International Journal of Scientific Engineering and Research (IJSER)
ISSN (Online): 2347-3878
Index Copernicus Value (2015): 62.86 | Impact Factor (2015): 3.791

Study of Effect of Temperature on Electrodeposition of Copper from Copper-Sulphate Solution

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Abstract: ***Electrodeposition of metals from electrolyte under certain conditions results in dendritic pattarns exhibiting fractal character. The underlying process responsible for development of dendritic tree like 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 temperature 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.***

Keywords: Electrodeposition, copper sulphate, fractal, fractal dimension, Diffusion Limited aggregation, Box counting

1. Introduction

In electrodeposition an electrolyte is placed between two electrodes and certain emf (Electro Motive Force) is applied; q is the charge on the ion and E is the applied electric field strength, magnitude of force is $f = qE$. In the presence of an emf V between two electrodes the region between the two plates has an electric field E = V/d, where d is the distance between the two parallel plate electrodes. If the geometry differs from parallel plate geometry, the field will get modified accordingly. The electrostatic force f on the charged ions makes them drift towards the respective electrodes which in turn result in accumulation of ions at the electrodes. The positive ions like Cu++, Zn++ and Ag+ are attracted towards the cathode and cations toward the anode. The accumulation of anions at the cathode results in an electrodeposition. Under certain operating conditions electrodeposition in circular cell geometry 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) [1]. In DLA, the movement of metal ions with positive charge (anions) in an electrolyte, in addition to electrostatic force f is under the influence of zigzag random motion (Brownian motion)[2]. Superimposition of this random motion on the directional motion due to electrostatic force makes the ions wander in the electrolyte and the path travelled becomes zigzag rather than straight. Electro deposition, viscous fingering, dendritic crystal growth, and DLA (Diffusion Limited Aggregation) [3, 5] are few examples of Diffusion controlled pattern formation. Fractal and non fractal aggregation concept is applicable in physics especially in turbulence [6, 7] polymerization [8, 9]. In many cases self-similarity and fractal character is exhibited by phenomena like coagulation, Gelation, dendritic growth, crystallization. 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. For experimental studies of growth of dendritic patterns and fractals electro-deposition process [10] is well suited. Concept of Fractal model is being used for the forecasting the trends of the random events like prices in the share market [11, 12].

Self-similar pattern formation also result in some solidification processes [13] and exhibit Fractals character. The fractals known as percolation clusters [14] are formed by seepage of liquids like water into the soil or materials in the form of powder or flows through coffee grains etc.

1.2 Effect of Temperature

Process of electrodeposition is always subjected to constraints arising from zigzag random motion (Brownian motion). In a typical electrodeposition cell employing circular cell geometry, there a circular anode at the centre of which a point cathode is located. The space between cathode and the outer anode ring is filled with a thin layer of electrolyte. Most of the studies related to electrodeposition of dendritic patterns in circular cell geometry or planar / linear cell geometry suffer from a drawback that the electric field is not uniform or constant throughout the entire region of space between cathode and anode. In circular cell geometry, the electric field is strong at the centre of the cell i.e. at the cathode initially This effect is more pronounced before the commencement of the electrodeposit, also when the size of electrodeposit is appreciably increased the distance between the outer anode ring and central cathode is appreciably reduced where as the applied voltage remains constant this in turn results in higher electric field. In electrodeposition the movement of the ions is of key value and electrodeposition is the result of drifting of ions. The electrostatic force F on an ion with charge q is given by

$$F = q E$$

Where E is the intensity of electric field at that point where the charge q is located. The movement of ions present in the electrolyte is governed by several conditions including the electrostatic force on the ions. In addition to the electrostatic forces the hydrodynamics of the fluids in the cell determine the migration of ions.

The two major factors affecting the migration of ions are;

- Radial applied electric field (due to voltage across the electrodes).
- Zigzag random motion due to temperature.

In the diffusion limited aggregation there is aggregation of metal ions from the electrolyte where the positive metal ions mover towards the cathode due to applied potential difference. At the same time there is zigzag random motion at all temperature, due to this the ions keep drifting in a zigzag random fashion. If the zigzag random motion becomes comparable to the radial motion, the migration of ions (diffusion) due to the applied electric potential is appreciably modified by the Brownian motion [15].

2. Experimental

2.1 Review Stage

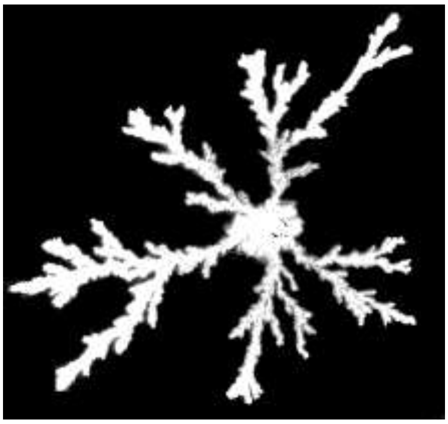
The experimental setup used for the study of effect of temperature on the morphology of the electrodeposits was not much different from previous work. It consisted of a electrodeposition cell constructed [16-18] from acrylic sheets with arrangement to permit a thin layer of electrolyte to be used for electrodeposition. A circular anode made of copper was provided at the centre of which a point cathode was arranged whose electrical connection was on the other side of the cell assembly. Leveling arrangements were provided for the cell assembly to ensure uniformity of the electrolyte in the form of thin layer and two dimensional growth of electrodeposit. The electrodeposition cell was fed with a regulated power supply with constant current facility capable of providing 2 A DC current at selected voltage (continuously variable from 0 – 16 V).

Figure 1: Photograph of setup of constant temperature bath

As the shape and morphology of electrodeposits was of interest, arrangements were made for photography of the electrodeposits using close-up lens assembly. Arrangements were made for placing the electrodeposition cell assembly in a constant temperature bath so that the electrodeposition at desired constant temperature could be studied.

Electrodeposition of copper from 1 M CuSO4 solution is studied at four different temperatures i.e. 45and 50°C at cell operating voltage of 6V. Electrodeposit obtained using cell operating voltage of 6 V and electrolyte temperature of 45°C is shown in Figure 2 along with it two color bitmap image in black and white.

(a)



(b)

Figure 2: Electrodeposit of copper from 1 M CuSO4 solution at a cell operating voltage of 6V at 45°C, a) actual deposit and b) two color bitmap of image.

The electrodeposit image was converted to gray scale and then to two colour bitmap image selecting suitable threshold to include all the prominent components of the image. Exterior parts of image like the edge of the outer anode ring etc. were removed from the image before the image was subjected to box counting. Box counting was implemented using a computer program that converted the image in to a matrix of pixels with occupied and unoccupied regions. The computer program selected square boxes of different sizes (r) starting from a lower value and counted the total number (N) of such boxes required to completely cover the entire image. This procedure of finding out the total number (N) of boxes of size (r) was repeated using all the selected values of r and finally the results were tabulated in a computer file that contained values of r, N, log(r) and log (N). Table –1 shows the results of box counting as applied to the two colour bitmap image of Figure 2 which is the output from the computer program on the analysis of the two colour bitmap image shown in Figure 2.

Table 1: Results of box counting applied to image from Figure 2

r	N	log(r)	log(N)		r	N	log(r)	log(N)
1	118070	0	5.0721		39	208	1.5911	2.3181
2	35995	0.301	4.5562		44	172	1.6435	2.2355
3	16657	0.4771	4.2216		50	141	1.699	2.1492
4	9779	0.6021	3.9903		57	112	1.7559	2.0492
5	6467	0.699	3.8107		64	100	1.8062	2
6	4661	0.7782	3.6685		72	82	1.8573	1.9138
7	3540	0.8451	3.549		81	70	1.9085	1.8451

8	2786	0.9031	3.445		91	52	1.959	1.716
9	2279	0.9542	3.3577		103	49	2.0128	1.6902
11	1599	1.0414	3.2038		116	39	2.0645	1.5911
13	1208	1.1139	3.0821		131	34	2.1173	1.5315
15	947	1.1761	2.9763		147	28	2.1673	1.4472
17	762	1.2304	2.882		165	26	2.2175	1.415
20	591	1.301	2.7716		186	19	2.2695	1.2788
23	464	1.3617	2.6665		209	16	2.3201	1.2041
26	393	1.415	2.5944		235	14	2.3711	1.1461
30	308	1.4771	2.4886		264	14	2.4216	1.1461
34	258	1.5315	2.4116		–	–	–	–

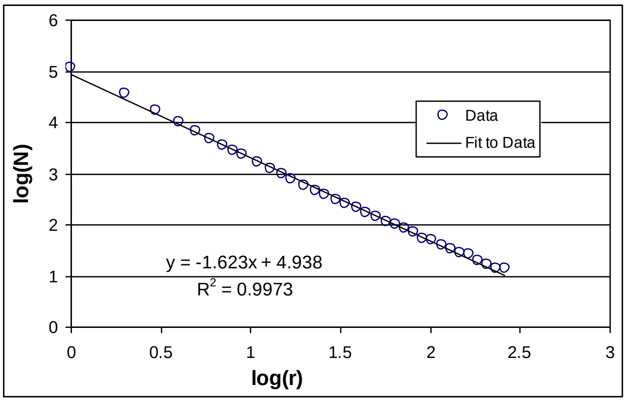


Figure 3: log (N) versus log (r) plot for Electrodeposit of copper from 1 M CuSO4 solution at a cell operating voltage of 6V at 45°C.

The graph of log (N) versus log(r) for the results of box counting applied to Figure 2 is shown in Figure 3. The points plotted are the actual data and taken from table –1 and the straight line joining these points is the best fitting straight line for these data points. This graph confirms the presence of self similarity and scale invariance as all the points lie well along a straight line and therefore the electrodeposit shown in Figure 2 is a fractal and possesses fractal characteristics.

Electrodeposit obtained using cell operating voltage of 6 V and electrolyte temperature 50°c is shown in the Figure 4 along with it two color bitmap image in black and white

(a)

(b)

Figure 4: Electrodeposit of copper from 1 M CuSO4 solution at a cell operating voltage of 6V at 50°C, a) is the image of actual deposit and b) is its two color bitmap

Same procedure is applied, the electrodeposit image was converted to gray scale and then to two colour bitmap image selecting suitable threshold to include all the prominent components of the image. After removing the exterior parts of image like the edge of the outer anode ring etc. the image was subjected to box counting. Box counting was implemented using a computer program that converted the image in to a matrix of pixels with occupied and unoccupied regions. The computer program selected square boxes of different sizes (r) starting from a lower value and counted the total number (N) of such boxes required to completely cover the entire image. This procedure of finding out the total number (N) of boxes of size (r) was repeated using all the selected values of r and finally the results were tabulated in a computer file that contained values of r, N, log(r) and log (N).

Table 2: Results of box counting applied to image from Figure 4.

r	N	log(r)	log(N)		r	N	log(r)	log(N)
1	108791	0	5.0366		39	219	1.5911	2.3404
2	34058	0.301	4.5322		44	190	1.6435	2.2788
3	16032	0.4771	4.205		50	152	1.699	2.1818
4	9518	0.6021	3.9785		57	132	1.7559	2.1206
5	6379	0.699	3.8048		64	107	1.8062	2.0294
6	4631	0.7782	3.6657		72	94	1.8573	1.9731
7	3533	0.8451	3.5481		81	76	1.9085	1.8808
8	2803	0.9031	3.4476		91	66	1.959	1.8195
9	2296	0.9542	3.361		103	52	2.0128	1.716
11	1659	1.0414	3.2198		116	44	2.0645	1.6435
13	1221	1.1139	3.0867		131	38	2.1173	1.5798
15	985	1.1761	2.9934		147	34	2.1673	1.5315
17	810	1.2304	2.9085		165	30	2.2175	1.4771
20	619	1.301	2.7917		186	23	2.2695	1.3617
23	503	1.3617	2.7016		209	19	2.3201	1.2788
26	404	1.415	2.6064		235	16	2.3711	1.2041
30	329	1.4771	2.5172		264	13	2.4216	1.1139
34	272	1.5315	2.4346		297	13	2.4728	1.1139

Table 2: Shows the results of box counting as applied to the two colour bitmap image of Figure 4 which is the output from the computer program on the analysis of the two colour bitmap image shown in Figure 4.

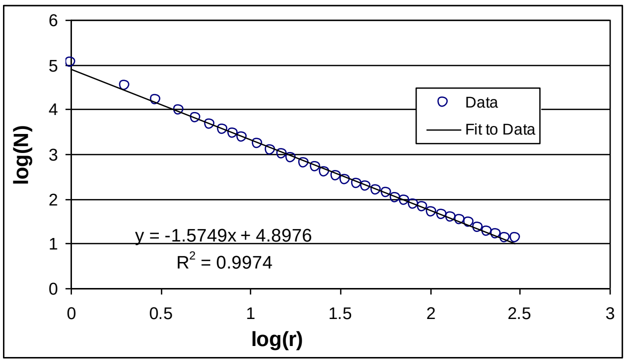


Figure 5: log(N) versus log (r) plot for Electrodeposit of copper from 1 M CuSO4 solution at a cell operating voltage of 6V at 50°C

The graph of log (N) versus log(r) for the results of box counting applied to Figure 4 is shown in Figure 5. The points plotted are the actual data and taken from table –2 and the straight line joining these points is the best fitting straight line for these data points. This graph confirms the presence of self similarity and scale invariance as all the points lie well along a straight line and therefore the electrodeposit shown in Figure 4.is a fractal and possesses fractal characteristics.

3. Conclusion

It is observed that electrodeposition of copper has been done at different temperature i.e 45 °& 50° C by maintaining concentration of the Cuso4 solution 1M and voltage (i.e 6V) of the cell constant the branching pattern obtained was found to be very much different in first case at 45°C temperature branching pattern with fewer but broad and thick branches and in second case at higher temperature 50°C branching pattern is more thick and number of branches was reduced. Thickness of branches increases because Brownian motion leads to electrodeposits to form thicker branches. Also fractal dimension of electrodeposits at 45°c is 1.623 where as that at 50°C temperature is 1.574, at 45°C the fractal dimension of the electrodeposit approaches the standard DLA fractal dimension of 1.66 which is seen in the following table-3

Table 3: Fractal dimension at different temperatures

Image	Cell operating conditions	FD	R^2
T1	Cuso4 1M-6v at 45°c	1.623	0.997
T2	Cuso4 1M-6v at 50°c	1.574	0.997

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