Multifractality of growth probability distribution in diffusion-limited-corrosion pit

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The multifractal structure of the growth probability distribution on the perimeter of a pit in the diffusion-limited pitting corrosion is derived by making use of the Monte Carlo estimation of the hitting probabilities by successive launching of a large number of random walkers. The multifractal spectrum $a-f(a)$ is determined, and compared with that of the diffusion-limited aggregation. It is found that the scaling exponent β of width w of the corrosion pit ($w \approx n^\beta$, where n is the particle number removed from metal) is given by $\beta = D_n(1)$ where $D_n(1)$ is the information dimension. It is also shown that the scaling exponent β is related to the maximum growth probability $p_{\max}$ at the edge of the corrosion pit and approximately given by $\beta = 1 - D_n(\infty)$.

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Recently, there has been increasing interest in the physical mechanisms governing the geometrical structure in diffusion-limited aggregation (DLA) [1-7]. It is well known that an aggregate cannot be fully characterized only by its fractal dimension. By using the multifractal formalism, Halsey, Meakin, and Procaccia [8] has suggested that there are two exponents for characterizing the DLA surface. Meakin *et al.* [9] and Amitrano, Coniglio, and di Liberto [10] have shown that the surface of DLA requires an infinite hierarchy of fractal dimensions for its characterization. They have presented the multifractal structure of the growth probability distribution. Nagatani [11] has presented a real-space renormalization-group method for calculating the multifractality of the growth probability distribution. The fact that an infinite set of exponents is necessary to characterize completely the properties of the DLA fractal has analogs in many fields, such as turbulence, self-similar resistor networks, localization, and dynamical system (see Refs. [12,13] for review articles).

Very recently, Nagatani presented a growth model to simulate the pit formation in pitting corrosion of metal surface [14]. The pit growth model was described in terms of the anti-DLA model. The profile of the corrosion pit was not a fractal but a dense structure. However, it was found that the width w and depth h of a pit scale as

$$w \approx n^\beta \quad (\beta = 0.66 \pm 0.05), \quad (1)$$

$$h \approx n^\gamma \quad (\gamma = 0.35 \pm 0.05), \quad (2)$$

where n is the particle number removed from metal. The width w and the depth h are defined, respectively, as the maximum value of the width and as the maximum value of the depth within the single pit. One can expect the multifractal structure of the growth probability distribution on the perimeter of the diffusion-limited-corrosion pit, similarly to the DLA fractal. However, until now, the scaling structures of the pitting corrosion have been little studied.

In this paper, we study the growth probability distribution on the perimeter of the corrosion pit. We derive the multifractal structure of the growth probability distribution in the diffusion-limited pitting corrosion. Similarly to

the DLA fractal, the growth probability on the perimeter of the corrosion pit is given by the harmonic measure. We calculate the growth probability by using the Monte Carlo estimation of the hitting probability by successive launching of a large number of random walkers. We compare the multifractal structure of the corrosion pit with that of the DLA fractal.

The pitting corrosion is induced by localized dissolution of an oxide-covered metal in the presence of a solution of certain anionic species [15]. The propagation of corrosion is generally thought to occur as follows: Anions such as chloride are concentrated into the corrosion pit from the external solution. The gradient in solution composition maintains the metal surface inside the corrosion pit in an active (dissolving) state. The local environment is acidified owing to the hydrolysis of the dissolving metal ions. This process is controlled by the diffusion of anions [14]. The pitting corrosion is described by the Laplace equation

$$\nabla^2 C = 0, \quad (3)$$

with the boundary conditions,

$$\frac{\partial C}{\partial y} = 0 \text{ on the oxide-covered metal surface}, \quad (4)$$

$$C = 0 \text{ on the surface within the corrosion pit}, \quad (5)$$

$$C = C_\infty \text{ at infinity}, \quad (6)$$

where $\partial C / \partial y$ is the derivative along the outward normal at the oxide-covered metal surface. In what follows we summarize the algorithm of the simulation of pit formation. The simulation is carried out with the use of a simple square lattice. We consider a subset of the square lattice enclosed by a square with 200×200 (units). We start out with a rectangle metal (200×100) with a flat oxide-covered metal surface positioned at the bottom of the square (see Fig. 1). Initially we put a single defect on the center of the metal surface. The pitting corrosion begins to propagate from the nearest-neighboring sites of the defect. The lateral boundary is periodic. A particle is introduced (one at a time) at a randomly chosen point on the upper boundary. The particle performs a random walk.

FIG. 1. Schematic representations of the pitting corrosion. The anions diffuse from the top toward the metal surface. When the diffusing anion lands on the surface of the corrosion pit, the metal particles are removed. When the diffusion anion lands on the oxide-covered metal surface, it is reflected.

The particle continues to move until it reaches a point adjacent to a surface site of the corrosion pit, reaches a point adjacent to an oxide-covered metal surface, or reaches the upper boundary. When the particle reaches a point adjacent to surface sites of the corrosion pit, the surface sites of the pit are removed. When the particle reaches a point adjacent to an oxide-covered surface, it is reflected. When the particle reaches the upper boundary, the random walker is annihilated. We repeat the above procedure. Thus we can obtain the typical patterns of corrosion pit.

We consider the growth probabilities on the perimeter sites inside the corrosion pit. From the growth probability

FIG. 2. (a) The growth probabilities (log plot) at each point on the perimeter of the typical pit with $n=500$ particles. There are 87 sites which are numbered from left to right along the horizontal axis. (b) The corresponding profile of the corrosion pit.

distribution one can obtain detailed information on the removability of each perimeter site to grow. The growth probabilities are given by the harmonic measure similarly to the DLA fractal. The measure is calculated by making use of the Monte Carlo estimation of the hitting probabilities. The probabilities to land at various sites on the typical pit are obtained by the successive launching of 100000 random walkers and recording of the point of first contact (while not allowing the pit to grow further). Figure 2(a) shows the growth probabilities at each point on the perimeter of the typical pit with the number $n=500$ of removed particles. There are 87 sites which are numbered from left to right along the horizontal axis. The vertical axis shows the log of the growth probability of such sites. Figure 2(b) indicates the profile of the corrosion pit. The maximum value of the growth probabilities appears at the edge of the pit or at the nearest neighbor of the edges. The growth probabilities changes alternately from site to site. The large difference between a site and its nearest neighbor is due to the step on the surface inside the pit. The growth probability is large at the upward vertex of the step, and is small at the downward corner of the step. Figure 3(a) shows the growth probabilities at each point on the perimeter of the typical pit with $n=1000$ particles. Figure 3(b) indicates the profile of the corrosion pit.

To study the multifractal structure of the growth probability distribution, for a corrosion pit of removed parti-

FIG. 3. (a) The growth probabilities (log plot) at each point on the perimeter of the typical pit with $n=1000$ particles. There are 130 sites which are numbered from left to right along the horizontal axis. (b) The corresponding profile of the corrosion pit.

FIG. 4. The generalized dimension $D_n(q)$ plotted against q for the growth probability distribution.

cles n , we consider the following moments as a function of n and their relative exponents:

$$Z(q) = \sum_i p_i^q \approx n^{-(q-1)D_n(q)}, \quad (7)$$

where p_i is the growth probability of site i . We note that the moments $Z(q)$ scale as a function of n since the width w and height h of a pit scale as Eqs. (1) and (2). In order to make a distinction between the ordinary $D(q)$ and that in Eq. (7), we represent the generalized dimension as $D_n(q)$. The generalized dimension $D_n(q)$ is calculated from the slope of the log-log plot of Eq. (7) for different values of n . Figure 4 shows the generalized dimension $D_n(q)$ plotted against q for the growth probability distribution. The negative moments $Z(q)$ ($q < 0$) do not diverge since the minimum value of growth probability is not sufficiently small. This is due to no existence of fjords. We introduce the partition of $D_n(q)$ into a density of singularities $f(q)$ with singularity strength $\alpha(q)$:

$$\alpha(q) = \frac{d}{dq} [(q-1)D_n(q)], \quad (8)$$

$$f(q) = q\alpha(q) - (q-1)D_n(q).$$

Figure 5 shows the α - f spectra of the growth probability distribution. The DLA fractal shows a left-sided multifractality or anomalous measure since the growth probability is very small in the fjords [16–18]. However, the α - f spectrum of the corrosion pit shows no left-sided multifractality since there is not a very small growth probability inside the pit. We derive the relationships between the exponent β and $D_n(q)$. Makarov showed that the information dimension $D(1)$ is exactly 1 for the harmonic measure of any connected object in two dimensions, i.e., $\sum_i p_i \ln p_i \approx \ln w$ [19]. Applying the theoretical prediction, we find the relationship

$$\beta = D_n(1), \quad (9)$$

by using $\sum_i p_i \ln p_i \approx \ln w$ and $\ln w \approx \beta \ln n$ [Eq. (1)].

FIG. 5. The α - f spectra of the growth probability distribution.

We obtain the information dimension $D_n(1) = 0.624$. The value is consistent with the exponent $\beta = 0.66 \pm 0.05$ [Eq. (1)] obtained from simulation within numerical accuracy. The information dimension $D_n(1)$ gives the scaling exponent β of the width w . We note that the generalized dimensions $D_n(q)$ are exponents of the number n of removed particles [see Eq. (7)]. Following the method of Turkevich and Scher [20], the variation of the width against that of the number of removed particles is given by

$$\frac{dw}{dn} = p_{\max}, \quad (10)$$

where $p_{\max}$ is the maximum value of the growth probability at the edge of the pit. The maximum growth probability $p_{\max}$ scales as

$$p_{\max} \approx n^{-D_n(\infty)} [D_n(\infty) = \alpha(\infty)]. \quad (11)$$

By using Eqs. (10) and (11), we find the following relationship:

$$\beta = 1 - D_n(\infty) = 1 - \alpha(\infty). \quad (12)$$

We obtain $1 - \alpha(\infty) = 0.613$. The value is also consistent with the exponent $\beta = 0.66 \pm 0.05$ within numerical accuracy. The dimension $D_n(0)$ represents the exponent of the length of the perimeter inside the corrosion pit. The value is given by $D_n(0) = 0.711$.

In summary, we derive the multifractal structure of the growth probability distribution on the perimeter inside the corrosion pit in the diffusion-limited pitting corrosion. By using the Monte Carlo estimation of the harmonic measure, we determine the multifractal spectrum α - f and compare it with that of the diffusion-limited aggregation. We find that the scaling exponent β of the width of the corrosion pit agrees with the information dimension $D_n(1)$. We also show that the scaling exponent β is related to that of the maximum growth probability.

- [1] T. A. Witten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
- [2] T. Visek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989).
- [3] P. Meakin, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and L. L. Lebowitz (Academic, New York, 1988), Vol. 12, p. 335.
- [4] *On Growth and Form*, edited by H. E. Stanley and N. Ostrowsky (Martinus Nijhoff, The Hague, 1985).
- [5] *Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).
- [6] J. Feder, *Fractals* (Plenum, New York, 1988).
- [7] *The Fractal Approach to Heterogeneous Chemistry*, edited by D. Avnir (Wiley, Chichester, 1989).
- [8] T. C. Halsey, P. Meakin, and I. Procaccia, Phys. Rev. Lett. **56**, 854 (1986).
- [9] P. Meakin, H. E. Stanley, A. Coniglio, and T. Witten, Phys. Rev. A **32**, 2364 (1985).
- [10] C. Amitrano, A. Coniglio, and F. di Liberto, Phys. Rev. Lett. **57**, 1016 (1986).
- [11] T. Nagatani, J. Phys. A **20**, L381 (1987); Phys. Rev. A **36**, 5812 (1987); **38**, 2632 (1988); J. Phys. A **21**, L655 (1988).
- [12] H. E. Stanley and P. Meakin, Nature (London) **335**, 405 (1988).
- [13] T. Tel, Z. Naturforsch. **43a**, 1154 (1988).
- [14] T. Nagatani, Phys. Rev. A **45**, 2480 (1992).
- [15] D. E. Williams, R. C. Newman, Q. Song, and R. G. Kelly, Nature (London) **350**, 216 (1991).
- [16] H. E. Stanley, A. Bunde, S. Havlin, J. Lee, E. Roman, and S. Schwarzer, Physica A **168**, 23 (1990).
- [17] B. B. Mandelbrot, C. J. G. Evertsz, and Y. Hayakawa, Phys. Rev. A **42**, 4528 (1990).
- [18] C. J. G. Evertsz, P. W. Jones, and B. B. Mandelbrot, J. Phys. A **24**, 1889 (1991).
- [19] N. G. Makarov, Proc. London Math. Soc. **51**, 369 (1985).
- [20] L. Turkevich and H. Scher, Phys. Rev. Lett. **55**, 1026 (1985).