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FRACTAL GROWTH MODELING OF ELECTROCHEMICAL DEPOSITION IN SOLID FREEFORM FABRICATION

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ABSTRACT

A new rapid tooling technique ElectroChemical Liquid Deposition Based Solid Freeform Fabrication (ECLD-SFF) was introduced in this paper. In the ECLD-SFF a substrate made of or coated with conductive materials is connected to a DC power supply, and the substrate is put into a plating bath. A very thin metal pin is connected to the DC power as a positive electrode. Between the substrate and the tip of the pin there is a thin layer of metal powder. Under the effects of electric field, metal ions from electrode moving to chemical liquid will deposit onto the powder particle and growing so that the metal particles can be bound by the deposited materials to form freeform solid. By controlling the pin's movement and electrified time, a desired 3-D shape will be built through layer by layer scanning. ECLD-SFF distinguishes itself from other SFF techniques with advantages of products: high build rate, high accuracy, high density, low shrinkage and controllable microstructures. It has been found that the electrochemical deposition among metal particles during ECLD-SFF is a fractal growth process. The fractal dimension and the width of the deposited metal band are all related to electric field density, composition of electroplating liquid and processing time. Several models on the fractal growth between electrodes or metal particles were developed in order to explain these fractal growth phenomena and obtain desired process parameters and conditions for the ECLD-SFF process.

INTRODUCTION

There have been many efforts to use gas-phase laser-induced reaction to make parts. The Selective Laser Sintering system has been used to form alumina parts by oxidation of aluminum powder in air, and to form silicon nitride by laser sintering of silicon in nitrogen or ammonia (Birmingham, 1995). Other efforts are focused on converting laser-induced Chemical Vapor Deposition (CVD) from a film-forming to shape-making technique (Maxwell, 1995, Lehmann, 1994). A technique called Selective Area Laser Deposition (SALD) has been proposed by Jakubenas et al., (1997). Their proposed process, depositing material from one or more organometallic gases on a substrate selectively heated by a scanning laser beam, offers an opportunity of forming shapes under lower temperature with a wide range of materials. The primary limitation of gas-phase reaction methods is their low deposition rates. According to the listed deposition rate of organometallics, 0.1-1.0 μm/min, (Sudarshan, 1989), it may take several weeks even months to make a cubic inch solid metal part by using conventional CVD. Solids can also be free-formed by electrochemical methods. There are two SFF techniques related to electrochemical reactions: tooling with Nickel Ceramic Composite (NCC) and Expresstool (Ashley, 1998). The NCC tooling method uses plastic RP models as a master pattern, it is first coated with a conductive silver-based material, then placed in an electroforming bath of nickel sulfamate where a thin nickel layer is plated over it. The typical nickel plating thickness varies from 0.04 to 0.2 inch (Ashley, 1997). After electroforming, Chemical Bonded Ceramic (CBC) is cast to support the nickel shell. Once the CBC is cured, the ejector pins are drilled and installed.

This technique is not a direct free-forming method, and the filled-in ceramic material usually has large shrinkage that will cause shear stress on the interface and tooling distortion. In Expresstool technique, a mandrel is first made with a CNC machine, then the mandrel is put in a bath of nickel sulfamate for electroforming. The formed nickel shell with a thickness of 1 to 2 mm needs to be backed with aluminum-filled epoxy. The aluminum fraction helps heat conduction. Two main advantages of this process are the ability to produce large parts and the high accuracy of the products due to a very small shrinkage. A key disadvantage is that deep holes do not electroform well; this is also the shortcoming of conventional electroforming techniques caused by the heterogeneity of electric current density. This technique is also not a direct freeform fabrication. A new SFF technique has been developed to overcome the main limitations of other gas-phase chemical reaction or electrochemical SFF techniques. It will be introduced briefly in this paper.

On the other hand, fractal geometry (Mandeibrot, 1967, 1982) has blossomed tremendously in the past few years and has helped reconnect pure mathematics research with both the natural sciences and engineering. Within the last decade fractal geometry and its concepts have become central tools in most of the natural sciences, including physics, chemistry, biology, geology, and meteorology. The application of fractal geometry in engineering, however, is still in its infancy. Although in its infancy in engineering practice, fractal geometry has already been introduced into many disciplines of engineering research and it has great potential in developing new technologies and solving real engineering problems. The engineering field that has benefited the most from fractal research is materials science. The microstructure of such materials as metals, composites, concrete, rocks, graphite, and the majority of synthetic materials can be characterized by fractal geometry. Particle distributions and aggregations also possess fractal properties. The fractal characterization of materials has greatly helped researchers in understanding the microstructures and operative mechanisms of materials, and in implementing the manufacture of new materials. In this paper, the authors will use fractal geometry as a modeling and analysis tool to study deposits and particle growing mechanism in the electrochemical liquid deposition process for solid freeform fabrication. If the fractal growth process is realized and understood thoroughly, then it can be used to predict and control various electrochemical liquid deposition processes used in coating, plating, solid freeform fabrication, and electronic circuit and device making (Bradley et al., 1997).

A NEW SOLID FREEFORM FABRICATION TECHNIQUE

A new SFF technique, called ElectroChemical Liquid Deposition based SFF (ECLD-SFF), has been developed by the authors to overcome the main limitations of other gas-phase chemical reaction or electrochemical SFF techniques**.** In the ECLD-SFF (see Fig.1), the substrate is made of or coated with conductive materials (metals or graphite), and is connected to a DC power supply as a negative electrode (cathode). Then the substrate is put into a plating bath that is filled with electroplating liquid. A very thin pin that is made of deposition metal is connected to the DC power as a positive electrode (anode). Between the substrate and the tip of the pin there is a thin layer of metal powder/particles. Between cathode and anode there is an electric field named Z direction field. Two assistant electric fields are arranged perpendicular to each other to form an X-Y surface electric field. A magnetic field is applied in the Z direction of the substrate to form a tight connection of ferrite material powders. Under the effects of the electric

and magnetic fields, metal ions from electrode moving to chemical liquid will deposit onto the powder particle and growing, and the metal particles will be bound by the deposited materials to form freeform solid. By controlling the pin's movement and electrified time, a desired 3-D shape can be built through layer by layer scanning. The formed product will be further treated, such as sintering and infiltration. Fig. 2 is a conceptual diagram of the ECLD-SFF system. It consists of six sub-systems: an X-Y-Z scanning & elevating; a pin anode feeding; a metal powder feeding system; a electroplating liquid treating and recovery system; a heating system; and a central computer control unit.

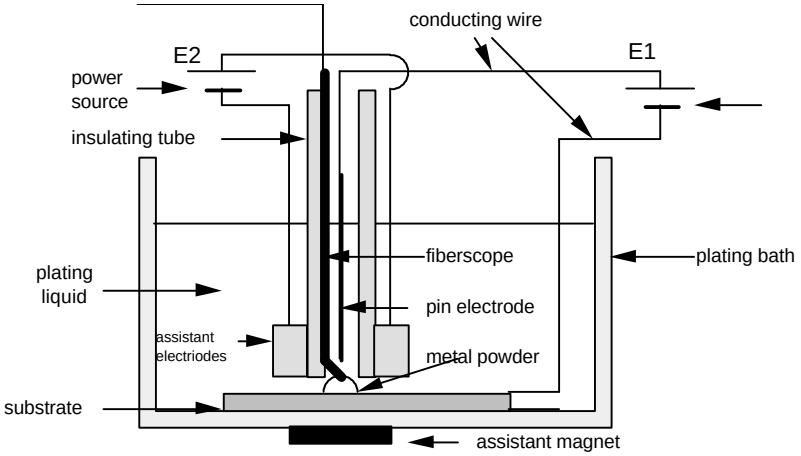


Fig. 1. A complete structure and mechanism of electrochemical liquid deposition

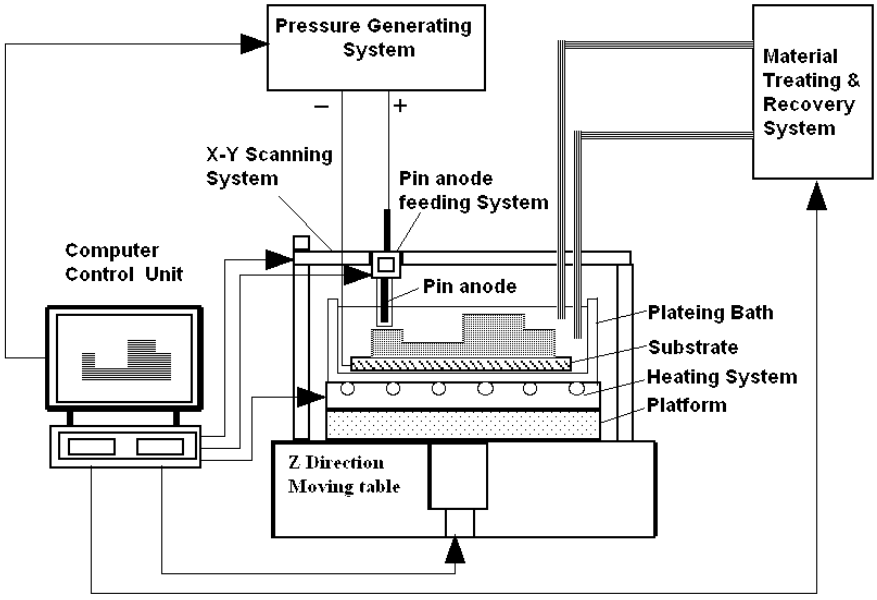


Fig. 2. The conceptual diagram of the ECLD-SFF system

The new ECLD-SFF distinguishes itself from other SFF techniques with the following advantages: (1) High build rate. In ECLD-SFF, the deposited material serves as the binder among the particles of metal powders, and the product is formed by many layers of the powders not only the deposited materials, thus a high producing rate can be expected. Additionally, the

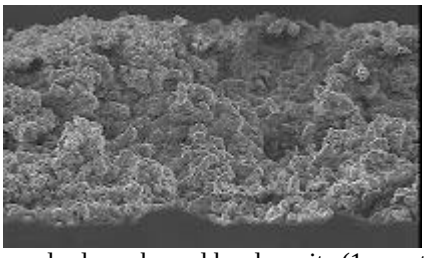
rate can be increased greatly by changing the shape of the anode. For example, for a part with large flat surface we can choose a similar shape metal plate as an anode. (2) High accuracy. In ECLD-SFF, a specially designed insulation tube is used to constrain the electric field of the pin anode, which will provide a concentrated electric field between the substrate and the pin so that the deposition occur only in a very small area. Since both the tube and pin wire can be made very thin, the scanning accuracy will be very high. (3) High density and low shrinkage. In ECDB-SFF, the assistant electric fields are used to increase the amount of the deposited materials among the powders, and the assistant magnetic field is used to increase the accumulation density of the ferromagnetic powders. Also, the layer thickness of the powder can affect the density. The thinner the layer of the powder, the higher the density should be. The high density will lead low shrinkage in later sintering and infiltration. (4) Controllable microstructure. In ECLD-SFF, the microstructures of the formed part can be controlled by changing the composition and the layer thickness of the powder. For example, for the working surfaces of a mold, which needs a higher hardness, we can reduce the layer thickness of the powder in order to increase the density or we can use a mixture of ceramic and metal powders.

FRACTAL PHENOMENA IN ECLD-SFF

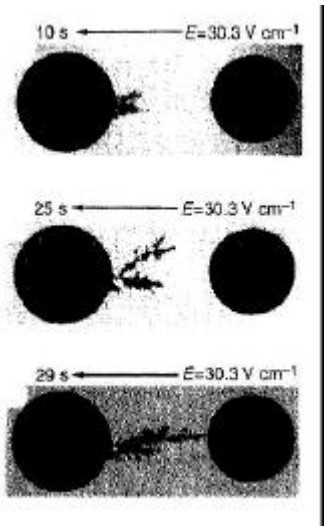
Existing researches on electrochemical deposition and our initial experiments on ECDB-SFF revealed the following interesting phenomena and also challenges. (1) Researches and experiments have shown that metal particles in a suitable electroplating medium can be connected by directed electrochemical growth (Bradley, et al., 1997, 1998). Our experiments further show that if some metal powders are laid on the cathode plate (substrate) and sunk into the liquid medium (Fig. 1), the powder particles can be bound under the action of electric fields and form a solid with a certain strength. In Fig. 3a, an SEM photo shows a ropelike deposit connecting to a particle at the initial growth stage. Our research result, in Fig. 3b, shows the formed powder layer bound by the deposits. (2) Researches and experiments have shown that the electrochemical deposition is a fractal growth process even the distance between two particles is very short, and the fractal growth always occurs in the direction of the electric field (Brady and Ball, 1984). The fractal dimensions of the growing branches and the width of the deposited metal band all decrease with the increasing electric field. Fig. 3c shows several stages of the fractal growth, from which one can see when some new fractal branches are forming, some formed fractal branches may disappear at the same time. After a longer time only a few main branches can survive. (3) Researches and experiments have shown that by using assistant electric fields in surrounding directions (Fig. 1), a web-like deposits among particles can be formed (Fig. 3d). (4) Our initial research has shown that the surface topography of the bound powder particles has fractal structures, and the fractal dimension depends mainly on the composition of the medium, the processing time and the strength of the electric and assistant magnetic fields (Fig. 3e). An assistant magnetic field can increase the particle density and affect the dimensions of the fractal surfaces. (5) Researches and experiments have shown that during the electrochemical process the voltage and current are unstable. There is a critical point of processing time for the deposition among each layer (see Fig. 4). At this critical point the constant voltage will drop sharply to a very low value. From then on the electrochemical deposition process will stop basically until new powders are added on the top surface, and then the voltage recovers to the initial value. This phenomenon can be used to detect and control the fractal growth process.

It is very obvious that the above mentioned electrochemical deposits growing process to bind metal powders under electric and magnetic fields is a complex fractal problem.

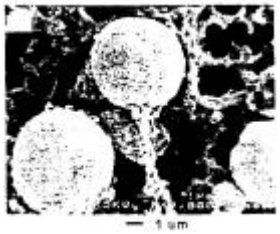
(a) A ropelike deposit on a particle at initial growing



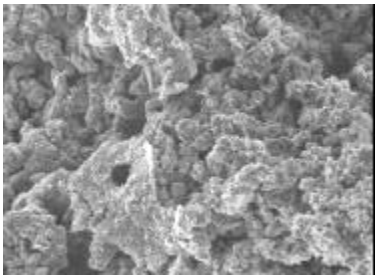
(b) The powder layer bound by deposits (1 mm thick)



(c) Three statges of fractal growth, at 10s, 25s, 29s

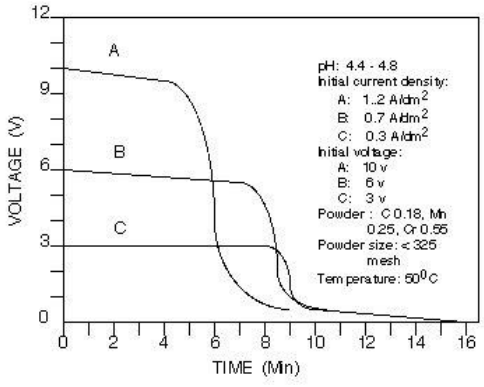


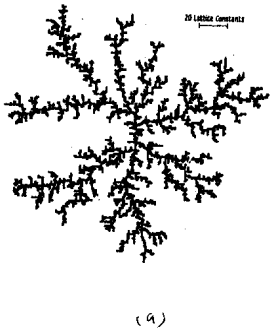
(d) Weblike deposits among particles



(e) The fractal surface topography of bound particles

Fig. 3. Five SEM photos showing fractal growth phenomena





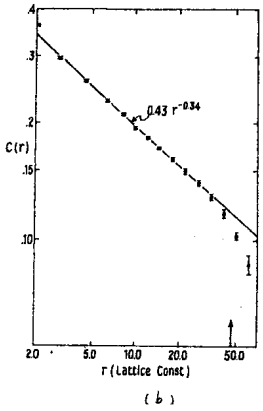


Fig. 4. Relation of the voltage and time, Fig. 5. (a) 3600 particles aggregation on a square lattice, (b) Simulation based on DLA model

FRACTAL GROWTH MODELS

The authors considered several fractal growth models to obtain information on the deposit and explain the above mentioned fractal growth phenomena. First, we consider the simplest case i.e., the fractal growth between two electrodes, then consider the model between two powder particles in single electric field. For the growth among the powders containing a large amount of particles, we will try to use the re-normalization group method.

1. Diffusion-Limited Aggregation (DLA) Model Between Two Electrodes

The goal of this model is to find the density distribution of the deposit in a small area between the pin anode and the plate cathode. It is expected that the density distribution is related to the microstructures and accuracy of the product. The pin anode with a diameter *d* is above the center of a metal disc and the cathode/disc has a diameter D. We assume that *d* is much smaller than D, and the end of the pin is so close to the disc surface that the deposition can be assumed as a 2-D process occurring on the disc. After a metal atom in the pin anode losses its electrons and become an ion, it will move into the plating liquid. Once the ion contacts the cathode surface it will get electrons and deposit on the disc. The second, ion walks randomly until it visits a site adjacent to the first one and the walking particle becomes part of the cluster. The next particle joins the cluster at a random distant point, and so forth. With the increase of deposited atoms the average walking distance of an ion before contacting the cathode will decease. The exposed ends of the cluster tend to grow more rapidly than other perimeter sites because these sites are "shadowed" by the deposits. The above mentioned growth process can be simulated with the Diffusion-Limited Aggregation (DLA) model. This model was first developed by Witten & Sander (1981), in which the so-called "shadow" effect is expressed as "diffusion-limited' In a 2-D DLA model a particles, i.e. ion is released from a random position on the boundary of a square lattice at regular intervals. The released particles will walk randomly in the lattice until join the aggregate. If assuming the distance ã separating two sites is much less than the size D of the aggregate, we can obtain information about the deposit-particle distribution from the following density correlation function:

$$C(g) = N^{-1}\sum_{g'} r(g')\,r(g'+g)\,, \qquad (1)$$

where ã' denotes the distance variable, N is the total number of deposit-particles, the density $\rho(\gamma)$ is defined to be 1 for the occupied site and 0 for the others. Fig. 5a shows a 3600-particle aggregate on the lattice. Fig. 5b shows the simulation results, in which the solid line is a least-squares fit over the range $\gamma = 3$ to ã = 27. The error bars represent the spreads of values among the six samples of aggregate. The arrow marks the average radius of the gyration. The simulation shows

$$C(g) = 0.43g^{\,-0.343\pm0.004}\,. \qquad (2)$$

From this we can get the following results. (1) The density distribution depends only on the distance separating two sites providing the distance is much less than the size of the aggregate. (2) The density correlation within the model aggregation falls off with distance obeying a fractal power law. (3) The maximum of density is only 0.43 (let ã =1 in Eq. (2)). The lower density of the deposit will cause large shrinkage, distortion and low strength of product. This is why we do not use direct electrochemical deposition between two electrodes. (4)

Considering that the real deposition occurs on a smaller circular area not a large square area and the ions is not released from the boundary of the deposition area, the density of the center region close to the pin anode must larger than that of others. This kind of distribution is desirous to the high accuracy of products. This 2-D model can be analogized to 3-D and was verified by experiments (Brady, 1984). However, DLA model is not so suitable to describe the fractal growth in our ECLD-SFF study. First, according to DLA model, we can not get any formula used to calculate the growth rate. Second, our experiments showed that the fractal growth occurs between the polarized powder particles not between the electric poles. Thus the space between particles, the size and shape of the particles all affect the growth. Thirdly, according to the DLA model, the growth process can continue forever without any critical points of cease-growing like illustrated in Fig. 4. Therefore, other two models were developed.

2. Modeling on the Fractal Growth between Two Metal Particles

The main goal of this model is to obtain a formula on the growth rate of deposits between powder particles. If the boundary and initial conditions can be got, according to the formula we can calculate the growth rate, then estimate the production rate. Production rate is very important not only to ECLD-SFF but also to other rapid tooling techniques. The fractal growth between two powder particles (not atoms) is shows in Fig. 6. After an electric field is applied to a pair of particles, both of them will be polarized (Fig. 6a). Initially the particle close to the anode will liberate metal ions while the particle close to cathode will reduce solvent (Fig. 6b). The concentration of the ions near the former one is much higher than that near the latter one. The ions will move towards the latter one by diffusion, and when the ion concentration around the latter particle reaches a critical value the electrodeposition will occur and the fractal branch begin to grow to facing the other particles (Fig. 6c). It is first assumed that the single electric field between two spherical particles has a cylinder shape (Fig. 6d), the ion concentrated along the X-axial direction has a continuous distribution. If the distance between the two particles is long enough, the effect of the shape of the particle can be neglected, then the concentration distribution along the radial r-direction will be uniform. Thus we can use U(x, t) denotes the concentration at point x at time t. If R denotes the radius of the particle, we have $-R< r <R$. In a very small area $\delta(x, r)$ around the center point C(x, r), the ion number will be $U(x, t)\delta(x, r)$. If assuming that ions all obey Brownian motion law and are independent with each other, then it can be deduced that the ion concentration at time t + h has the following normal distribution:

$$U(x', t + h) = (2\pi h)^{-1/2} \exp[-(x - x')^2/(2h)]U(x, t)dx \quad (3)$$

By differentiating x' and h, we obtain

$$\partial U/\partial t = 0.5 \nabla^2 U \quad (4)$$

where ∇^2 denotes the second order partial differentiation. The boundary conditions of this differential equation are assumed as follows: On the surface of the particle near the cathode the ion concentration is a constant during the process, i.e., $U(x = 0) = U_0$. Using F_t denotes the depositing bound at time t, on F_t all ions will lose their electric charges, so we have $U(F_t) = 0$. The growing rate of F_t in its orthogonal direction will be

$$V_n = K_n \nabla U \quad (5)$$

where ∇ denotes the first order partial differentiation and K is a coefficient of per unit time growing rate.

This model also can not describe the critical phenomenon shown in Fig. 4, because it is related to only a few particles. As we know most critical phenomena occur in the systems consisting of a large number of individual units.

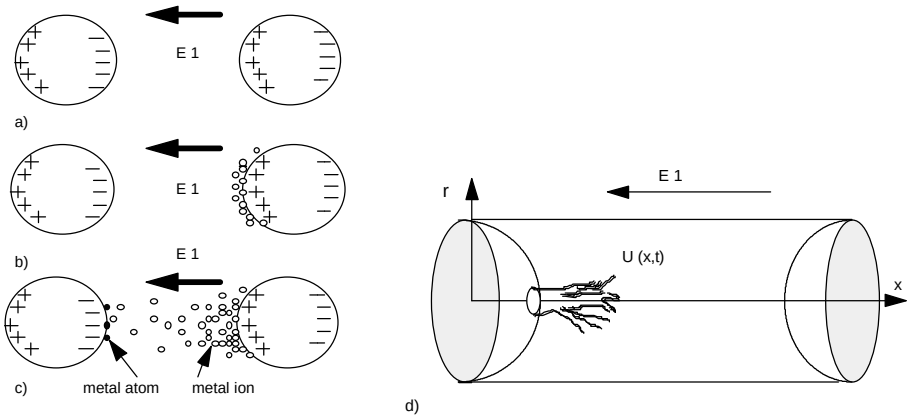


Fig. 6. Fractal growth of deposits between two parcicles

3. Modeling on the Fractal Growth among a Large Amount of Particles

It is impossible to treat fractal growth related to many particles by conventional analytic methods. Even if we can deduce a very complex model to describe the growth among ten particles, we are still not sure if it can be used to describe the case of more than ten particle, and whether the results can be used to explain the complex growth phenomena. So we will try to use the re-normalization group method which has been used to treat various phase transformation or critical problems (Wilson and Kogut, 1974). Considering a 2-D array which contains a large amount of particles, if four neighbor particles can be connected by deposited material just like that shown in Fig. 3, we call the unit containing four connected particles breakover cell. Under the action of the electric fields, some units in the array may become breakover cells, but others may not. With the time increasing, the number of breakover cell will be more and more. But when the number reaches a critical value the whole array will become breakover by connecting a lot of neighbor breackover cells and forming some breakover cell clusters. Once the array becomes breakover, the distribution of electric fields on the array will be changed greatly. Further depositing new material among the remained individual particles will be very difficult, so the process will stop. We think it may be the main reason why the voltage will drop down very quickly after a period in the ECLD-SFF process in Fig. 4. The goal of this model is to find the conditions that the cluster can form and the density of the breackover. If the formed clusters have the fractal structure, we also want to know their fractal dimension.

In the 2-D array model, assuming the breackover probability of a four-particle unit is p_0, critical point probability $p_{c.}$ It has been known when $0 < p_0 < p_{c,}$ the cluster forming probability P is very small. However, when $p_c < p_0 < 1$, P will be very close to 1. Although by using Monte Carlo method one can calculate the value of $p_{c,}$ when there are a lot of particles, the calculation will be very difficult and time-consuming. Here we are introducing the re-normalization group method. As shown in Fig. 7a, four adjacent particles form into an initial unit, and it has the breackover probability p_0. Four adjacent initial units form into a first degree unit with breackover probability p_1, and four first degree units form a second degree unit with probability p_2, and so

on. Based on the principle of re-normalization group, p_2 can be calculated from p_1, p_3 can be calculated from p_2, p_4 can be calculated from p_3, and so on. Fig. 7b-7f show all probable cases of four first degree units. The probability that all four initial units are not breackover is $(1- p_0)^4$ (Fig. 7b). The probability that only one initial unit is breackover will be $p_0(1-p_0)^3$ (Fig. 7c). The probability that only two initial units are breackover should be $p_0^2(1-p_0)^2$ (Fig. 7d). The probability that only one initial unit is not breackover is $p_0^3(1-p_0)$ (Fig. 7e). The probability that all initial units are breackover is p_0^4. Therefore, the probability that a first-degree unit is breackover will be

$$p_1 = 2\, p_0^{\,2}(1 - p_0)^2 + 4\, p_0^{\,3}(1 - p_0) + p_0^{\,4} = 2\, p_0^{\,2} - p_0^{\,4} \qquad (6)$$

Then considering the second degree unit with the same method, we get $p_2 = 2\, p_1^{\,2} - p_1^{\,4}$. A general equation is

$$p_{n+1} = 2\, p_n^{\,2} - p_n \qquad (7)$$

Figure 8 shows the iteration relationship between p_{n+1} and p_n. This equation can be rewritten as

$$f(x) = 2x^2 - x^4 \qquad (8)$$

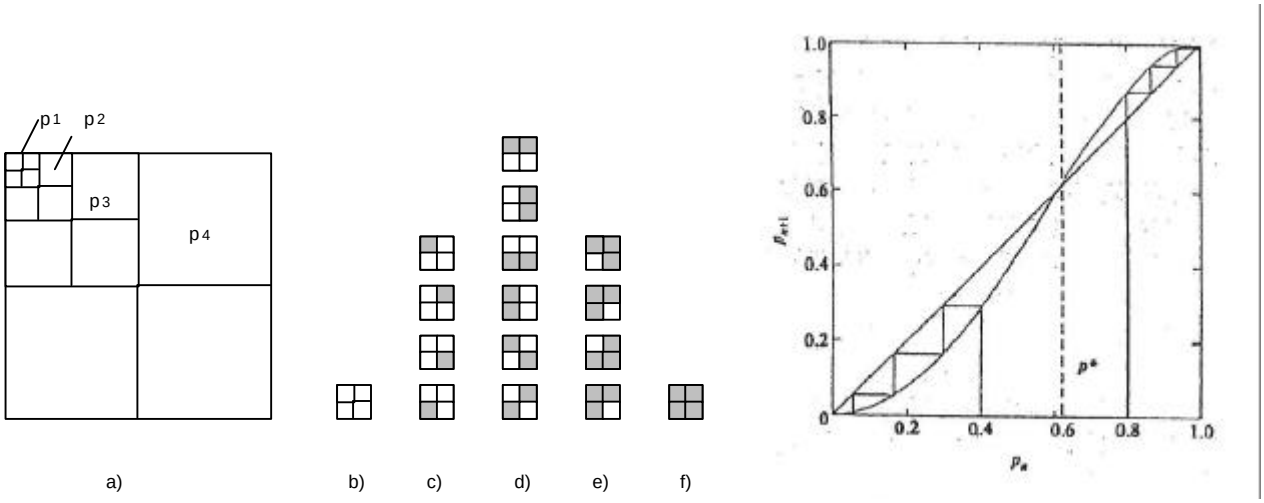


Fig. 7. The breakover probabilities of the first degree unit, Fig. 8. Iteration between p_n and p_{n+1}

Let $f(x) = x$ ($0< x <1$) and we get three solutions (fix points): $x_1= 0$, $x_2 = 0.618$ and $x_3 = 1$. Their corresponding values of $df(x)/dx$ will be $\lambda_1= 0$, $\lambda_2= 1.582$ and $\lambda_3= 0$. Therefore, both x_1 and x_3 are stable, but x_2 is unstable because $\lambda_2 >1$. So the critical probability p_c will be 0.618. It is an approximate value. In order to improve the accuracy we can chose 3×3 unit instead of 2×2 unit and obtain,

$$p_{n+1} = 3\, p_n^{\,3} + 3\, p_n^{\,4} - 2\, p_n^{\,5} - 15 p_n^{\,6} + 18\, p_n^{\,7} - 7 p_n^{\,8} + p_n^{\,9} \qquad (9)$$

According to this equation, we calculate $p_c = 0.609$ that is closer to the value obtained from Monte Carlo method. From the obtained critical value, we can deduce the critical particle number n_c of the cluster,

$$n_c \approx n^{0.5 d_f} \qquad (10)$$

where n is the total number of the particles in a 2-D array, and d_f denotes the fractal dimension of the cluster. If n is big enough we can get $d_f \approx 1.896$. Then the ratio between n_c and n can be calculated. For example, when n = 10,000, the ratio is about 55%. It means when the depositing process stops, over a half of the metal particles can be connected. However, the real ECLD-SFF process should be considered in 3-D models. In the simplest case, the initial unit will include $2 \times 2 \times 2$ particles. But there are three ideal stacking modes of the metal particles, i.e., Body Centered Cubic(BCC), Face Centered Cubic(FCC) and Hexagonal Close-packed (HCP). For different stacking mode the critical probability will be very different. In addition, we must consider the effects of voids in real metal powders. The 3-D model of fractal growth is very challenge and promising.

CONCLUSIONS

It has been found that the electrochemical deposition among metal particles during ECLD-SFF is a fractal growth process. The fractal dimension and the width of the deposited metal band are all related to electric field density, composition of electroplating liquid and processing time. Based on the DLA model of the fractal growth between two electrodes we know that the density distribution depends only on the distance separating two sites, the density correlation within the model aggregation falls off with distance obeying a fractal power law, and the maximum of density is only 0.43. According to a 2-D re-normalization group model, the critical phenomenon on the fractal growth will occur when the whole powder layer becomes breakover. In the critical case the formed powder cluster's fractal dimension is 1.896, the ratio of the particles connected by the deposits is about 55%. Based on the fractal model we can calculate growth rate of deposits.

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