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Study of Electro-Deposition from Mixture of Copper-Sulphate And Zinc-Acetate Solution

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ABSTRACT

Electro-deposition of metals from mixture of electrolytes results in growth of dendritic patterns exhibiting fractal character under certain cell operating conditions. Electro-deposition of copper and zinc in the form of dendritic patterns exhibiting fractal character is studied in circular cell geometry using mixture of copper-sulphate and zinc-acetate as electrolyte in circular electro-deposition cell geometry. It is shown that the electro-deposits obtained from the mixture of electrolyte exhibit different character in terms of the branching pattern morphology and complexity of structure. The electro-deposited patterns obtained and different stages are analysed for fractal character using box counting technique and the results and findings are presented.

KEYWORDS: Electro-deposition, copper-sulphate, zinc-acetate, fractal, fractal dimension, Diffusion Limited, Aggregation, Box counting

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INTRODUCTION

Electro-deposition of metal ions[1, 2, 3, 4] from electrolytes under certain operating conditions results in development of branching patterns exhibiting dendritic shapes. The branching patterns exhibits self avoiding tendency such that the growing branches try to avoid neighboring branches and they never touch each other during growth of electro-deposit. Such electro-deposits have a tendency to allow the growth of branches that are already well developed and very limited or no electro-deposition is present at the branches that remain under developed as compared to the rest of the competing branches. This effect where developed branches tend to grow faster than the under developed branches is known as the masking effect and is the characteristic of Diffusion Limited Aggregation (DLA)[5,6,7,8,9,10]. The reason for such a masking effect is that in the region between two growing branches is such that a wandering metal ion in this region has higher probability of sticking to the branches on one side or the other as compared to reaching deeper in the space between the two branches and sticking to a under developed shorter branch.

EXPERIMENTAL SECTION

Electro-deposition from mixture of electrolytes i.e 1M cuso4 and 0.5M Znacetate has been done using electro-deposition cell at cell operating voltage 12V.If the electrolyte is a mixture of more than one salt solution, there will be more than one metal ion with positive charge that is drifting towards the cathode and two respective anions that get discharged at the anode. The movement of the ions in the electrolyte is governed by several factors like hydrodynamics of the electro-deposition cell, the surface tension and viscosity of the liquid, size of the ion, the charge on the ion and the applied electric field and the local electric field. Under a given set of cell operating conditions like type of electrolyte, operating voltage and temperature condition, the force acting on the two different type of metal ions could be different and their size and hydrodynamics will allow certain type of movement in the presence of zigzag random motion. This results in sizable difference of the rate of deposition of metal ions at the cathode and the relative proportion of the two types of metals at the site of deposition is governed by the movement of the ions under the DLA like conditions and their sticking properties at those sticking sites. The circular geometry of electro-deposition cell was designed by keeping in mind for recording photography of growth of fractal pattern Fig 1.1 shows electro-deposition cell In the present work the electro-deposition cell consisted of a circular anode at the centre of which a point cathode was situated.

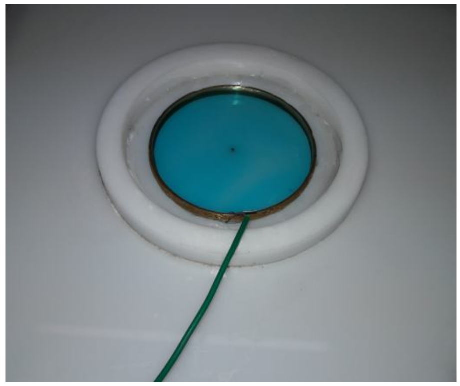

Fig.1.1 Electro-deposition cell

Electro-deposition under cell operating conditions

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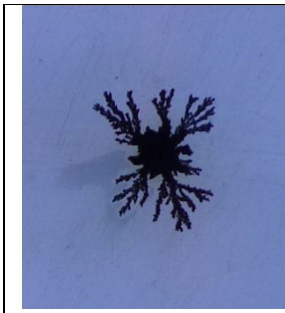	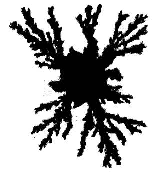
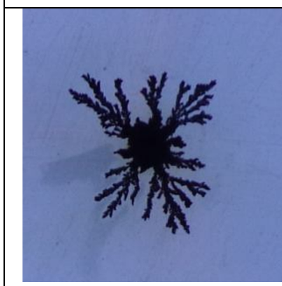	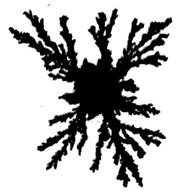
	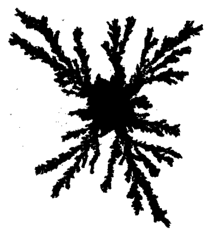
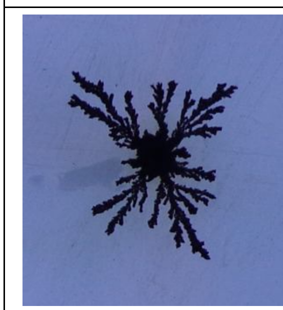	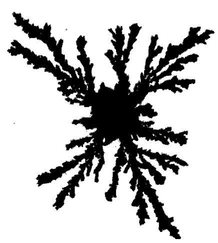
	

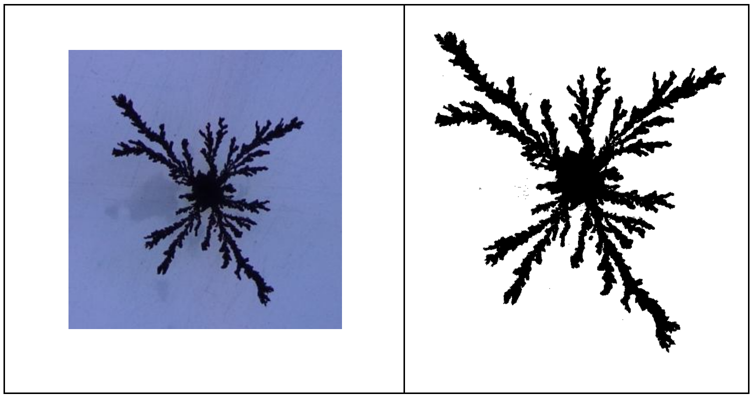

Fig.1.2Nine stages of Development of electro-deposits using Mixture of copper sulphate 1 M zinc acetate 0.5 M

It is seen from the shapes of electro-depositions presented in Fig. 1.2 that during initial stages like first three stages the major component of the electro-deposit is in the form of central lump. Such a lump formations is because of the fact that during initial stages the size of the cathode is very small and in the circular cell geometry electrical lines of force are concentrated at the centre representing a strong electric field. The force acting on the drifting ions is due to the applied electric field and if the electric field is strong the force acting toward the central cathode is also strong. At room temperature there is a component of zigzag random motion or Brownian motion. In Diffusion Limited Aggregation (DLA) the effect of DLA becomes prominent when the two components of driving force i.e. the force due to electric field and the force due to Brownian motion become comparable. In the initial stages of growth of electro-deposit the force due to electric field happens to be much stronger than that due to Brownian motion therefore there is a tendency of development of lumpy structures. As the growth proceeds and development of branches commence, the presence of branches start showing masking effect and growth proceeds along the existing branches. Branches that are growing tend to grow faster and most of the electro-deposit is at the tips of the branches and the region between two branches remains under developed as the ions have higher possibility to stick to the tip of the growing branch than sticking elsewhere. As the growth proceeds further and further the shape of electro-deposit is more and more close to DLA like shapes.

For the characterization of shape of electro-deposits the images of electro-deposits are cleaned up to remove unwanted extra structures like the outer electrode etc and then is converted to gray scale images. The gray scale images are then converted to two colour bitmap images for further processing using box counting technique. We developed program for implementation of box counting technique in Matlab. The image is read in Matlab and the bitmap image in converted into a matrix and the matrix is padded on all the four sides with zero to facilitate box counting. Table 1.1 shows the results of box counting as applied to the first stage of image shown in Fig. 1.2.

Table-1.1 Results of box counting for first stage of electro-deposits- of fig 1.2

r	N	log(r)	log(N)		r	N	log(r)	log(N)
1	11695	0	4.068		15	91	1.1761	1.959
2	3257	0.301	3.5128		17	72	1.2304	1.8573
3	1535	0.4771	3.1861		20	56	1.301	1.7482
4	924	0.6021	2.9657		23	48	1.3617	1.6812
5	606	0.699	2.7825		26	38	1.415	1.5798
6	442	0.7782	2.6454		30	26	1.4771	1.415
7	335	0.8451	2.525		34	28	1.5315	1.4472
8	269	0.9031	2.4298		39	21	1.5911	1.3222
9	218	0.9542	2.3385		44	18	1.6435	1.2553
11	155	1.0414	2.1903		50	15	1.699	1.1761
13	116	1.1139	2.0645		57	16	1.7559	1.2041

The results of box counting presented in Table – 1.1 are plotted using log (N) on the y – axis and log(r) on the x – axis. The points plotted represent actual data from Table 1.1 and the straight line joining these points is the best fitting straight line to this data. Equation of the best fitting straight line is also shown in the inset. The fractal dimension of the shape analyzed is found from the slope of the straight line as Fractal dimension D_f= – slope of the straight line. For the log(N) versus log (r) plot shown in Fig. 1.3 the resulting fractal dimension is 1.6723 and almost all the points lie along a straight line indicating that the shape analyzed is a fractal and possess self similarity and scale invariance.

A similar procedure is adopted for the next stages by implementing the box counting technique and fractal dimensions are obtained which are close to fractal dimension according to DLA (Diffusion Limited Aggregation) characteristic.

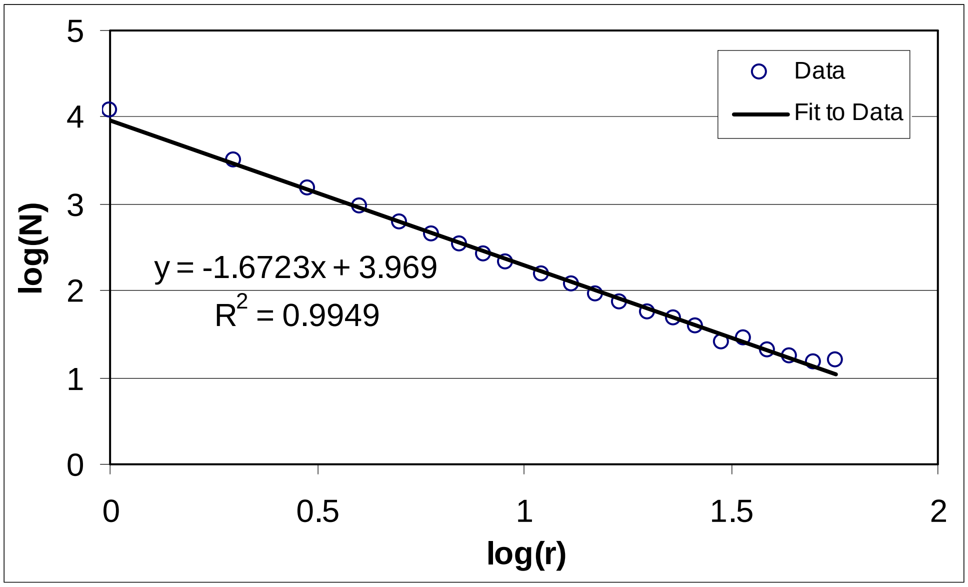

Fig.1.3Log (N) versus log(r) for first stage of electro-deposits of Fig 1.2

RESULT AND DISCUSSION

We successfully studied the electro-deposition from mixture of 1 M copper sulphate and 0.5 M zinc acetate solution at a cell operating voltage of 12 V. For investigation of temporal changes as the growth of electro-deposit proceeds we studied 8th stages of the growth of electro-deposited pattern shown in Fig. 1.2. The electro-deposit contains both the metals i.e. copper and zinc however as the zinc ions require smaller potential difference as compared to copper, the deposition of zinc is at a faster rate as compared to that of copper. The electro-deposit is a mixture of copper and zinc, however as the electro-deposits are dull in colour without metallic luster the electro-deposit does not exhibit colour like brass and the colour of electro-deposit is grayish. The fractal dimension determined at different stages of deposition shown in Fig. 1.2 is presented in the table 1.2

It is seen from Table 1.2 that the fractal dimension of the electro-deposit is high in the beginning and during the major period of electro-deposition the fractal dimension is more of less constant indication that the degree complexity of shape associated with the growing pattern is more or less same and in the present case it is consistent with the fractal dimension of ideal DLA.

Table 1.2 Fractal dimension at different stages of growth of electro-depositof Fig. 1.2

Sr.No.	Image	Slope	Fractal Dimension	R2
1	F6	-1.672	1.6723	0.9942
2	F8	-1.659	1.6589	0.9960
3	F9	-1.665	1.6654	0.9985
4	F11	-1.665	1.6650	0.9975
5	F12	-1.665	1.6646	0.9980
6	F14	-1.66	1.6598	0.9985
7	F15	-1.665	1.6649	0.9984
8	F17	-1.628	1.6278	0.9976
9	F19	-1.622	1.6219	0.9972

At the last stages of growth of the electro-deposition the fractal dimension slightly decreases and is around 1.62 indicating that it is still close to DLA fractal dimension however the increase in the overall size of the electro-deposit results in higher electric field condition for the migration of ions in the electrolyte which results in a slightly lower fractal dimension.

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