Dynamic Scaling of Pit-Size Distribution in Corrosion Patterns

Takashi Nagatani
College of Engineering, Shizuoka University, Hamamatsu 432, Japan
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A growth model is presented to simulate the corrosion pattern in pitting corrosion in three dimensions. The pitting corrosion is controlled by diffusion of anions toward the metal surface. The computer simulation is performed to study the scaling structure of pit-size distribution in the corrosion pattern. It is shown that a transition occurs in the overall corrosion pattern from disconnected pits to a percolating structure at the percolation threshold. Below the percolation threshold, it is found that the pit-size distribution $n_s(t)$ obeys the dynamic scaling $n_s(t) \approx t^{-w} s^{-\tau} f(s/t^z)$ ($\tau = 0.93 \pm 0.03$, $z = 1.43 \pm 0.02$, and $w = 0.66 \pm 0.02$), where the cutoff function $f(x)$ is a constant for $x \ll 1$.

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Metallic corrosion is an important field of materials science. Pitting corrosion is a major cause of failure of metal structures. The corresponding corrosion patterns observed experimentally display a complex ordering on many length scales. The corrosion is induced by localized dissolution of passivated (oxide-covered) metal in the presence of a solution of certain anionic species [1]. 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 keeps the metal surface inside the corrosion pit in an active (dissolving) state. The local environment is acidified owing to hydrolysis of the dissolving metal ions. Recently, the formation of pitting corrosion of binary alloys in two dimensions has been investigated with the use of computer simulation by Williams *et al.* [1]. They have shown a mechanism for the triggering of pitting corrosion of stainless steels. Sieradzki *et al.* [2] have also suggested a similar computer model which is based on the Eden model on the percolating cluster. Their model does not take into account the diffusion of anions and the oxide-covered metal surface, and therefore, in their model, corrosion pits are not localized. The pit-size distribution does not indicate a dynamic scaling law except for the percolation threshold. Costa, Sagues, and Vilarrasa [3] found that the overall structure of the corrosion-pit profile can be described in terms of fractal geometry in the steel pitting corrosion experiment. They also showed that the pits observed on corroded surfaces are small or large in diameter, drawing a variety of sizes and shapes. However, until now, there have been no simulations for analyzing the pit-size distribution of the corrosion pattern on an oxide-covered metal surface. Open questions include the scaling behavior of the pit-size distribution in the corrosion pattern.

Recently, there has been increasing interest in a variety of nonequilibrium aggregation and growth models such as the diffusion-limited aggregation (DLA) model and the cluster-cluster aggregation (CCA) model [4–10]. A variety of computer simulations have been carried out to investigate the relationships between the cluster geometry and growth mechanisms. The DLA model presents a prototype of the pattern formation of diffusive systems including electrochemical deposition, crystal growth, viscous fingering, dielectric breakdown, chemical dissolution, and bacterial colonizing. The CCA model presents the prototype of colloidal aggregation, smoke aggregation, and droplet coalescence. In this model, there is dynamic scaling of the cluster-size distribution. Until now, very few investigations of pitting corrosion have been performed from the point of view of growth models. Paterson [11] called the DLA model of decay the anti-DLA model. The anti-DLA model has attracted little attention because the interface becomes stable in the decay process. Sahimi and Tsotsis [12] and Sahimi [13] have studied the disaggregation process on the percolating cluster by using the diffusion-reaction-consumption (DRC) model. They have found the dynamic scaling law of the fragment distribution. Pitting corrosion cannot be simulated by the diffusion-reaction-consumption model since it does not take into account the oxide-covered metal surface.

In this Letter, we present a growth model for the corrosion pattern in the pitting corrosion of an oxide-covered metal. We simulate the corrosion pattern formation by using the growth model, analyzing the scaling structure of the pit-size distribution in the corrosion pattern. If the consumption of the metal is continued for a long enough time, corrosion pits (finite clusters) with a wide variety of shapes and masses appear. This distribution in the number of pits (clusters) is somewhat similar to the cluster-cluster aggregation process [9] and the disaggregation process of reactive porous media [12,13]. There are, however, significant differences between the phenomenon studied here, that of CCA, and that of DRC. The system in CCA is conserved (i.e., the total number of particles does not change), and a large fractal structure is eventually formed. The phenomenon in DCR is dissipative in the sense that the density of occupied sites decreases with time and eventually vanishes. On the other hand, in pitting corrosion, corrosion pits nucleate continuously and coalescence between pits occurs simultaneously. Despite these differences, we show that a dynamic scaling holds for the pit-size distribution. The different mechanism of the pit formation process from the CCA and DRC models results in the different values of the scaling exponents.

First, we present the basic equation and the boundary conditions in corrosion pattern formation. In the pitting corrosion, anionic species diffuse toward the metal surface. After the diffusing anions land on the metal surface, the metal dissolves into solution as a result of hydrolysis of the metal ions. This process is controlled by the diffusion of anions. The corrosion pattern formation is described in terms of the anti-DLA with an appropriate boundary condition. Figure 1 shows a schematic representation of the pitting corrosion. The concentration C of the diffusing anions satisfies the Laplace equation under the quasistationary approximation,

$$\nabla^2 C = 0 . \tag{1}$$

The metal surface is covered with oxide except within the corrosion pit and the oxide-covered metal surface only dissolves with difficulty. We define a dissolution probability P_d to represent the tendency of the oxide-covered metal surface to dissolve. When the diffusing anion lands on the oxide-covered metal surface, the metal dissolves into solution with probability P_d and the diffusing particle reflects from the metal surface with probability $1-P_d$. Then, the boundary condition on the metal surface except for the corrosion pit is given by

$$(1-P_d)\partial C/\partial z - P_d C = 0 \quad \text{on the oxide-covered metal surface ,} \tag{2}$$

where $\partial C/\partial z$ is the derivative along the outward normal at the flat metal surface. In general, the dissolution probability P_d is expected to be sufficiently small. On the other hand, the metal surface inside the pit dissolves easily. On the surface of the pit, we assume that the dissolution time of the metal is significantly shorter than the diffusion time of anions. Then, the boundary condition is given by

$$C = 0 \quad \text{on the surface of the corrosion pit .} \tag{3}$$

The concentration far from the metal surface remains constant,

$$C = C_\infty \quad \text{at infinity .} \tag{4}$$

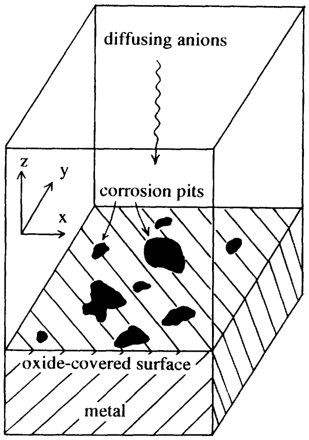

FIG. 1. Schematic representation of corrosion pattern formation on the oxide-covered metal surface. The anions diffuse toward the metal surface. When a diffusing anion lands on the oxide-covered metal surface, the metal component is removed with a small dissolution probability P_d. The metal component on the surface inside the corrosion pit is removed with probability 1.

We consider the simulation of the corrosion pattern formation on the oxide-covered metal surface satisfying Eq. (1) with boundary conditions (2)-(4) (see Fig. 1). The diffusive particle governed by the Laplace equation (1) can be simulated by using an isotropic random walk. The simulation is carried out with use of a simple cubic lattice. We consider a subset of the cubic lattice enclosed by a cube with 100×100×100 (x,y,z) units. We start out with a cube of metal (100×100×50) with a flat surface positioned at the bottom of a cube (see Fig. 1). The metal with a flat surface is covered by an oxide. The lateral boundary is periodic. Particles are introduced one at a time at a randomly chosen point on the upper boundary $(x,y,100)$. Each particle performs a pure random walk resulting from diffusion. The particle continues to move until it reaches a point adjacent to surface sites of the corrosion pit, or until it reaches a point adjacent to the oxide-covered metal surface, or until it 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 the oxide-covered metal surface, it is reflected with probability $1-P_d$ and the oxide component is removed with probability P_d. When the particle reaches the upper boundary, the random walker is annihilated. We repeat the above procedure. The corrosion pattern is developed until the number of particles removed from the metal reaches 14000. Figure 2 shows the time evolution of corrosion patterns in the overall picture for $P_d = 0.01$. We note that for a sufficiently small P_d the number of pits increases with P_d but the scaling property does not change. Figures 2(a)-2(d) indicate, respectively, the overall pictures of corrosion patterns with $t = 2000$, 6000, 8000, and 12000. Here, we define the time t as the particle number removed from the metal. The corrosion patterns obtained from the simulation display a complex ordering on many length scales. The size of the corrosion pit increases with time t. When the area of the corrosion pattern reaches the percolation threshold, the corrosion pit percolates over the entire system.

We study the scaling structure of the corrosion pattern. Figure 3 shows the log-log plot of the mean pit size $S(t)$ against t. Below the percolation threshold the mean pit size $S(t)$ scales as

$$S(t) = \frac{\sum_{s=1}^{\infty} s^2 n_s}{\sum_{s=1}^{\infty} s n_s} \approx t^z \quad (z = 1.43 \pm 0.02) , \tag{5}$$

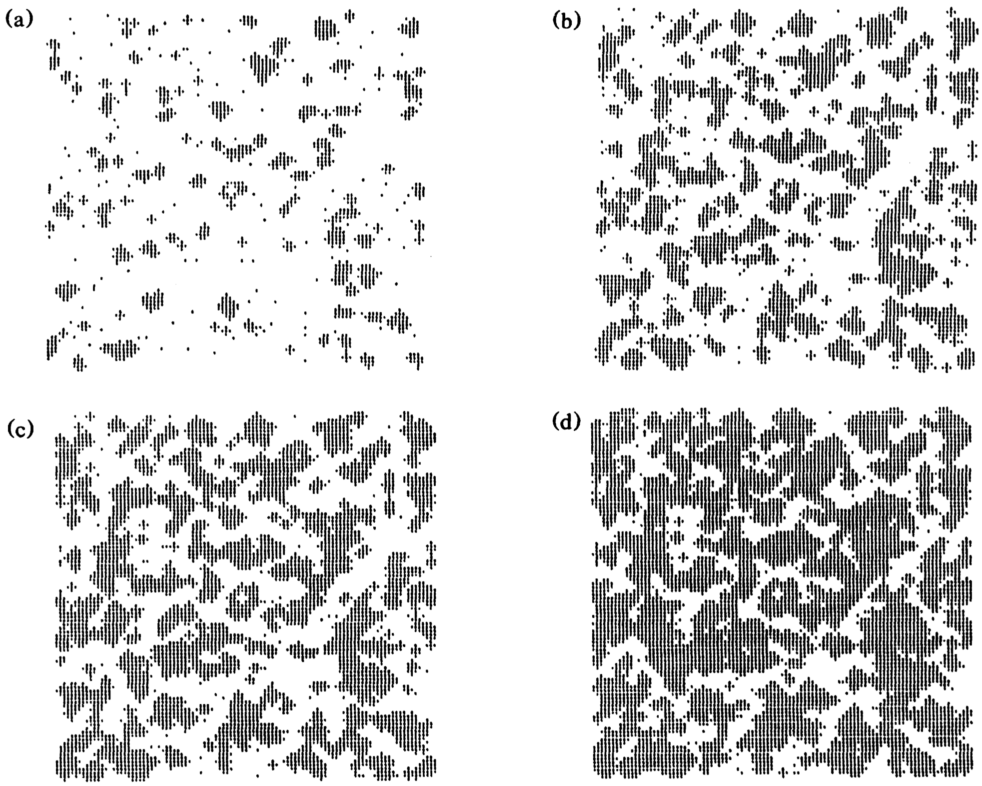

FIG. 2. Overall pictures of corrosion patterns for $P_d = 0.01$ obtained by simulation. (a) Corrosion pattern at $t = 2000$, (b) corrosion pattern at $t = 6000$, (c) corrosion pattern at $t = 8000$, (d) corrosion pattern at $t = 12000$.

where $n_s(t)$ is the pit-size distribution function. When the time t approaches the percolation threshold $t_c \approx 10000$, the mean pit size deviates from the power law. Figure 4 shows the log-log plot of the number density $\rho(t)$ against t. The number density $\rho(t)$ scales as

$$\rho(t) = \sum_{s=1}^{\infty} s n_s \approx t^{-w+(2-\tau)z}$$
$$[-w+(2-\tau)z = 0.87 \pm 0.02] . \tag{6}$$

The mean pit size diverges faster than the number density. This means that smaller pits gradually die out, forming larger pits. Figure 5 shows the log-log plot of $\sum s n_s$ against the number s of particles in the pits for fixed times $t = 2000$, 4000, and 6000. The quantity $\sum s n_s$ scales as

$$\sum_{s=1}^{s} s n_s \approx s^{2-\tau} \quad (2-\tau = 1.07 \pm 0.03) . \tag{7}$$

These observations can be well represented by the scaling assumption [14]

$$n_s(t) \approx t^{-w} s^{-\tau} f(s/t^z) , \tag{8}$$

$w = 0.66 \pm 0.02$, $\tau = 0.93 \pm 0.03$, and $z = 1.43 \pm 0.02$, where the cutoff function $f(x)$ is approximately a constant for $x \ll 1$ and decays faster than any power law as $x \to \infty$. In order to give direct evidence for the cutoff function $f(x)$, a log-log plot of $t^{0.66} s^{-1.07} (\sum s n_s)$ against $t^{-1.43} s$ is shown in Fig. 6. It is found that the data collapse. The data determined for various times fall onto a constant line between the lower limit ($t^{-1.43} s \approx 3 \times 10^{-4}$) and the upper limit ($t^{-1.43} s \approx 6 \times 10^{-3}$). The lower limit corresponds to $s \approx 5$ for $t \approx 1000$ and the

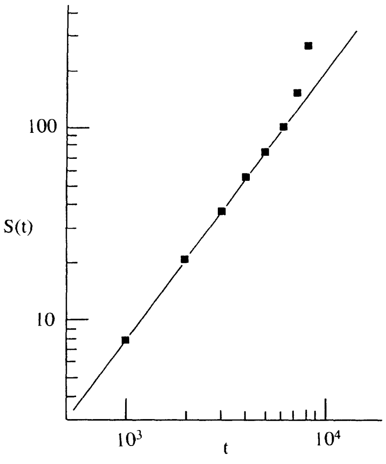

FIG. 3. The log-log plot of the mean pit size $S(t)$ against t.

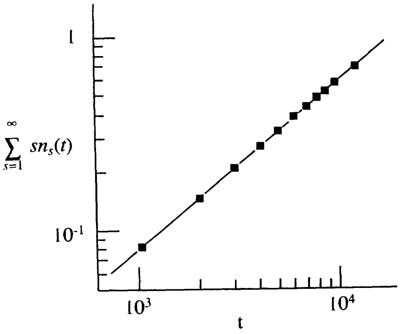

FIG. 4. The log-log plot of the number density $\rho(t)$ against t.

upper limit corresponds to $s \approx 100$ for $t \approx 1000$. In the range that the mean cluster size and the first moment of the size distribution can scale, the cutoff function $f(x)$ becomes a constant.

The data collapse supports the claim that the proposed form for the size distribution is correct and it obeys dynamic scaling. The term t^{-w} corresponds to a process typical for corrosion patterns; the pits which are much smaller than s/t^z gradually die out, forming larger pits. The characteristic cluster size is determined by the denominator t^z. The scaling form (8) corresponds to that of cluster-cluster aggregation. The exponent $w=0.66$ is much smaller than $w=1.7$ [14] of the two-dimensional diffusion-limited CCA. This is due to supplying new corrosion pits. In the CCA model, the cluster number decreases with time by collapsing under the constant number density. However, in our model, new corrosion pits are supplied at some rate and each pit grows by both three-dimensional diffusion and collapsing. The dynamic exponent $z=1.43$ agrees with $z=1.4$ [14] of the two-dimensional diffusion-limited CCA. This means that the growth rate of a single pit is nearly equivalent to that of CCA. The growth rate at the edge of a single pit may be governed by a two-dimensional diffusion on the oxide-covered metal surface. Except for the casual agreement of the exponent z, the exponents w and τ are different from those of the CCA model. The corrosion-pit model belongs to a different universality class from the CCA model.

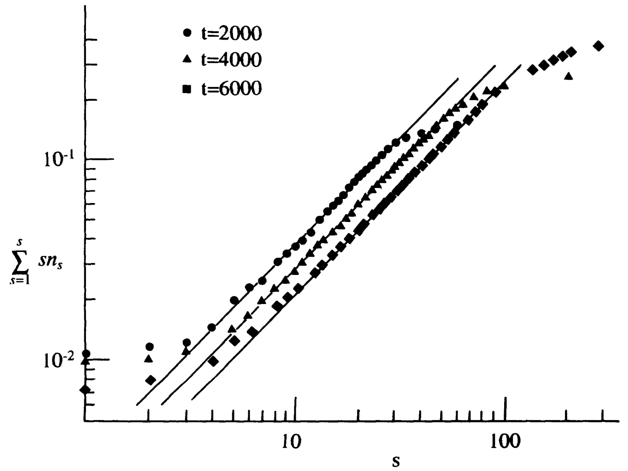

FIG. 5. The log-log plot of $\sum sn_s$ against the number s of particles in the pits for fixed times $t=2000$, 4000, and 6000.

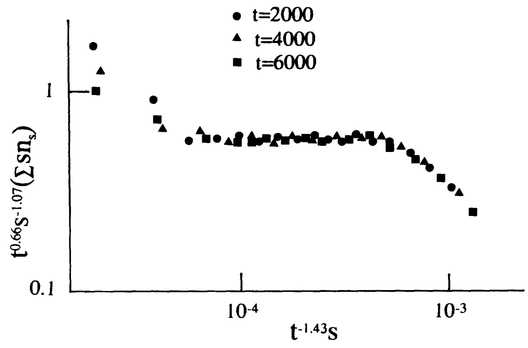

FIG. 6. The log-log plot of $t^{0.66}s^{-1.07}(\sum sn_s)$ against $t^{-1.43}s$. The data determined for various times fall onto a constant line between the lower limit ($t^{-1.43}s \approx 3\times10^{-4}$) and the upper limit ($t^{-1.43}s \approx 6\times10^{-3}$).

In summary, we present a simulation model for corrosion pattern formation on the oxide-covered metal in three dimensions. We find that below the percolation threshold the pit-size distribution obeys a dynamic scaling law.

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