Chaos, Solitons and Fractals 116 (2018) 381–385

Contents lists available at ScienceDirect

Chaos, Solitons and Fractals

Nonlinear Science, and Nonequilibrium and Complex Phenomena

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

A fractal dimension minimum in electrodeposited copper dendritic patterns

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ARTICLE INFO

Article history:
Received 9 April 2018
Revised 1 September 2018
Accepted 24 September 2018

Keywords:
Dendritic patterns
Electrodeposition
Fractal dimension
Self-similarity

ABSTRACT

Dendritic growth processes occur in a plethora of natural systems and play a relevant role in materials science and engineering. Models based on diffusion-limited aggregation (DLA) have been extensively used to study the mechanisms underlying this class of particle aggregation phenomena. One of the main features of DLA clusters is their fractal character, evinced by self-similarity at different scales. The physical and chemical properties of systems in which DLA aggregates emerge are determined by their fractality. In this work, two-dimensional copper dendritic patterns are grown by electrodeposition in a circular cell at applied voltages in the 5 – 10 V range using a 1 M copper sulfate aqueous solution. The box counting method confirms that the electrodeposited dendritic structures manifestly exhibit fractal character. Although the growth rate increases exponentially with the applied voltage, it is reported for the first time that the fractal dimension has a minimum value for patterns grown at an applied voltage between 7 and 8 V. The results reflect the active role of applied voltage in the physical mechanisms driving dendritic growth in the system, mainly controlled by the copper ion concentration gradient. However, it also suggests the existence of two growth regimes: one corresponding to patterns grown under voltages lower than *circa* 7–8 V; the other to patterns grown at higher voltages. This evidence is supported by the determined mass values of the copper electrodeposits.

1. Introduction

Order in nature has been widely studied since the earliest days of philosophy in Greece. Natural patterns are found in butterflies' wings, honeycombs, leaves and other plant structures. Many such patterns are so irregular and fragmented that they used to be considered *formless*. However, much attention has been paid to these complex structures since Mandelbrot addressed their geometry. It was Mandelbrot who coined the term *fractal* in 1977 [1], loosely defined by himself as “a shape made of parts similar to the whole in some way” [2]. This feature is known as self-similarity or scale invariance. Fractals are also characterized by fractal dimension, a measure of complexity.

Fractal geometry has made it possible to mathematically describe order in naturally occurring complex patterns. Dendritic growth processes, i.e., the development of self-similar objects far from equilibrium, may, in some cases, be modelled using methods of fractal geometry [3]. One such example is the diffusion-limited aggregation (DLA) model of Sander and Witten [4,5], which simulates irreversible particle aggregation by diffusion, a phenomenon found in colloid physics, materials science, phase transitions, etc.

The DLA algorithm can be pictured as follows: on a lattice, one defines the origin as the first seed particle of a cluster (commonly called point attractor); then a random walker, i.e., a Brownian moving particle, is launched and wanders around until it reaches the neighborhood of the first particle, where it sticks; further particle liberation leads to the formation of a cluster, which exhibits fractal characteristics [6,7]. Notwithstanding its simplicity, the DLA model does not provide a method for computing particle aggregates' fractal dimension. In fact, it is not possible to prove DLA clusters are fractals [8].

This model has a wide range of applications, from Hele-Shaw fluid flows to cosmological large-scale structure [9]. A particularly simple experimental system that produces DLA-like patterns is the irreversible growth of clusters by electrodeposition of metal ions provided by an aqueous solution [6]. Pioneer works by Brady and Ball [10] and by Matsushita et al. [11] showed good agreement with computer simulations based on the theoretically proposed DLA model. The fractal nature of metallic patterns grown by electrodeposition has been addressed over the last years from different theoretical and experimental points of view [12–19], given

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https://doi.org/10.1016/j.chaos.2018.09.042
0960-0779/

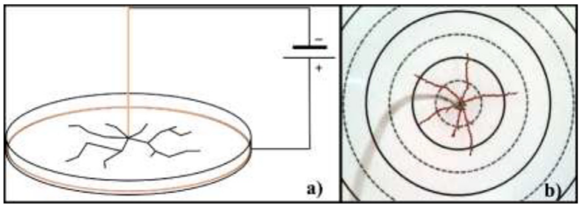

Fig. 1. a) Fractal-like copper structures are radially grown by electrodeposition in a thin layer of copper sulfate aqueous solution between two Petri dishes; b) Frame of video record of a copper dendritic pattern grown by electrodeposition at 8 V.

its practical implications in nanofabrication processes and technology [17,20,21]. It is well known that this irreversible aggregation process results from a complex interplay between convection, migration and diffusion [22,23], whose macroscopic effects chiefly depend on the concentration of the aqueous solution as well as on the applied voltage (or, alternatively, the applied current) [12,13,24]. The morphology of the metallic aggregates is mainly determined by these two independent observables, although other parameters such as the concentration of oxygen dissolved in the solution may lead to significant morphological perturbations [15]. Most experiments in the past were conducted in quasi-two-dimensional (linear or circular) geometries and focused on single-metal deposits (e.g., Zn, Cu) grown at low concentrations and low voltages [12,13,15,25,26], whereas pattern formation in two-metal electrodeposition systems started being explored more recently [27,28]. However, despite the high number of studies involving single-metal deposits, there is still missing information on the mechanisms that rule their tree-like growth.

In this work, copper dendritic patterns are grown two-dimensionally by electrodeposition in a circular cell geometry using copper sulfate ($CuSO_4$) solution. Their fractal dimension is studied under operating voltages in the 5 – 10 V range. Different algorithms to compute the fractal dimension of real aggregates can be found in the literature, each one corresponding to a particular definition of that mathematical quantity [12–14]. Here, the fractal dimension of the copper electrodeposits is calculated using the box counting method [6,12–14], one of the simplest available algorithms, allowing the identification of a not so straightforward relation between the applied voltage and fractal dimension.

2. Experimental

Copper dendritic patterns are electrodeposited in a circular cell made of two acrylic Petri dishes, as depicted in Fig. 1a. Firstly, the outer Petri dish (8 cm diameter) is filled with 5.5 mL of 1 M $CuSO_4$ (anhydrous, > 99%, Sigma-Aldrich) aqueous solution. Then a ring-shaped copper wire (~1.5 mm diameter) is placed along the inner edge of the outer Petri dish (anode), on which the inner Petri dish (7.6 cm diameter) is fit in so that the copper electrodeposits' growth is nearly two-dimensional (~2 mm depth). The inner Petri dish has a tight hole in its center in which a copper rod cathode (~0.3 mm diameter) is inserted using a clamp. A digital SLR camera (Canon EOS 200D + EF-S 18–55 mm f/4–5.6 IS STM Lens [29]) is installed over the setup for shooting (Fig. 1b), with the lens parallel to the Petri dishes' bases and aligned with their symmetry axis. Fig. 1b shows a frame of the video record of a copper dendritic pattern grown by electrodeposition at 8 V. This video (with approximately 30 × the original speed) can be found in the article supplementary material.

Copper electrodeposition at the cathode is triggered by applying a DC voltage between the cathode and the ring-shaped anode. The experiment was performed at room temperature (~22 °C) using a 1621A BK Precision DC regulated power supply. When dissolved in water, $CuSO_4$ dissociates into copper cations (Cu^{2+}) and sulfate anions (SO_4^{2-}), which follow Brownian paths at room temperature. On the other hand, when a voltage is applied, the Cu^{2+} cations in solution are drifted towards the cathode under the influence of the electric field, where they stick upon reduction. Dendritic growth under weak electric fields results in DLA patterns, since ions nearly follow Brownian paths. However, the original DLA model is no longer valid for strong electric fields (or, in other words, for high voltages, such as those used in the present work). Although the electric field drift dominates, fractal-like structures are still formed due to the ever-present thermal motion. A few minutes after the start of the experiment, branching fingers become noticeable. The growth is stopped, i.e., the power supply is turned off, as soon as one of the branches is 2 cm apart from the original cathode. A white sheet of paper with concentric circles, 0.5 cm apart, placed under the outer Petri dish and with the center aligned with the inner Petri dish's hole, is used to measure that distance (Fig. 1b). Total growth time, i.e., the time necessary for the fractal electrodeposits to reach the fourth concentric circle around the copper cathode, is measured, as is the electric current over time. The dendritic pattern is then photographed for image processing and analysis.

The image processing and analysis procedures can be summarized as follows: photographs are first converted into black and white images, whose contrast and brightness are then adjusted so that the dendritic patterns stand out on the background. Besides, each image is reduced to its region of interest. These steps can be done using PhotoScape 3.7 [30], a free photography editing software, or similar. The fractal dimension of dendritic patterns can be determined using FracLac [31], a plug-in for ImageJ based on a box counting algorithm [6,12–14]. In this method, the image, after being converted into a binary file, is fully covered by squares of fixed width, *N*, and the number of squares required to cover the pattern, *S*, is determined. Repeating this task for several different square widths, one can compute the fractal dimension of the pattern, once known the dependence of *S* on *N*.

When analyzing patterns using FracLac, box counting scan settings should be carefully defined. Although in most cases default values do work, some parameters should be changed in order to take into account image quality, namely sharpness. These include the number of grid positions and the box size. The former refers to where the grid is placed in the image [12,31]. In fact, the number of boxes needed to cover the pattern depends on the grid position, meaning that fractal dimension should be computed for different grid positions. Herein, this value was set to 12. As for the box size, it is related with the minimum and the maximum size of the grid caliber. The minimum size should match the resolution of the image being analyzed.

3. Results and discussion

Grey scale images of copper dendritic patterns grown at different operating voltages are shown in Fig. 2, together with the delimiting 4 cm-diameter circle. The patterns resemble those found by DLA-based simulations, exhibiting a tree-like structure, with primary branches (those borne on and grown from the cathode) originating secondary branches, and so on [16]. The number of primary branches, quasi-evenly distributed in space, increases as the applied voltage increases, except for the case when $U = 9$ V, for which second and third generation branches start to appear. As a result, the average angle between primary branches decreases from 120° to 36° as the voltage increases from 5 to 10 V (cf. Table 1). The branches' thickness varies between 0.1 and 1.0 mm, decreasing as the applied voltage increases. However, the patterns grown under voltages above 8 V are characterized by branches of the same width (~0.1 mm). In addition, from Fig. 2 it is clear that some branches are significantly smaller. Indeed, notwithstanding their