Structural transition in pitting corrosion of binary alloys

Takashi Nagatani

College of Engineering, Shizuoka University, Hamamatsu 432, Japan

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A growth model is proposed to simulate the pit formation in pitting corrosion of binary alloys. The metal is modeled by a random binary alloy where one species is easy to dissolve and the other species is hard to dissolve. The pit growth model is described by the anti-diffusion-limited aggregation model. A computer simulation is performed to form the corrosion pit in two dimensions for various composition ratios. It is shown that at the percolation threshold, a structure transition of the corrosion pit occurs between the diffusion-limited corrosion and the dissolution-limited corrosion. Above the percolation threshold of easily dissolving species, the pitting corrosion is controlled by the diffusion of anions and the width w of the pit scales as $w \approx h^{1.86 \pm 0.05}$ where h is the depth of the pit. Below the percolation threshold, the pitting corrosion is controlled by dissolution of metal and the width w of the pit is proportional to the depth h of the pit.

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I. INTRODUCTION

Metallic corrosion is an important field of materials science. The pitting corrosion is a major cause of failure of metal structures. The corrosion is induced by localized dissolution of a passivated (oxide-covered) metal in the presence of a solution of certain anionic species [1,2]. The propagation of corrosion is generally thought to occur as follows. Anions such as chloride are concentrated into the pit from the external solution. The gradient in solution composition maintains the metal surface inside the pit in an active (dissolving) state. The local environment is acidified owing to hydrolysis of the dissolving metal ions. The formation of pitting corrosion of binary alloys has been investigated with the use of the computer simulation by Williams *et al.* [1]. They have found a mechanism for the triggering of pitting corrosion of stainless steels. Their model is based on the Eden model and does not take into account the diffusion of anions and the dissolution rate of the metal. Open questions include the asymptotic behavior of the corrosion pit profiles and their dependence upon such parameters as the diffusion constant of anions and the dissolution rate of metal. However, until now, there have been no simulations for analyzing the structure of the corrosion pit of binary alloys.

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 Eden model. A variety of computer simulations has 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 the electrochemical deposition, crystal growth, viscous fingering, dielectric breakdown, chemical dissolution, and bacterial colony [3–9]. Until now, very few investigations for pitting corrosion have been performed from the point of view of growth models. Paterson called the DLA model of decay the

anti-DLA model [10]. The anti-DLA model has attracted little attention because the interface becomes stable in the decay process.

In a previous work [11], we presented a growth model for pit formation in the pitting corrosion of a simple metal. We extended the anti-DLA model to apply the pitting corrosion by taking into account the surface reaction. We found that the width w of the pit against the depth h scales as $w \approx h^{1.86 \pm 0.05}$ in the diffusion-limited corrosion. We showed that the crossover of the pit profile occurs from the reaction-limited corrosion at small length scales to the diffusion-limited corrosion at large length scales.

In this paper, we extend the previous model to apply the pitting corrosion of binary alloys. The metal (for example, stainless steel) is modeled by a random binary alloy with a easily dissolving species (Fe) and a hardly dissolves species (Cr). By using computer simulation, we investigate the pit structure of the pitting corrosion of binary alloys in two dimensions for various composition ratios. In the limit of 100% Fe, the pitting corrosion is controlled by the diffusion of anions because the dissolution time of metal is sufficiently smaller than the diffusion time of anions. On the other hand, in the limit of 100% Cr, the pitting corrosion is controlled by the dissolution of the metal because the diffusion time of anions is sufficiently smaller than the dissolution time of metal. We show that at the percolation threshold a structure transition of the corrosion pit occurs between the diffusion-limited corrosion and the dissolution-limited corrosion. Above the percolation threshold of an easily dissolving species, the corrosion pit is governed by the diffusion-limited corrosion. Here, the width w of the corrosion pit against the depth h scales as $w \approx h^{1.86 \pm 0.05}$. Below the percolation threshold, the corrosion pit is governed by the dissolution-limited corrosion where the width w is proportional to the depth h : $w \approx h$.

The organization of the paper is as follows. In Sec. II we present the basic equation and the model for pit formation in the pitting corrosion of binary alloys. In Sec.

III we present the simulation results. We show the structure transition of the corrosion pit in the pitting corrosion of binary alloys. Section IV presents the summary.

II. BASIC EQUATION AND MODEL

We consider the basic equations for pit formation in the pitting corrosion of binary alloys. We extend the anti-DLA model to apply the pitting corrosion of binary alloys. We introduce the dissolution probability P_d into the original anti-DLA model. We assign the dissolution probability $P_d=1$ for an easily dissolving component (Fe). For a hardly dissolving component (Cr), we assign the sufficiently small value of the dissolution probability. The dissolution probability is similar to the sticking probability in the DLA model [12,13]. In the pitting corrosion of binary alloys, anionic species diffuse toward the metal surface. After diffusing anions land on the metal surface, each component dissolves into the solution with the dissolution probability P_d . The process is controlled by both diffusion of anions and dissolution of metal. We restrict ourselves to formation of a single pit. We assume that the corrosion pit starts to grow from a single defect on the metal surface. The metal is given by a random binary alloy. Figure 1 shows a schematic representation of the pit formation in pitting corrosion of binary alloys. The concentration C of the diffusing anions satisfies the Laplace equation under the quasistationary approximation

$$\nabla^2 C = 0. \quad (1)$$

The metal surface is covered with oxide except for the corrosion pit. The metal surface which is not a neighbor to the corrosion pit does not dissolve. The boundary condition on the metal surface except the corrosion pit is given by

$$\frac{\partial C}{\partial y} = 0 \quad (2)$$

on the flat metal surface, where $\partial C / \partial y$ is the derivative along the outward normal at the flat metal surface. The boundary condition far from the metal surface maintains a constant concentration C_∞ ,

$$C = C_\infty, \quad (3)$$

FIG. 1. Schematic representations of the pit formation in pitting corrosion. The anions diffuse toward the metal alloy surface. After the diffusing anions react with the metal alloy on the surface of the corrosion pit, the metal alloy dissolves into solution.

at infinity. We consider the boundary condition on the surface of the corrosion pit. If the diffusing anion lands at the site of an easily dissolving component (Fe) on the surface of the corrosion pit, the easily dissolving component dissolves into solution soon since the dissolution time of the easily dissolving component is sufficiently shorter than the diffusion time of anions. On the other hand, when the diffusing anion lands at the site of a hardly dissolving component (Cr), a small amount of the hardly dissolving component dissolves into solution since the dissolution time of the hardly dissolving component is sufficiently longer than the diffusion time of anions. The number of particles which dissolve per unit time is assumed to be given by $q = kC$ where k is the dissolution rate. Under steady-state conditions, the number of particles which dissolve into solution per unit time equals the number of particles arriving at the surface. This mass flux to the surface equals $j = D(\partial C / \partial n)_{\text{surface}}$, where $(\partial C / \partial n)_{\text{surface}}$ is the derivative along the outward normal evaluated at the surface of the pit and D is the diffusion constant. The boundary condition on the surface of the corrosion pit is given by

$$C = 0 \quad (4)$$

on the site of the easily dissolving component, and

$$D \left[\frac{\partial C}{\partial n} \right]_{\text{surface}} = kC \quad (5)$$

on the site of the hardly dissolving component. A growth velocity of the growing interface of the pit is assumed to be proportional to the mass flux at the surface. We rewrite Eq. (1) with the boundary conditions (2)–(5) in dimensionless form:

$$\nabla^{*2} C^* = 0, \quad (1')$$

$$\frac{\partial C^*}{\partial y^*} = 0 \quad (2')$$

on the flat metal surface,

$$C^* = 1 \quad (3')$$

at infinity,

$$C^* = 0 \quad (4')$$

at the site of the easily dissolving component on the surface of the pit, and

$$\frac{\partial C^*}{\partial n^*} = k^* C^* \quad (5')$$

at the site of the hardly dissolving component on the surface of the pit, where $x^* = x/L$, $y^* = y/L$, $C^* = C/C_\infty$, and $\nabla^* = L \nabla$. The dimensionless parameter k^* is given by

$$k^* = kL/D. \quad (6)$$

The dimensionless parameter k^* represents the ratio of the diffusion time to the dissolution time. The limit of $k^* \rightarrow 0$ indicates the dissolution-limited process. The limit of $k^* \rightarrow \infty$ represents the diffusion-limited process.

Here it is convenient to introduce the parameter

$$P_d = k^* / (1 + k^*) . \quad (7)$$

The boundary condition (5) or (5') is rewritten in terms of P_d as

$$(1 - P_d) \frac{\partial C^*}{\partial n^*} - P_d C^* = 0 . \quad (5'')$$

In the limit of $P_d = 0$ the anti-Eden model is reproduced. In the limit of $P_d = 1$ the anti-DLA model is reproduced. The parameter P_d corresponds to the dissolution probability. The parameter P_d is similar to the sticking probability in the DLA model [13].

III. SIMULATION AND RESULT

We consider the simulation of the pit formation on the flat metal satisfying Eq. (1') with boundary conditions (2')–(5') (see Fig. 1). The diffusive particle governed by the Laplace equation (1') can be simulated by using an isotropic random walker. The boundary condition (5'') can also be simulated by introducing the dissolution probability into the anti-DLA model. The dissolution probability is similar to the sticking probability in the DLA model. On what follows we summarize the algorithm of the simulation process. The simulation is carried out with the use of a simple square lattice. We consider a subset of the square lattice enclosed by a rectangle with 400×200 (units). We set a rectangular metal (400×100) with a flat surface at the bottom of the rectangle (see Fig. 1). The metal is modeled by a random binary alloy where the one component is easily dissolving and the other component is hardly dissolving. Each site of the rectangular metal is randomly occupied by an easily dissolving component with probability p and by a hardly dissolving component with probability $q (= 1 - p)$. The random alloy is described in terms of the site percolation on the square lattice. Above the percolation threshold, the sites occupied by the easily dissolving component are connected each other and an infinite cluster of the easily dissolving component appears [14]. Initially we put a single defect on the center of the metal surface. The pitting corrosion starts to propagate from the nearest-neighboring sites of the defect. The lateral boundary is periodic. A particle (anion) is introduced one at a time at a randomly chosen point on the upper boundary. The particle performs a pure random walk resulting from diffusion. The particle continues to move until it either reaches a point adjacent to a surface site of the corrosion pit, until it reaches a point adjacent to a flat metal surface or until it reaches the upper boundary. When the particle reaches a point adjacent to surface sites of the corrosion pit and the surface sites are the easily dissolving component, the surface sites of the pit remove with probability 1. If the particle reaches a point adjacent to surface sites of the corrosion pit and the surface sites are the hardly dissolving component, the surface sites of the pit are removed with probability P_d and the diffusing particle is reflected with $1 - P_d$. When the particle reaches a point adjacent to a flat metal surface

and the point is not a neighbor to the corrosion pit, it is reflected with probability 1. When the particle reaches the upper boundary, the random walker is annihilated. We repeat the above procedure. The corrosion pit is grown until the number of particles removed from the metal reaches 6000. Figure 2 shows typical patterns of the corrosion pits obtained by varying the occupation probability p for $P_d = 0.01$. Figures 2(a), 2(b), 2(c), 2(d), and 2(e) indicate, respectively, the corrosion pits for $q (= 1 - p) = 0.1, 0.3, 0.5, 0.7$, and 0.9 . With increasing concentration q of the hardly dissolving component, the corrosion pit becomes deeper. The limit of $q = 0$ gives the diffusion-limited corrosion. On the other hand, the limit of $q = 1$ gives the dissolution-limited corrosion. In the binary alloy with a small quantity of the hardly dissolving component, the diffusion of anions governs the pitting corrosion. Then, the hitting probability of diffusing particles at the edges of the pit becomes higher than that at the bottom of the pit. Therefore, in the diffusion-limited corrosion, the pit profile shows the shallow structure. In the binary alloy with a large quantity of the hardly dissolving component, the pitting corrosion is governed by the dissolution of metal. The diffusing particle visits all the surface sites of the pit many times before dissolution. Then the hitting probability becomes uniform over the whole surface as in the Eden model. The anti-Eden model is reproduced. Figure 3 shows the plot of the width w against h (in the log-log plot) for $P_d = 0.01$. The width w and the depth h are, respectively, given by the maximum values of the corrosion pit. For smaller values of q than 0.4, the scaling form of the diffusion-limited corrosion is found:

FIG. 2. Typical patterns of the corrosion pit obtained by varying the concentration $q (= 1 - p)$ for the dissolution probability $P_d = 0.01$. (a) $q = 0.1$, (b) $q = 0.3$, (c) $q = 0.5$, (d) $q = 0.7$, (e) $q = 0.9$.

FIG. 3. The log-log plot of the width w against the depth h obtained by varying the concentration q for $P_d = 0.01$.

$$w \approx h^{1.86 \pm 0.05} \quad \text{for } q < 0.4 \quad (8)$$

where w is the maximum width of the pit and h is the maximum depth of the pit. For larger values of q than 0.4, the scaling form of the dissolution-limited corrosion is found:

$$w \approx h \quad \text{for } q > 0.4. \quad (9)$$

We find that near the percolation threshold a structure transition occurs between the diffusion-limited corrosion and the dissolution-limited corrosion. In the site percolation, the threshold is given by $p = 0.593$ ($q = 0.407$) in the literature [14]. Our result $q = 0.4$ of the transition point is nearly in agreement with the accurate value of site percolation on the square lattice. Above the percolation threshold, the sites of the easily dissolving component are connected to each other. On larger scales than the correlation length ξ of percolation, the pit formation is controlled by diffusion. Therefore, the structure transition of corrosion pit is induced by the percolation transition.

We study the effect of dissolution probability on the pit profile. We choose the dissolution probability $P_d = 0.1$. In this case, the hardly dissolving component is easier to dissolve than the above case $P_d = 0.01$. Figure 4 shows typical patterns of the corrosion pits obtained by varying the occupation probability p for $P_d = 0.1$. Figures 4(a), 4(b), 4(c), and 4(d) indicate, respectively, the corrosion pits for $q = 0.3, 0.5, 0.7$, and 0.9 . With increasing concentration q , the corrosion pit almost does not change compared with the case of $P_d = 0.01$. Figure 5 shows the plot of the width w against h (in the log-log plot) for $P_d = 0.1$. For all values of q , the scaling form $w \approx h^{1.86 \pm 0.05}$ is found. The pit formation is governed by diffusion. The structure transition at the percolation threshold does not appear.

In the corrosion pit of a one-component metal with small dissolution probability, a crossover occurs from the dissolution-limited corrosion at small length scales to the diffusion-limited corrosion at large length scales [11]. The crossover length r_c is assumed to be given by

FIG. 4. Typical patterns of the corrosion pit obtained by varying the concentration $q (=1-p)$ for the dissolution probability $P_d = 0.1$. (a) $q = 0.3$, (b) $q = 0.5$, (c) $q = 0.7$, (d) $q = 0.9$.

$r_c \approx P_d^{-1}$. The crossover length r_c is approximately given by $r_c \approx 10$ for $P_d = 0.1$. For $P_d = 0.01$, $r_c \approx 100$. Therefore, for $P_d = 0.1$ the diffusion-limited corrosion is found on larger length scales than $r_c \approx 10$ even below the percolation threshold. The structure transition of corrosion pit at the percolation threshold appears if the following relation holds:

$$\xi \ll l \ll r_c, \quad (10)$$

where l is the size of a typical pit. When the pit size l is sufficiently small compared with the crossover length r_c , the structure transition occurs.

FIG. 5. The log-log plot of the width w against the depth h obtained by varying the concentration q for $P_d = 0.1$.

IV. SUMMARY

We present the simulation model for the pit formation in pitting corrosion of binary alloys. We investigate the pit formation governed by diffusion of anions and dissolution of metal by computer simulation. We find that at the percolation threshold a structure transition of the corrosion pit occurs between the diffusion-limited corro-

sion and the dissolution-limited corrosion. We also show that above the percolation threshold the pitting corrosion is controlled by diffusion of anions and below the threshold the pitting corrosion is controlled by dissolution of metal. We find the scaling forms $w \approx h^{1.86 \pm 0.05}$ for the diffusion-limited corrosion and $w \approx h$ for the dissolution-limited corrosion.

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- [1] D. E. Williams, R. C. Newman, Q. Song, and R. G. Kelly, *Nature* (London) **350**, 216 (1991).
 - [2] J. M. Costa, F. Sagues, and M. Vilarrasa, *Corros. Sci.* **32**, 665 (1991).
 - [3] T. A. Witten and L. M. Sander, *Phys. Rev. Lett.* **47**, 1400 (1981).
 - [4] *Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).
 - [5] *On Growth and Form*, edited by H. E. Stanley and N. Ostrowsky (Nijhoff, The Hague, 1985).
 - [6] P. Meakin, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1988), Vol. 12, p. 336.
 - [7] J. Feder, *Fractals* (Plenum, New York, 1988).
 - [8] T. Vicsek, *Fractal Growth Phenomena* (World-Scientific, Singapore, 1989).
 - [9] *The Fractal Approach to Heterogeneous Chemistry*, edited by D. Avnir (Wiley, Chichester, 1989).
 - [10] L. Paterson, *Phys. Rev. Lett.* **52**, 1621 (1984).
 - [11] T. Nagatani (unpublished).
 - [12] P. Meakin, *Annu. Rev. Phys. Chem.* **39**, 237 (1988).
 - [13] T. Nagatani, *Phys. Rev. A* **40**, 7286 (1989).
 - [14] D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).

FIG. 2. Typical patterns of the corrosion pit obtained by varying the concentration q ($=1-p$) for the dissolution probability $P_d=0.01$. (a) $q=0.1$, (b) $q=0.3$, (c) $q=0.5$, (d) $q=0.7$, (e) $q=0.9$.

(a)

(b)

(c)

(d)

FIG. 4. Typical patterns of the corrosion pit obtained by varying the concentration $q (=1-p)$ for the dissolution probability $P_d=0.1$. (a) $q=0.3$, (b) $q=0.5$, (c) $q=0.7$, (d) $q=0.9$.