Studies on the Effect of Electrolytic Parameters on the Growth and Fractal Dimensions of Fractal Dendrites formed by Electrodeposition of Copper with a reference to their Economic Aspects

[1]Viji. V.R, [2]Sreedevi Gopalakrishnan
[1]Assistant Professor of Physics, [2]Assistant Professor of Economics
[1]University College, Palayam, Thiruvananthapuram, Kerala-695034, India
[2]Sree Narayana College, Chengannur, Kerala-689 508, India.

Abstract

Electrodeposition of metals from electrolyte under certain conditions results in dendritic patterns exhibiting fractal character. The underlying process responsible for development of dendritic treelike structures with complex branches is the Diffusion Limited Aggregation (DLA). In order to realize DLA like conditions the cell operating conditions play an important role. We studied the growth of electrodeposits from copper sulphate solution under different cell operating conditions and the effect of voltage, time and concentration on the nature of electrodeposit is studied using the concept of fractal dimension. Box counting technique is used for the estimation of fractal dimension of the electrodeposit, details are presented. Models based on diffusion-limited aggregation (DLA) have been extensively used to explore the mechanisms of dendritic particle aggregation phenomena. The box counting method confirms that the electrodeposited dendritic structures manifestly exhibit fractal character. It was found that with the increase of the voltage and copper ion concentration, the fractal copper size becomes larger and its morphology shifts towards a dendritic structure, with the fractal dimension fluctuating.

The electrodeposition market is a specialized sector that involves the deposition of materials onto a substrate through electrochemical processes. As a fractal structure emerges – the repeating of a simple rule – it appears to share direct properties familiar to classical economics, including production, consumption, and equilibrium

Key words: *Electrodeposition, copper sulphate, fractal, fractal dimension, Diffusion Limited aggregation, Box counting, morphology, fractal attractor, electrodeposition market, marginalism etc.*

Introduction

In electrodeposition an electrolyte is placed between two electrodes and certain emf (Electro Motive Force) is applied between the electrodes. In the presence of an emf between two electrodes the region between the two plates has an electric field. The electrostatic force due to the electric field on the charged ions makes them drift towards the respective electrodes which in turn result in deposition of ions at the electrodes. The positive ions are attracted towards the positive electrode and negative ions toward the positive electrode. The accumulation of positive ions at the negative electrode results in an electrodeposition. Under certain operating conditions electrodeposition gives rise to formation of dendritic patterns with branching patterns. These dendritic electrodeposits in most of the cases exhibit scaling Fractal Characteristics. Objects having self-similarity and scale invariance are fractals. The peculiar dendritic patterns exhibiting fractal character develop because of a process called Diffusion Limited Aggregation (DLA). In the recent past, practical applications of the principle of Diffusion limited growth processes has increased the pace of research and development in this area. Concept of Fractal model is being used for the forecasting the trends of the random events like prices in the share market.

Copper powder forms the most important part of powder metallurgy, in comparison to other metal powders. Among copper powders, dendritic ones prepared by electrolysis have a wide range of applications in different fields of industry due to their unique microscopic morphology, large relative specific surface area and better chemical properties. The generation of dendrites by electrolysis has gained attraction due to formal symmetry and substantive complexity. DLA problems like dendrites are tedious to study using conventional Euclidean geometry, and even numerical solutions cannot be obtained. Until 1977, when Mandelbrot investigated the geometry of nature and introduced the term fractal, fractal geometry has developed rapidly. The complexity of the growth of electrodeposited metal dendrites is due to the instability of the flow field morphology, providing new ideas for the study of metal dendrite factorisation.

This paper we attempt by using electrolysis to prepare fractal products of copper deposition by controlling the applied voltage, time of deposition and copper ion concentration, and to investigate the morphology and fractal dimension relationship of electrodeposited copper dendrites.

Economic aspects of fractal dimensions and electrodeposition

Fractal geometry is found universally and is said to be one of the best descriptions of our reality – from clouds and trees to market price behaviour. As a fractal structure emerges – the repeating of a simple rule – it appears to share direct properties familiar to classical economics, including production, consumption, and equilibrium. The mathematical principles behind 'the market' – known as marginalism – is an aspect or manifestation of a fractal geometry or attractor. It was found the fractal attractor demonstrates properties and best models' classical economic theory and from this, it was deduced the market is a fractal attractor phenomenon where all properties are inextricably linked.

The electrodeposition market is influenced by various drivers that affect its growth and development. These drivers can vary based on industry trends, technological advancements, and economic factors. Here are some key market drivers for the electrodeposition market. Increasing Demand for Electronics, Automotive Industry Growth Aerospace and Defence Applications, Advancements in Technology, Growing Renewable Energy Sector, Demand for Improved Surface Properties, Cost-Effectiveness, Customization and Precision Coating etc.

The electrodeposition market is a specialized sector that involves the deposition of materials onto a substrate through electrochemical processes. One of the primary market segments within this sector is categorized by type, encompassing various methodologies, including electroplating, electrodeposition of polymers, and electroforming. Electroplating is a widely utilized technique that involves the deposition of a metallic layer onto a substrate to enhance its appearance, corrosion resistance, and overall durability. This process is prevalent in industries such as automotive, electronics, and jewellery, where aesthetic appeal and functional properties are paramount. The electrodeposition market is a critical segment within the broader coating and surface finishing industry, showcasing significant applications in automotive, electronics, aerospace, and consumer goods, among others. The primary segmentation of this market is categorized by material, reflecting the diversity of substrates and applications for electrodeposition processes. The first sub-segment, metals, plays a pivotal role as it encompasses a wide range of applications from decorative finishes to functional coatings that enhance resistance to corrosion and wear. This sub-segment includes various metals such as nickel, copper, and gold, which are crucial for enhancing electrical conductivity and providing aesthetic value in electronic components and decorative items. The electrodeposition market, a pivotal segment within the broader electrochemical deposition industry, focuses on the application of electric current to deposit materials onto substrates, primarily for metal finishing, corrosion protection, and decorative purposes.

Experimental

The process of electrolysis in two-dimension is carried out using copper sulphate solution for the study of fractal geometry formed during the electro-deposition of copper. Add 25g of copper sulphate granules to 100 ml of water to get 1m copper sulphate solution. The mixture is not vigorously shaken because it may result in bond breakage. Using a heating furnace to heat the solution and stirring it with a glass rod, we can dissolve the solid copper granule present in the experimental solution. The freshly prepared solution is allowed to cool for the upcoming procedure. For the electrolysis process of copper sulphate solution in two-dimension, we need two glass slides, a DC source, copper stands pure copper wire, clip, camera, filler and an illuminating source. Proper hygienic have to be checked in the beginning of the experiment, since a single impurity may result in broken fractal structure. Then the two glass slides are cleaned with cotton and a cleansing solution. The cleaned glass slides are pressed against each other horizontally and copper sulphate solution is poured between the glass slides using filler.

The positive terminal of 12V DC source is connected to the negative of the ammeter using a pure copper wire. Cu wire drawn from the negative end of DC source and the positive end of ammeter are properly placed between two glass slides filled with $CuSO_4$ solution and they are firmly clipped. It is illuminated with a proper illuminating source, so that no shadow falls on the background. Here copper strand which extend from positive terminal act as anode and that from negative terminal of battery act as cathode. If potential of few volts is applied between the electrodes, then after a few minutes, a deposit of copper starts to form around the cathode. After a few minutes the copper deposit will have extended into fractals.

In solution, between the copper slides, the copper sulphate splits into copper Cu^{2+} and sulphate so_4^{2-} ions which drift around in random manner. When voltage is applied, the copper ions that hit the cathode receive two electrons and deposited as copper. Copper ions that hit any Cu already formed are also deposited as copper, so that the Cu ions move in a sufficiently random manner. i.e., following Brownian path ions are more likely to hit the exposed end and undergo aggregation which results in the formation of fractal. Thus, the growth of copper deposition will be thin, branching rather than in a solid block around the cathode. On other hand the SO_4^{2-} get attracted towards anode and at anode it gives up two electrons and become SO_4 radical, the attack copper anode to form copper sulphate which again react with water again to form Cu^{2+} and SO_4^{2-} ions.

Photographs of copper deposition are taken for 5, 10, 15, 20 and 25 minutes successively using a camera. Camera itself is chosen so that the fractal can be seen with great accuracy. Experiment is carried out for different voltages say 2V, 4V, 8V, and 12V. The whole process is repeated for solution of each 0.01M, 0.02M, 0.03M, 0.04M, and 0.05M concentrations. During the above process the Cu ions aggregates at copper cathode to form the fractals. The photographs which are taken during the process are analysed. The photographs taken during the experiment are converted into 2-dimensional arrays using Python programming. This conversion involves translating the images into a numerical format where each pixel is represented by its intensity values. To determine the fractal dimension of the structures, we employ the box counting method. This method involves covering the fractal pattern with a grid of boxes of varying sizes. We count the number of boxes required to cover the fractal pattern completely for each box size. By plotting the logarithm of the number of boxes needed against the logarithm of the inverse of the box size, we can analyse the scaling behaviour of the fractal. The slope of this plot corresponds to the fractal dimension. Thus, by fitting a line to the data, we can estimate the fractal dimension of the structures. This experiment provides insights into the fractal nature of copper electrodeposition. By varying experimental parameters such as voltage and concentration, and by analysing the resulting fractal patterns using the box counting method, we gain a deeper understanding of the factors influencing fractal growth. The ability to quantify fractal dimensions helps in comparing and contrasting different growth conditions and contributes to the broader study of fractal geometry in electrochemical processes.

Results and discussion

The main concept behind fractal geometry is the fractal dimension. Fractal dimension is a dimension that can be a fraction. The fractal dimension was first coined by Haus Dorff in 1919, hence known as the Haus Dorff dimension. Later, Mandelbrot generalized the fractional dimension to form fractal geometry. Fractal dimension is a statistical measure of complexity of a geometric shape. In more general terms, the fractal dimension describes how the shape changes in detail as the measurement scale changes. Different morphology of copper electrodeposits can be described by fractal geometry.

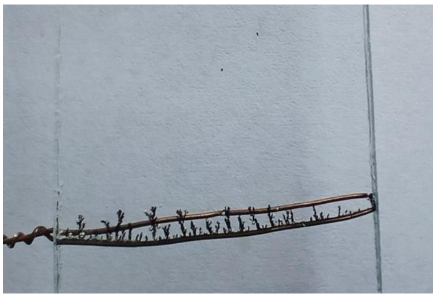
For irregular shapes with the electrodeposited copper fractals, the box counting dimension method is used to calculate the fractal dimension. This paper investigates the effect of different growth conditions on the growth morphology and fractal dimension of copper dendrites during electrodeposition.

0.01 M	6 V	1.3988799627197264	1.5186142991779337	1.5523959595108363	1.5697360577990846	1.5739699910314948
	8 V	1.3678716816847682	1.498946482027818	1.499948860643746	1.5112199977168062	1.558066605833443
	10 V	1.3614808817808086	1.458641709265628	1.4768539235653648	1.5207796330772212	1.5855935304478144
	12 V	1.3273438163807383	1.3831636757505121	1.4446124448740016	1.5055289440551034	1.5136557755090099
0.02 M		5 MIN	10 MIN	15 MIN	20 MIN	25 MIN
	6 V	1.6037611245213732	1.6077319516817157	1.6647150909801414	1.6936458030817694	1.7278124502442982
	8 V	1.523349410850872	1.6542218757138103	1.699696143464133	1.7174168627936168	1.7446017538948664
	10 V	1.5601666767000744	1.6384696724520222	1.6653581271955267	1.6900637898910809	1.7407074419302009
	12 V	1.5976649250199813	1.6117705850740063	1.7358403997829017	1.7656738175371507	1.7873473736266636
0.03 M		5 MIN	10 MIN	15 MIN	20 MIN	25 MIN
	6 V	1.5532427570858869	1.6036041941521486	1.6122527035849172	1.6701922361542711	1.6766457894583162
	8 V	1.5750906984809803	1.638568070284802	1.6506278000485028	1.6665050105193482	1.6738927561899872
	10 V	1.5236823482487936	1.602309028636261	1.6199710352741974	1.650929320915635	1.7056377195250219
	12 V	1.5452209160031258	1.6233516065682567	1.6692137185728597	1.6745583804638808	1.6770497092037588
0.04 M		5 MIN	10 MIN	15 MIN	20 MIN	25 MIN
	6 V	1.3419287036838377	1.5342805860643252	1.5602880206847636	1.585535525764207	1.6292656436946018
	8 V	1.480508777634225	1.4898451445117666	1.6124097289892296	1.6155252997477876	1.6353091306059326
	10 V	1.5105230429655458	1.5867321187096484	1.5878202047532095	1.6694234930550016	1.6950547561559628
	12 V	1.4856740632059577	1.5921766152572372	1.6954030991853484	1.7373831437681577	1.7457817907166677

0.05 M		5 MIN	10 MIN	15 MIN	20 MIN	25 MIN
	6 V	1.4996108718337668	1.5031374556714285	1.6722670625094287	1.7042027558059676	1.7318087747279955
	8 V	1.4708359962246564	1.5028470072913982	1.5799546979402868	1.585661296988356	1.6538855037854068
	10 V	1.5799693976574951	1.6247985574194563	1.6565029673262357	1.6748415937926697	1.7224892669546925
	12 V	1.549935659374912	1.5851874080668569	1.624166095560585	1.6790582085424341	1.6813929914189478

The variation of fractal dimensions of as deposited copper dendrites at various time, voltage and copper ion concentrations are shown above.

The photographs of fractals obtained for same concentration at different voltages at different times are shown below.



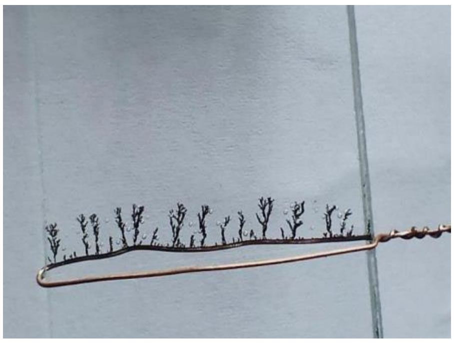
0.01 M, 6 V, 5 min

0.01 M, 6 V, 10 min

0.01 M, 6 V, 15 min

0.01 M, 6 V, 20 min

0.01M,6V,25min



0.01M,8V, 5min

0.01 M, 8 V, 20 min

0.01 M, 8 V, 25 min

0.01 M, 10 V, 15 min

0.01 M, 10 V, 20 min

0.01 M, 12 V, 20 min

0.01 M, 12 V, 25 min

0.02 M, 12 V, 20 min

0.02 M, 12 V, 25 min

0.03 M, 12 V, 20 min

0.03M, 12 V, 25 min

0.04 M, 12 V, 20 min

0.04 M, 12 V, 25 min

0.05, 12 V, 20 min

0.05 M, 12 V, 25 min

Effect of time on morphology and fractal dimensions

In order to study the variation of fractal growth and fractal dimensions with time, photographs of fractals for a constant voltage, at different time are analysed for each concentration of the electrolyte. The dendrites grow more intensively over a short period of time. As the reaction time increases, some of the dendrites stop expanding, new dendritic branches appear on the tips of the dendrites, the number of branches increases and the fractal character becomes clearer. The fractal dimension of the dendrites gradually increases with increasing deposition time and then gradually stabilises. This means that after the initial growth and development of the copper fractal dendrites are complete.

Effect of voltage on morphology and fractal dimensions

It is found that the morphology of electrodeposited copper fractals varies from denser, multi-branched growth to open, thick and short branched growth as the applied voltage between the cathode and anode increases. This is mainly due to the increase in current density, a greater probability of binding of free copper ions to electrons, an increase in the rate of nucleation. In the range of our experimental measurements, the fractal dimension of the electrodeposited product morphology varies irregularly with the applied voltage. The fractal dimension of the deposited copper morphology does not show a clear and regular trend with the applied voltage.

Effect of copper ion concentration on morphology and fractal dimensions

The diffusion of copper ions is the controlling aspect of the electrolytic copper fractal deposition process. The effect of copper ion concentration on the electrodeposited copper fractal morphology was investigated. The morphology of the deposited copper products shows that as the concentration of copper ions in sulphate increases, the morphology of the deposited products varies from a dense type consisting of shorter and finer branches to an open type consisting of thicker branches, which are gradually thicker and looser. Fractal dimensionality of the deposited copper products increases with the rise of concentration of copper ions in the electrolyte when other electrolytic parameters are kept constant. The cluster fractal structure arises because the fast-growing parts of the sediment branches shield other parts, making it harder for particles to reach the shielded parts. Thus, creating more branches of the copper dendrites and forming a multi-branched fractal structure. Our analysis suggests that during the electrodeposition of copper fractals, the substances in the electrolyte solution follow Brownian motion. The increased concentration of copper ions increases the deposition of copper ions near the cathode. As the deposition rate of copper ions increases, the effect of inter-branch shielding decreases and the chance of particles reaching the interior of the cluster is increased, so that the fractal dimension of the deposited product becomes larger as the concentration of copper ions in copper sulphate increases; the branching of the deposited fractals also becomes more complex and coarser with the increase of copper ion concentration.

Conclusion

It is showed that with the increase of voltage, time of deposition and copper ion concentration, the deposited copper size becomes larger. The fractal dimension showed irregular fluctuations. The sediment morphology showed high similarity to the DLA cluster with fractal characteristics. The box counting method confirms that the electrodeposited dendritic structures manifestly exhibit fractal character. It was found that with the increase of the voltage and copper ion concentration, the fractal copper size becomes larger and its morphology shifts towards a dendritic structure, with the fractal dimension fluctuating.

Optimizing parameters improves process efficiency, reducing energy use and production costs. For instance, slurry electrolysis in e-waste recycling lowers copper recovery costs by controlling dendrite morphology. The electrodeposition market is a specialized sector that involves the deposition of materials onto a substrate through electrochemical processes. As a fractal structure emerges – the repeating of a simple rule – it appears to share direct properties familiar to classical economics, including production, consumption, and equilibrium

References

1. Written T.A (Jr.) and Sander L.M., Diffusion Limited Aggregation- Kinetic critical phenomenon phy Rev Let.47, 19, 1400 -1403(1981)
2. Paul S. Addision Fractals and Chaos, An illustrated Napier University Edinburgh IOP Publishing Ltd. (1997)
3. The Fractal geometry of nature, By Benoit B. Mandelbrot, W.H Freeman and Company, New York (1992)
4. N.D. Nikolić, L.J. Pavlović, M.G. Pavlović and K.I. Popov, *Powder Technol.*, **2008**, *185*(*3*), 195–201.
5. N.D. Nikolić, L. Pavlović, M. Pavlović and K.I. Popov, *J. Serb. Chem. Soc.*, **2007**, *72*(*12*), 1369–1381.
6. B.B. Mandelbrot, The fractal geometry of nature. WH freeman, New York, **1982**.
7. I.B. Murashova, N.E. Agarova, A.B. Darintseva, A.B. Lebed and L.M. Yakovleva, *Powder Metall. Met. Ceram.*, **2010**, *49*, 1–7.
8. A. Ďurišinová, *Powder Metall.*, **1991**, *34*(*2*), 139–141.
9. Razdan Ashok „Bombay Stock Exchange Index" Pramana
   J. of physics 58, 537. (.2007)
10. N.M. Santos and D.M.F. Santos, *Chaos Soliton. Fractals*, **2018**, *116*, 381–385.
11. B.H. Kaye, *Powder Technol.*, **1978**, *21*(*1*), 1–16.
12. N.D. Nikolić, K.I. Popov, L.J. Pavlović and M.G. Pavlović, *J. Electroanal. Chem.*, **2006**, *588*(*1*), 88–98
13. N. Leventis, M. Chen, X. Gao, M. Canalas and P. Zhang, *J. Phys. Chem. B*, **1998**, *102*(*18*), 3512–3522.
14. N.D. Nikolić, K.I. Popov, L.J. Pavlović and M.G. Pavlović, *Surf. Coat. Technol.*, **2006**, *201*(*3–4*), 560–566.
15. M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo and Y. Sawada, *Phys. Rev. Lett.*, **1984**, *53*, 286.
16. Landolt, D. Electrodeposition science and technology in the last quarter of the twentieth century. *J. Electrochem. Soc.* **2002**, *149*, S9–S20
17. Kang, H.S.; Lee, J.Y.; Choi, S.; Kim, H.; Park, J.H.; Son, J.Y.; Kim, B.H.; Noh, S. Do Smart manufacturing: Past research, present findings, and future directions. *Int. J. Precis. Eng. Manuf. Technol.* **2016**, *3*, 111–128.
18. Future Market Insights Electroplating Market: Global Industry Analysis and Opportunity Assessment, 2016. Available-online : https://www.futuremarketinsights.com/reports/electroplating-market