, relative movement between heavy phase and light phase is inhibited or accelerated based on two extreme situations in Fig. 1 according to the direction of concentration reduction (i.e. electric field direction) and gravity. As shown in Fig. 1A, under opposite direction of gravity and concentration reduction, solution density increases along gravity direction and convection is inhibited, which is unfavorable to mass transport of metal ions. Otherwise, mass transport is enhanced by gravity-induced convection to eliminate concentration difference in Fig. 1B.

It is an interesting work to adjust concentration difference of metal ions by gravity-induced convection. In our previous papers,

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http://dx.doi.org/10.1016/j.jelechem.2015.03.003
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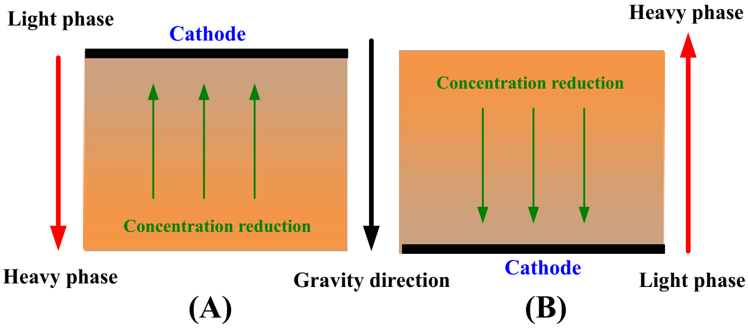

Fig. 1. The illustrations for two extreme situations of natural convection during metal electrodeposition.

amorphous NiW films with refined grains were electrodeposited under super gravity field and exhibited good catalytic activity for hydrogen evolution reaction [6]. The rate and efficiency of metal electrodeposition were also improved by enhancing gravity-induced convection [3,4,7,8]. Eftekhari [7] found that Cu electrodeposition rate was increased one times under gravity acceleration of 210 g (*g*: earth gravity acceleration, 9.8 m s^{-2}). Although the structure evolution of deposits and enhancement of metal electrodeposition by gravity-induced convection were confirmed, the effects of the relationship between gravity and concentration difference direction on metal electrodeposition were unclear. In addition, the kinetic of metal electrodeposition under enhanced gravity-induced convection was not studied. In this paper, Cu^{2+} and Ni^{2+} were used as model ions. The effects of gravity-induced convection on metal electrodeposition were studied based on the adjustment of gravity acceleration and action direction. The kinetic behaviors of metal ion reduction were analyzed quantitatively.

2. Experimental

High gravity acceleration was obtained by a centrifuge with a 250 ml electrolytic cell (Fig. 2). The equipment was similar with that reported in previous paper [6]. The electrolytic cell was horizontal under super gravity field (i.e. rotating), while vertical under normal gravity condition (i.e. not rotating). The electrochemical signals were transferred by the gold slip ring (EC 3848-10, MOOG Inc.) which was fixed on the top of axis. Gravity coefficient (*G*) was defined as the ratio of practical gravity acceleration and earth gravity acceleration (9.8 m s^{-2}). It was adjusted by rotating electrolytic cell with different speeds and was calculated as follows:

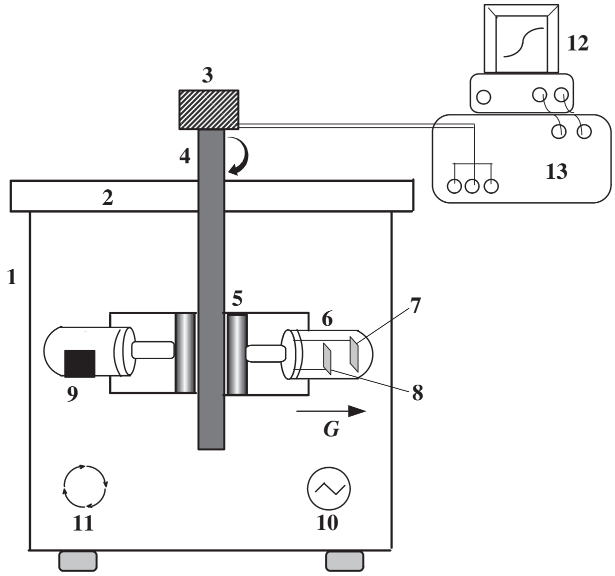

Fig. 2. Experimental equipment for metal electrodeposition under super gravity field. (1) Centrifuge; (2) lid of the centrifuge; (3) mercury slip ring; (4) axis; (5) rotating bracket; (6) electrolytic cell; (7) cathode; (8) anode; (9) counter part for balance; (10) control button; (11) revolution meter; (12) computer; (13) electrochemical working station.

$$G = \frac{\omega^2 L}{g} = \frac{N^2 \pi^2 L}{900g} \tag{1}$$

where *N* is rotating speed (rpm), *g* is earth gravity acceleration (9.8 m s^{-2}) and *L* is the distance between electrode center and axis, being 0.25 m in this experiment. *G* value is 1 under normal gravity condition.

The solution for Cu electrodeposition consisted of 62.5×10^{-3} mol L^{-1} $CuSO_4$ and 0.10 mol L^{-1} H_2SO_4. Pure copper plate with an area of 1.5 cm^2 and nickel foil with an area of 1.0 cm^2 were used as anode and cathode, respectively. The electrodeposition experiments with a current density of 0.15 A cm^{-2} were controlled by a WYK-3010 DC Power. The electrolytic time was 75 min. Copper products on cathode surface were collected completely and their morphologies were observed by SEM (JEOL, JSM6700F). Current efficiency η was calculated as following:

$$\eta = \frac{M}{qIt} \times 100\% \tag{2}$$

where *M* is the mass of copper products (g); *q* is electrochemical equivalent, 1.186 g $(A\,h)^{-1}$; *I* is current intensity (A); *t* is electrodeposition time (h).

All electrochemical measurements were carried out on CHI 760C electrochemical working station (CH Instrument, Inc.). Working electrode was glassy carbon electrode of 3.14 mm^2. Platinum foil and solid state electrode (GD-IV, Beijing Research Institute of Chemical Engineering and Metallurgy) were used as counter electrode and reference electrode, respectively. The potential of solid state electrode was 0.19 V vs SHE. Unless marked, the solution for electrochemical measurement consisted of 0.01 M $CuSO_4$ or $NiSO_4$ and 0.10 M Na_2SO_4. pH value was adjusted to 3. Cu^{2+}concentrations were examined using atomic absorption spectrometry (TAS-990, Beijing Purkinje General Instrument Co., Ltd). All chemical reagents were analytical grade. Fresh double-distilled water was used throughout.

3. Results and discussion

Generally, mass transport was controlling step for most of metal electrodeposition. When the concentrations of metal ions were enough low, limiting diffusion current density was reached due to the limitation of mass transport and metal powders were easily