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Growth rate of fractal copper electrodeposits: Potential and concentration effects

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Experiments are reported on fractal copper electrodeposits. An electrochemical cell was designed in order to obtain a potentiostatic control on the quasi-two-dimensional electrodeposition process. The aim was focused on the analysis of the growth rate of the electrodeposited phase, in particular its dependence on the electrode potential and electrolyte concentration.

INTRODUCTION

Presently we are witnessing a renewed interest in different growth phenomena that result in irregular structures with mass distributions that do not follow the usual constant-density-based scaling laws.¹ This is particularly true in referring to electrochemical surface processes, which, under appropriate conditions, may lead to the formation of dendritic or other similar tenuous morphologies. As in most pattern-forming phenomena, the texture of these structures is the result of the interplay between the different mechanisms participating in the growth process. These different mechanisms, comprising the transport processes inside the electrolyte solution as well as the interface mechanisms at the boundary of the growing electrodeposit, introduce different length scales delicately balanced to reproduce the observed morphologies of the aggregates, both in a micro and macro scale.²⁻⁴ An understanding of this complicated phenomenology stimulates most of the present theoretical and experimental basic research in this field, although its implications for electrodeposited materials technology⁵ are also important.

Beyond the identification of the diverge electrodeposition patterns observed in experiments,⁶⁻¹³ a crucial question that has received little attention in the past, but one which is certainly fundamental for an understanding of electrodeposition phenomena concerns the growth velocity of the metallic aggregate. We therefore report experiments conducted with the primary aim of evaluating growth rates for a wide range of aggregation textures. Preliminary results on zinc electrodeposits indicate that growth velocities measured at the outermost parts of the aggregates vary greatly for ramified as opposed to dendritic patterns.¹⁰ More recent results on interfacial velocities, mostly referring to zinc electrodeposits, either focused on a particular deposit morphology, the so-called dense-branching morphology (DBM)^{2,14} or were primarily aimed at testing the influence of the electrode potential.¹³ Actually, in the DBM regime most nonpotentiostatic experimental results suggest that interfacial velocities at constant applied potential are largely independent of solute concentration.^{2,14} However, it has been suggested in the literature^{3,15} that when concentrations are varied, the applied potential across the cell may not be

the appropriate control parameter. Our experiments address this problem by working under potentiostatic conditions; in order to get a better electrochemical control of the actual deposition process taking place at the metallic interface, we kept constant the potential applied to the cathode. Computed interfacial velocities are presented here in relation to both the potential of the electrode and the concentration of the electrolyte. The range of selected experimental conditions enabled us to evaluate growth velocities for different morphologies including but not restricted to DBM. The constancy of the interfacial velocity with respect to concentration is found to be a nongeneric behavior limited to a concentration range that is actually potential dependent. Finally, several considerations regarding the relation between growth rates and morphologies are proposed.

EXPERIMENT

Experiments were carried out in the electrochemical cell schematically shown in Fig. 1. Pure copper wires of 0.2 mm diameter were used for both working (*W*) and auxiliary (*A*) electrodes. They were placed between two parallel Plexiglas plates and separated by a distance of 50 mm. These electrodes were cleaned immediately before use. The reference electrode (Ref.), a saturated Calomel electrode (SCE), was positioned near the working electrode, as indicated in the figure.

Solutions of different concentrations in CuSO_4 were prepared from analytical grade reagents. These solutions filled the space limited by the working and auxiliary electrodes and the Plexiglas plates. Care was taken in order to prevent solution losses during the experiment. Before transferring the solution into the cell, the solutions were deaerated by injecting nitrogen gas.

The experiments, conducted under constant-potential conditions, were controlled by an Amel Potentiostat, Mod. 551. All potentials quoted in this paper refer to the SCE (0.2412 V with respect to the standard reversible hydrogen electrode). The experiments were performed at room temperature.

The experimental system was illuminated from below and the growing structures were photographed from above. The photographs were processed using a standard image-analysis system, and digitized with a resolution of

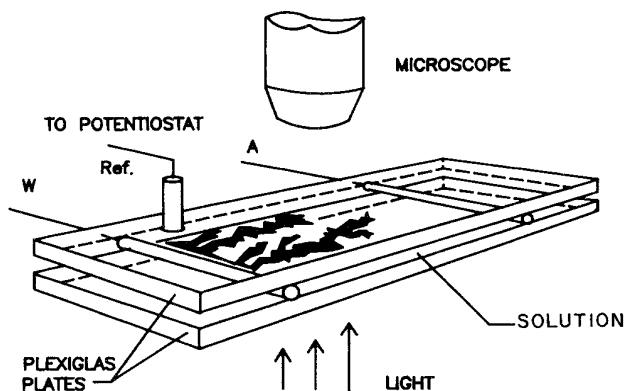


FIG. 1. Schematic view of the electrochemical cell used in the experiments.

512×512 pixels. The digitized patterns were then transferred onto an IBM PS/2 computer for further analysis.

RESULTS AND DISCUSSION

The growth speed was determined from measurements of the time dependence of the average thickness of the deposit. This was evaluated in terms of the averaged height of the so-called "upper surface," i.e., the surface that an observer would see looking straight down at the deposit. As previously reported in both nonpotentiostatic^{2,14} and potentiostatic¹³ experiments, the velocity selected by the interface is apparently constant over much of the cell except for a short transient after initiation and, eventually, during the late growth stages when the growing aggregate approaches the auxiliary electrode. Typical aggregates, grown at ca. 10 min after initiation, are shown in Figs. 2 and 3, corresponding, respectively, to a 0.05M electrolyte concentration with different electrode potentials and to a constant -5.0-V electrode potential (measured against the SCE) with different electrolyte concentrations.

The results for the growth speed under different values of the electrolyte concentration and electrode potential are summarized in Fig. 4. The order of magnitude of the calculated velocities agrees with previous results quoted in the literature,^{2,10} although it differs by nearly two orders of magnitude with respect to the zinc electrodeposition experiments conducted by Kahanda and Tomkiewicz,¹³ probably due to the different experimental setup.

In our discussion here we make when appropriate, an intuitive use of the notion of electrode potential and correlate growth velocities with pattern morphology. Regarding the dependence of the growth speed on the electrode potential, it is clear that higher potentials result in larger growth velocities. This effect is generic and, from a qualitative point of view, is applicable irrespective of the range of concentrations considered. Similar conclusions were also extracted from the experiments by Kahanda and Tomkiewicz¹³ and those conducted by Garik *et al.*² This behavior admits a simple interpreta-

tion if we consider the electrode potential as a basic parameter that governs the actual deposition mechanism at the interface, or in other words as a sort of sticking coefficient of the depositing cations. Higher potentials would represent more favorable sticking conditions and concomitant larger aggregation rates. Actually, results from computer simulations of diffusion-limited aggregation (DLA) routines with different sticking probabilities are sometimes introduced and analyzed with this motivation.¹⁶ On the other hand, deposit morphologies and growth rates may also be easily correlated at constant concentrations (Fig. 2) by noting that in going from lower to higher electrode potentials, mossy and slowly growing aggregates turn into ramified and less-dense structures whose interfaces propagate at larger rates.

It is also apparent from Fig. 4 that this effect is, from a quantitative point of view, far from being uniform when concentrations are varied. In general, one would say that in going to larger concentrations the interfacial velocities tend to decrease, this effect being much more pronounced in the limit of the higher concentrations considered here. At small concentrations and specially under high electrode potentials, the growth rate appears to be fairly insensitive to concentration changes. Actually, this region corresponds to the DBM regime, where analogous conclusions were raised based on experiments for zinc^{2,14} and copper² deposition under standard nonpotentiostatic conditions. We try to interpret this behavior with the understanding that the interfacial motion in electrodeposition

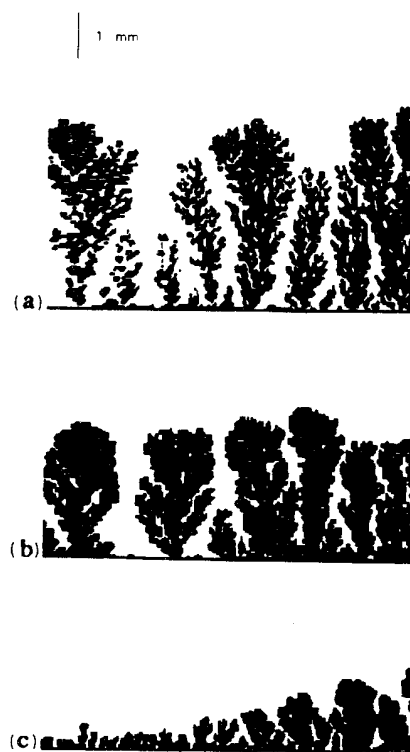


FIG. 2. Digitized growth patterns of copper deposited from a 0.05M CuSO_4 solution at different electrode potentials: (a) -5.0 , (b) -4.0 , and (c) -3.0 V measured against the SCE. Time was approximately 8–10 min.

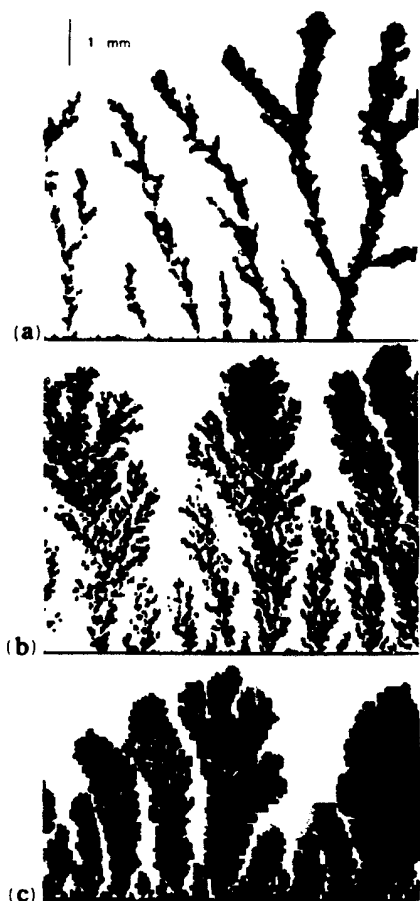


FIG. 3. Digitized growth patterns of copper deposited at an electrode potential of -5.0 V measured against the SCE, from solutions of different CuSO_4 concentrations: (a) 0.01 , (b) 0.05 , and (c) 0.1 M. Time was approximately 10 min.

is likely to involve a velocity-selection mechanism not only based on the electrochemical driving force, but also depending on the branching development and on the thickness of the branches. In our experiments (Fig. 3), when restricted to largely ramified deposits [Figs. 3(a) and 3(b)], an increase of concentration results in a smaller spacing between trees whereas their widths increase, finally resulting in growth rates that were approximately independent of electrolyte concentration. Thus the appropriate picture of electrodeposits growing in the DBM regime is that of a moving, ideally equipotential front that limits a dense and barely restructured metallic de-

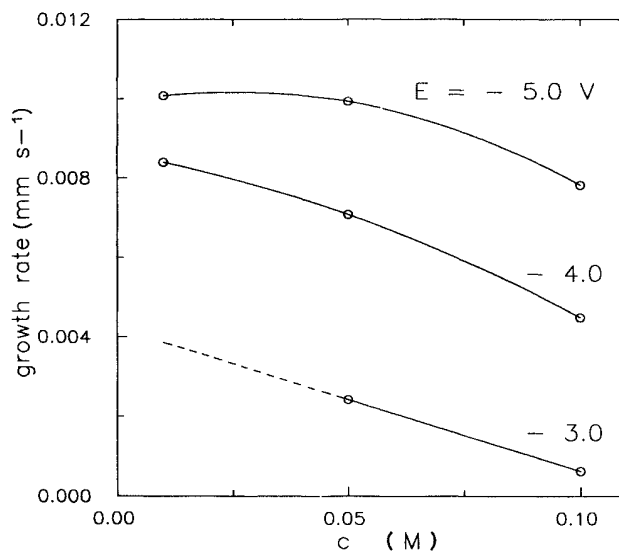


FIG. 4. Growth rate vs CuSO_4 concentration at different electrode potentials, measured against the SCE.

posit. Actually, this idea has been recently proposed¹⁷ in connection with an Ohmic model as the basis of theoretical approaches aimed at describing DBM in real electrodeposition experiments. On the other hand, in the limit of the large concentrations and mostly under low potentials, this picture completely breaks down. A front motion is then completely meaningless, the actual metallic boundary being more appropriately described by an irregular interface enclosing what would be a very dense fractallike aggregate [Fig. 3(c)]. As a result, electrodeposition progresses with larger portions of new accreted material compacting and restructuring the inner parts of the deposit, thus lowering the interfacial velocity.

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