



Modelling the dynamic growth of copper and zinc dendritic deposits under the galvanostatic electrolysis conditions



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ARTICLE INFO

Article history:

Received 29 December 2014

Received in revised form 1 April 2015

Accepted 22 April 2015

Available online 23 April 2015

Keywords:

Dendritic deposit

Zinc

Copper

Current efficiency

Phenomenological model

Empirical equation

Shell formation time

ABSTRACT

This paper investigates the process of crystallisation of the copper and zinc dendritic deposits under galvanostatic conditions on the rod electrode. The effect of the value of current and metal ion concentration in solutions on the growth dynamics of loose deposits is studied. It is shown that the current efficiency of the metal increases, and the growth rate decreases during the elongation of dendritic particles, and an increase in the surface area on which the electrocrystallisation takes place. Empirical equations for the quantitative description of changes in time of the lengths of the dendrites and the current efficiency of copper and zinc are proposed, which well approximate the experimental data obtained under various conditions of electrolysis.

A phenomenological model is worked out that helps to calculate the variation of structural parameters in time (the number and the radius of tips of the dendrite branches) of the loose deposit growth and to determine the moment of transition from a loose deposit to a compact one.

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1. Introduction

The metal electrocrystallisation mechanism, texture and morphology of deposits depend on the electrolysis conditions. In the creation of deep diffusion limitations on the delivery transport of the discharging ions to the cathode surface, it becomes possible to form a powdery dendritic metal structure characterised by high porosity [1]. The electrolytic deposits obtained through this method are used to prepare powders. Electrolytic powders have a highly-developed surface and a branched particle structure thus making it possible to use them in the preparation of parts by powder metallurgy (copper, iron and nickel), as a raw material in the manufacture of electrodes of chemical current sources (zinc, nickel etc.) and in the manufacture of metal-filled composite materials.

Methods for the quantitative description of the formation of dendritic deposits date back to the middle of the last century, when the classical works of Bockris, Diggle and Despić [2,3] to explain the growth of a dendrite branch by the spherical diffusion mechanism were released. There are many works dedicated to the influence of overpotential, electrolysis regime, concentration of the discharging ions and supporting electrolyte on the morphology of

loose deposits [4–11]. The model description of the electrocrystallisation of dendritic deposits was proposed by different authors for both potentiostatic [2,3,12,13] and galvanostatic electrolysis conditions [14–18].

The current which is applied to the electrode is not fully used for the growth of dendrites, as simultaneously with the reduction of metal ions, hydrogen gas production can be recorded. This fact was noted earlier [19,20] but researchers began to put special focus on it in later works [4–11,21]. In most studies [4–10] the current efficiency of hydrogen was determined by the volume of the gas evolved and taken into account in the form of a constant average value. There is an article by a group of scientists [11] who associate the fact of the dendrite formation (particularly zinc) with the presence of hydrogen bubbles on the deposit-branching mechanism. A detailed research of the current efficiency of copper was performed in the work by Murashova et al. [21], which introduced the 'differential current efficiency' concept. This value has been particularly important in the description of dendritic deposit formation for a long time since the differential current efficiency takes into account changes in the part of the current going to the metal discharge at each point in time.

The data on the number of the dendrite nucleation centres is quite important in modelling the growth of dendritic deposit. Most studies assume that the starting points of dendrite growth are the rough surfaces. As far as we know, the first work which attempts to determine the number of growing dendrites according

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to electrochemical measurements is work [21]. The authors studied the deposition of dendritic copper deposits in setting DC on a cylindrical rod cathode. They presented an equation for calculation of the number of growing tips per overall surface deposit unit (N), based on the data of dendrite length change and overpotential. However, this ratio does not take into account the fact that alongside the elongation of the dendrite branches, they are also thickening. This makes the value of N quite uncertain as part of the current, which is used for the metal ion discharge on the lateral faces of the dendrites, changes visibly as the deposit grows. In particular, from the practice of the electrodeposition of dendritic deposits in the galvanostatic mode, it is known that as long as the surface develops, the current density of the metal deposition decreases. This leads to a significant decrease in the dendrite elongation rate. Dendritic branches thicken and eventually separate branches merge into a solid deposit [18].

To describe the dendritic deposit formation from the very beginning to dendrite fusion into a compact deposits, we need data on potential and structure change in dendrites while growing. In addition, the quantitative dependencies describing all associated processes (the elongation of dendrites, tip radius, values of the differential current efficiency) are required. An analytical form of presentation is needed to extrapolate them for the time of the formation of the compact deposit. These phenomena have hardly been studied from the experimental point of view or in terms of their model description.

The general properties of the dendritic deposit growth can provide the basis for the construction of such a model. There are papers in which the authors study the morphology of the particles of copper and zinc [4–10]. Researchers address a variety of issues. However, in all these studies it is indisputable that loose deposits are branched dendrites, the bases of which are located on the substrate surface; the dendrites themselves retain the electrical (and mechanical) contact with the electrode during the period of electrodeposition. Thus, the deposit characteristics during the growth are determined by the regime of electrolysis.

This study was aimed at finding some general empirical dependencies to describe the growth rates of dendritic deposits of copper and zinc on the cylindrical electrode. We also developed a phenomenological model allowing us to evaluate the structural parameters of the deposit and the transition period from the crystallisation of loose deposits to compact ones (the so-called ‘shell formation time’; that is, the solid layer of metal on the outer surface of the loose deposit).

2. Experimental background

To assess the general issues of the proposed model approach to the description of the dendritic deposit formation, a comparative analysis of the structure and kinetics of deposition of the two metals, copper and zinc was performed. The study is aimed at obtaining the empirical data on the deposition kinetics, dendrite dynamics, metal deposition morphology and determination of the actual fraction of the current that constitutes to metal precipitation. The collection of the data allowed us to build a model and then evaluate how the model representation matches the actual dendritic deposit development.

3. Experimental procedure

For the deposition of zinc, zincate electrolytes containing zinc oxide (0.12; 0.24 and 0.36 M) and 4 M NaOH were used, and for copper electrolytes, different concentrations of copper sulphate (0.12, 0.24 and 0.36 M) and 1 M of sulphuric acid. Dendritic metal deposits were obtained in the galvanostatic conditions and the

current setting (I) exceeded the value of the limiting diffusion current on the smooth surface of the electrode (I_d) by $K_{\text{dep}} = I/I_d$ times. The concept of the depletion factor K_{dep} as the characteristics of the depth of diffusion limitations was introduced by Pomosov [22]. Electrodeposition of the dendritic deposits of metals under review was carried out at K_{dep} values equal to 3, 6 and 9. The limiting diffusion current was calculated based on the experimentally determined limiting current density and the area of a smooth electrode.

The dendritic deposits growth of copper and zinc is usually accompanied by the evolution of hydrogen but at current densities below the limiting diffusion current density of the hydrogen evolution reaction can be neglected for both metals. Therefore, the kinetic and diffusion parameters of the ion discharge of the investigated metals from the corresponding solutions were determined using the method of stationary polarisation curves and chronopotentiometry.

Polarisation measurements were carried out in a three-compartment standard electrochemical cell with a Solartron 1280C and a ZIVE SP5 electrochemical test system. For the manufacture of a rod electrode, copper and zinc wires with a diameter $d_0 = 1.8$ mm were used. The working surface of the electrode was the side surface of a cylinder 8 mm high, the rest of the electrode was insulated. Before the experiments, the working surface was polished, etched in nitric acid, then rinsed thoroughly with distilled water and air dried. Counter electrode were made of a corresponding metal foil. Saturated silver chloride electrodes or the unpolarised electrodes made of the same metal in the test solutions were used as reference electrodes. The measured potentials, if necessary, were recalculated with a NHE scale. The overpotential (η) was calculated as a difference between the potential under the current-applied (E_i) from the equilibrium potential (E_{eq}) $\eta = E_i - E_{\text{eq}}$.

To study the dynamics of dendritic deposit growth over time, a unit was used which allowed us to film a videotape recording of an electrode with the growing deposit, simultaneously with electrochemical measurements. Videotape recording was performed with the Sony DSR-200SE video camera. To determinate the amount of evolved hydrogen over the electrode a funnel connected to the burette [4,9,21] was set up, so that all the extracting gas got into the burette which was filled in with electrolyte. The amount of the evolved gas and overpotential were being registered in the process of electrolysis.

The diameter of the working electrode with the growing deposit ($d_0 + 2y$) (Fig. 1) was measured by video tape recording at

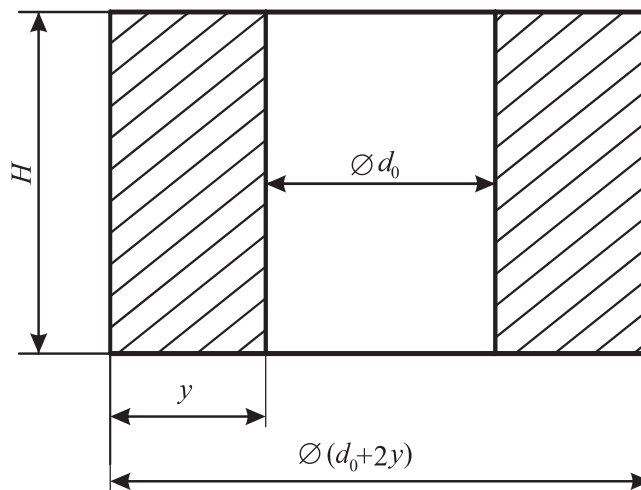


Fig. 1. Diagram of the cylindrical electrode with a height of H and a layer of loose deposit; d_0 – initial diameter of the electrode.

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