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Nucleation and early stages of growth of lead onto copper electrodes from dilute electrolytes

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Abstract: The processes of nucleation and growth of lead from the dilute electrolytes on copper substrates were investigated by chronoamperometry and by scanning electron microscopic (SEM) analysis of the deposits obtained in the potentiostatic regime of electrolysis. In the dependence of electrodeposition conditions, the nucleation of Pb followed either progressive or instantaneous type. The type of nucleation changed from progressive to instantaneous one with increasing the concentration of Pb(II) ions and the overpotential of electrodeposition. Regardless of the type nucleation, a novel type of Pb particles like cobweb was formed by the potentiostatic electrodeposition in the moment of nucleation and at the early stages of growth. On the basis of the shape of cobweb-like particles and the electrodeposition conditions leading to their formation, these particles were situated in the group of spongy-like ones. Also, comparative morphological analysis of Pb deposits obtained in the conditions of progressive and instantaneous nucleation confirmed the existence of two limiting types of nucleation.

Key words: electrodeposition; lead; nucleation; growth; morphology; chronoamperometry

1 Introduction

Electrodeposition technique is very promising way to obtain metal at the micro or nano scale in the form suitable for application in various technologies. The desired morphology of electrodeposited pure metals or alloys is attained by the choice of regime and by easy control of parameters of electrolysis, such as current density or overpotential of electrodeposition, temperature of electrolysis, solution composition, type of working electrode, time of electrolysis, addition of additives [1−4]. Simultaneously, the morphology of metal deposits strongly depends on the nature of metals, and metals are usually classified in the dependence of values of the exchange current density and overpotential for hydrogen discharge on normal, intermediate and inert ones [5]. The similar effects of parameters of electrolysis on the surface morphology were observed during electrolysis from both the aqueous electrolytes and ionic liquids [6−8].

Lead (Pb) is the typical representative of normal metals which attracts both academic and technological attention thanking its specific characteristics, such as extremely high reactivity and superconductivity [9]. Due to these characteristics, Pb has found wide application as high purity active material for acid batteries [10], semiconductors [11,12] and in the fabrication of electrochromic devices [13]. The processes of Pb electrodeposition belong to the fast electrochemical processes because they are characterized by the extremely high exchange current density and high hydrogen overpotential discharge values. The main characteristics of these processes are fast charge-transfer step, formation of irregular deposits starting from relatively small overpotentials and the absence of obtaining of compact deposits without use of additives [1]. The electrolysis from the aqueous electrolytes is the most often used way to obtain Pb in the form suitable for some of above mentioned applications. The different electrolytes including both acid [14−18] and alkaline [19−21] ones are widely used for the processes of Pb electrodeposition. In the last time, electrolysis from choline chloride−urea deep eutectic solvents is also used to obtain Pb in the desired form [22,23].

In the dependence of conditions of electrolysis, Pb electrodeposition processes from aqueous electrolytes lead to the formation of both isotropic and anisotropic

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morphological forms, such as octahedrons, hexagons, twinned particles, wires, needle-like and honeycomb-like structures, as well as two-dimensional (2D) dendrites of different shapes (fern-like and tooth of saw ones) [9,15,16,24−29]. There was no any difference in Pb surface morphologies obtained by electrolysis from aqueous electrolytes and those obtained from deep eutectic solvents [22,23].

Chronoamperometry is widely often way to analyze the processes of nucleation and the early stages of growth. SCHARIFKER et al [30−32] developed the theoretical model enabling to determine the type of nucleation by comparison of the experimental data obtained by the analysis of the potentiostatic current transients with their model. The model proposed by SCHARIFKER et al [30−32] was based on the three-dimensional (3D) nucleation with diffusion-controlled growth and they predicted two limiting cases for nucleation processes: progressive and instantaneous. In the instantaneous nucleation, all nuclei are formed simultaneously at the very beginning of electrodeposition process, while in the progressive nucleation type the number of nuclei increases with time prolonging. This model is widely used for the analysis of nucleation/growth processes from both aqueous electrolytes [33−36] and deep eutectic solvents [37,38]. However, in these investigations, little attention is devoted to morphological analysis of deposits formed in the early stages of metal growth without clear correlation between the type of nucleation and the surface morphology. Considering the fact that the morphology is the most important characteristic of electrodeposited metal, in this study, we correlate the limiting types of nucleation with morphology of lead deposits formed in the moment of nucleation and at the early stages of growth.

2 Experimental

Lead was electrodeposited at the overpotentials of 25, 37.5, 50 and 62.5 mV from the following electrolytes: (a) 0.010 mol/L $Pb(NO_3)_2$ in 2.0 mol/L $NaNO_3$, (b) 0.030 mol/L $Pb(NO_3)_2$ in 2.0 mol/L $NaNO_3$, and (c) 0.045 mol/L $Pb(NO_3)_2$ in 2.0 mol/L $NaNO_3$.

All electrodepositions were performed in open cell at room temperature, using Autolab potentiostat/galvanostat PGStat 128N (ECO Chemie, The Netherlands). Electrodeposition of lead was performed on the cylindrical copper electrodes. The surface area of Cu electrodes was 0.25 cm^2. The reference and counter electrodes were of pure lead. The counter electrode was a lead foil with a surface area of 0.80 dm^2 that was placed close to the cell walls. The reference electrode was a lead wire of which the tips were positioned at a distance of about 0.2 cm from the surface of the working electrodes. The working electrodes were placed in the centre of cell, at the same location for each experiment. Doubly distilled water and analytical grade chemicals were used for the preparation of electrolytes for Pb electrodeposition.

Lead deposits electrodeposited from 0.010 mol/L $Pb(NO_3)_2$ in 2.0 mol/L $NaNO_3$ at overpotentials of 25 and 62.5 mV were characterized using a scanning electron microscope (SEM)−TESCAN Digital Microscope.

3 Results and discussion

3.1 Nucleation and kinetics of Pb electrodeposition processes

Figure 1 represents the potentiostatic current transients obtained in the Pb electrodeposition processes at overpotentials of 25, 37.5, 50 and 62.5 mV from 0.010, 0.030 and 0.045 mol/L $Pb(NO_3)_2$ in 2.0 mol/L $NaNO_3$ electrolytes. All shown the potentiostatic current transients represent the typical diffusion controlled ones characterized by the increase in the current density up to maximum and the sharp decrease until the limiting diffusion current density was reached. The increase in the current density corresponds to the process of nucleation and to the growth of existing nucleus, while the descending part corresponds to the linear diffusion to the planar electrode surface. From Fig. 1, it can be noticed that the decrease in the time corresponding to the maximum current density was observed with increasing the overpotential of electrodeposition.

The shape of the potentiostatic current transients clearly indicates that it is possible to apply a model proposed by SCHARIFKER et al [30−32] to determine the type of nucleation. For the determination of type of nucleation, the dimensionless dependencies $(J/J_m)^2-t/t_m$ were derived from the potentiostatic current transients and compared with the theoretical predictions for instantaneous:

$$\left(\frac{J}{J_m}\right)^2=\frac{1.9542}{(t/t_m)}\left\{1-\exp\left[-1.2564\left(\frac{t}{t_m}\right)\right]\right\}^2 \tag{1}$$

and progressive:

$$\left(\frac{J}{J_m}\right)^2=\frac{1.2254}{(t/t_m)}\left\{1-\exp\left[-2.3367\left(\frac{t}{t_m}\right)^2\right]\right\}^2 \tag{2}$$

nucleation and growth [30−32]. In this way, the dependencies shown in Fig. 2 are obtained from the potentiostatic current transients shown in Fig. 1.

In Eqs. (1) and (2), a time t_m corresponds to the maximum of current density (J_m) in the potentiostatic current transients. It can be seen from Fig. 2 that