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Simple passivation and depassivation model for pitting corrosion

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A simple two-dimensional passivation and depassivation model for pitting corrosion has been developed. This model describes corrosion processes that are limited by the diffusion of either a corrosive agent or the diffusion of corrosion products that inhibit the corrosion process. Despite its simplicity, this model exhibits both stable and unstable pit growth, along with distinctive current fluctuations. For the case of a single corrosion pit, the corrosion current $I(t)$ has the form $I(t)=f(t/t^*)/\ln(t)$ if there is no depassivation. The function $f(x)$ has the form $f(x)=\text{const}$ for $x \ll 1$ and $f(x)$ decays faster than any power of x for $x \gg 1$. The characteristic time t^* is given by $t^*\ln(t^*)\simeq k_p^{-2}$, where k_p is the passivation rate constant.

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I. INTRODUCTION

The corrosion of metals has been studied for many years primarily because of its economic importance. In 1962 Uhlig [1] "conservatively" estimated the cost of direct losses (losses attributed to the cost of replacing damaged components or structures and the cost of corrosion protection) to be $\$5.5\times 10^9$ per year in the United States alone and estimated a comparable cost due to indirect losses. In general, corrosion processes involve a combination of physical and chemical phenomena. In most cases the development of an adequate theoretical understanding (of predictive value) poses severe challenges that have not yet been met. The rich phenomenology associated with corrosion processes [1,2] suggests that many models and theoretical approaches will be required. However, the development of a better understanding of a few simple corrosion models may provide valuable insights into experimental results and may stimulate new research directions. The importance of morphology in corrosion processes has been recognized for a long time but the main focus of research has been on the chemical and electrochemical aspects of corrosion. Here we are concerned with simple models for pitting corrosion processes for which the structure of the corrosion front is one of the primary characteristics. For well over a century the idea that the formation and breakdown of a corrosion resistant "passive" layer occurs has played a central role in attempts to understand corrosion or resistance to corrosion [1–7]. At present considerable uncertainty exists concerning the nature of the passive layer [8], its formation [7–9] and breakdown [7–17]. The wide variety of materials and environments for which pitting corrosion has been studied contribute to these uncertainties and make it difficult to describe a typical scenario for pitting corrosion. However some types of pitting corrosion (such as the corrosion of ferrous metals in aqueous systems containing chloride ions) have been studied extensively because of their practical importance and they are relatively well understood. The fact that pitting corrosion is found under a wide range of conditions encourages the belief that this is a universal phenomenon that does not depend on the details of the corrosion mechanism(s) and may be represented in terms of a simple model. Apart from the formation of pits there appear to be several other characteristics that are common to most pitting corrosion processes. These include the generation of distinctive current fluctuations [11,18–20,21–28] and an induction period before pitting corrosion commences [6,10,15,16,25,29–34]. However, a broad distribution of induction times is often observed and there is no consensus concerning either the significance or interpretation of the induction time (distribution). Many authors [11,35–37] have suggested that pit initiation may be a consequence of cracking of the passive layer [38]. For many systems there is good evidence that pitting corrosion is associated with defects, inclusions, phase boundaries, etc. [2,6,10,39–43].

Depending on the electrochemical conditions pitting corrosion may be either "stable" or "unstable" [44–46]. In stable pitting corrosion the pitting corrosion process proceeds indefinitely after the pitting process has been initiated. In unstable pitting corrosion the protective layer can reform inside the corrosion pit leading to at least a temporary cessation of the pit-growth process. The model that we use in the work described here is a model for both stable and unstable pitting corrosion. In at least some systems the transition between stable and unstable pit growth appears to be associated with a morphological transition (from a smooth to a rough pit surface) [45,46]. Because of the complexity and uncertainty associated with pitting corrosion processes it is quite natural that attempts have been made to develop statistical models for pitting corrosion that, for the most part, neglect mechanistic details [16,25,47–52].

The simulations described here were all carried out using simple two-dimensional square-lattice models in which the sites of the lattice can, in general, be in four different states. These four states are (1) unreactive fluid or corrosion product (empty); (2) corrosive fluid or particles (●); (3) reactive metal (□); (4) passive, nonreactive (■). The indices (1)–(4) can be used to label each of the sites on the lattice.

The basic assumption used in these models is that corrosion is a result of a diffusion-limited reaction between a mobile corrosive chemical species and the bare, unprotected metal surface. The corrosion dynamics in this model is controlled by diffusion of the mobile corrosive sites and by the passivation and depassivation of perimeter sites at the boundary between the metal and corrosive fluid. We assume that the passive layer provides a perfect barrier to the corrosive species so long as it remains intact. In most of the simulations all of the passive sites can be coverted to reactive (bare metal) sites via the depassivation reaction. In some simulations a broken outer layer of permanently passive sites is used. These sites are labeled by an additional index (5).

II. COMPUTER MODELS

Most of our simulations have been carried out using two versions of the model outlined in the Introduction. The first of these models (model I) is illustrated in Fig. 1. At the start of a simulation all the sites in a $L_x \times L_y$

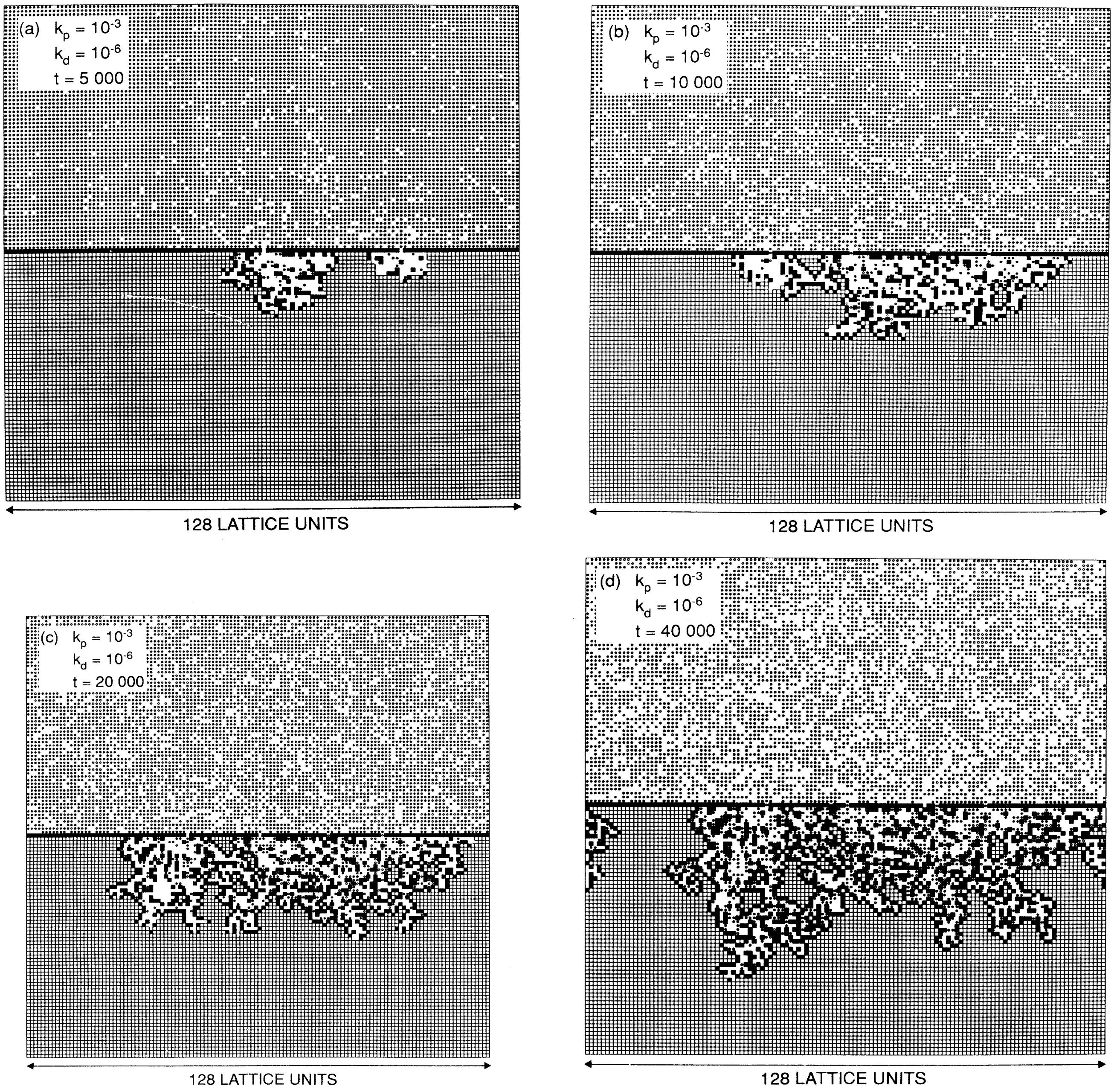

FIG. 1. Four stages in a small-scale simulation carried out using a simple passivation and depassivation model for pitting corrosion. In this (and other) figures the passive sites are filled, the substrate sites are open squares, and the corrosive particle sites are indicated by a small circle (which appears as a dot in these figures). In the corrosion-product diffusion-limited version of the model, the empty sites represent corrosion product.

square lattice with y coordinates in the range of 1 to t (t is the thickness of the corroding material) are labeled with an integer (3 if the labeling scheme described above is used). The next layer of sites with a y coordinate of $t+1$ are then given a different label (4) to represent sites associated with the protective surface layer [except for one site in this layer which is empty (1) to represent a gap or defect in the protective layer]. The remaining sites are then given the label (2) to represent sites occupied by corrosive particles. Throughout all of the simulations periodic boundary conditions are used in the lateral x direction.

The dynamics of the model is contained in the following rules applied at each stage of the simulation. Here N_c is the number of corrosive (2) fluid sites, N_p is the number of (4) sites in the protective passive layer, and N_s is the number of unprotected reactive (3) surface sites of the metal.

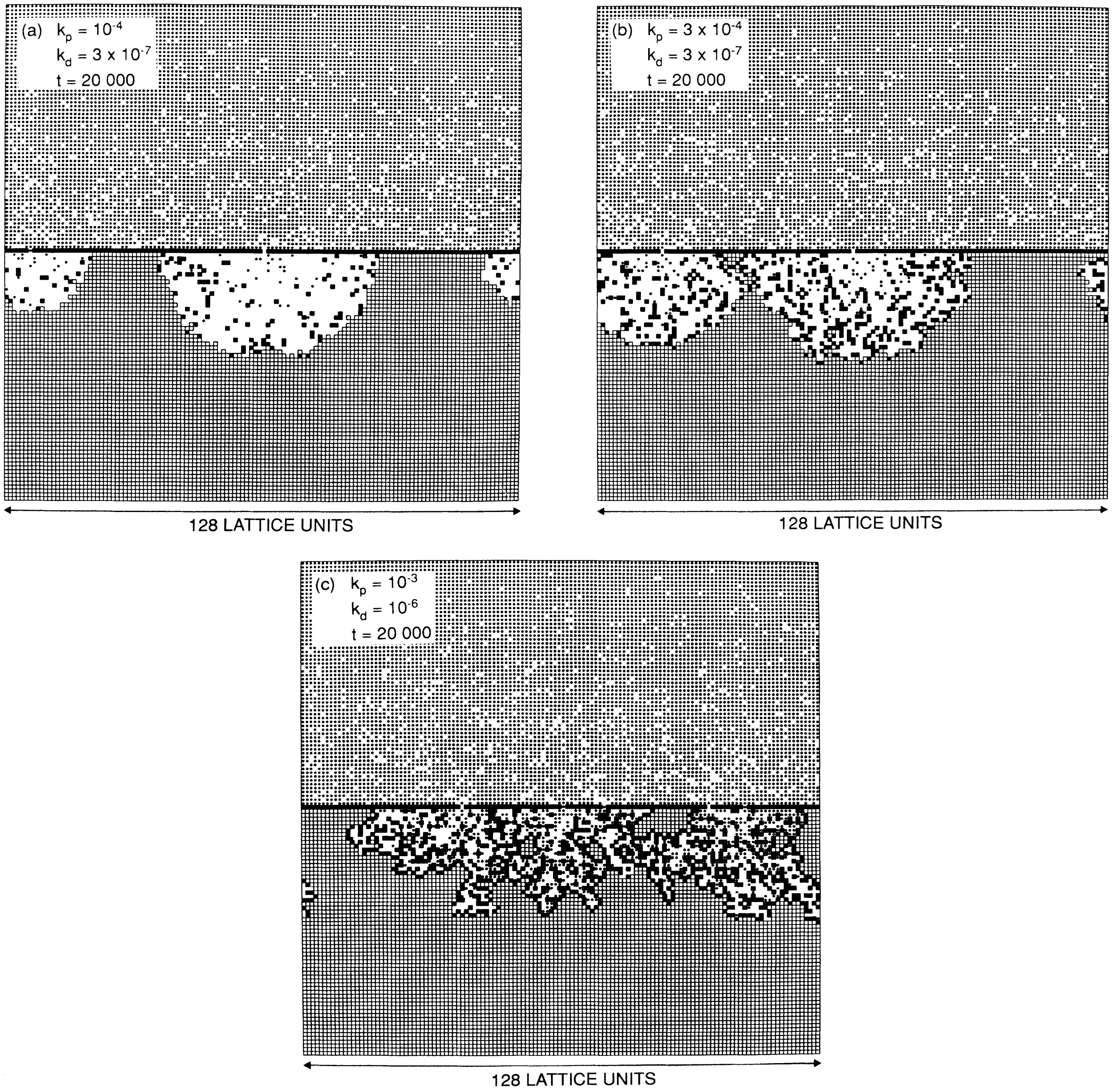

FIG. 2. Corrosion patterns obtained from simulations carried out using a version of model I (like that illustrated in Fig. 1) in which the density ρ of corrosive particle sites was maintained at a constant value ($\rho=1$) adjacent to the upper boundary. This figure shows results for several combinations of the passivation rate constant k_p and the depassivation rate constant k_d.

A. Diffusion

Increment time by $\delta t = 1/N_c$. Select at random a corrosive fluid (2) site and attempt to move it in a random direction to a neighboring site that is in the state (n). The $(2)(n)$ pair follows the following transition rules:

$$(2)(n) \rightarrow \begin{cases} (1)(2) & \text{diffusive step if } n=1 \text{ (empty)}, \\ (1)(1) & \text{corrosive step if } n=3 \text{ (metal)}, \\ (2)(n) & \text{do nothing if } n=2 \text{ or } n=4 . \end{cases} \tag{1}$$

B. Passivation and depassivation

In this model passivation and depassivation are considered to be spontaneous random events that can be characterized by rate constants (k_p and k_d). After each diffusion step two random numbers (X and X') uniformly distributed over the range 0–1 are generated. If $X < k_p N_s \delta t$ then one of the N_s reactive metal perimeter sites that is exposed to empty (1) or corrosive (2) fluid sites is converted to a passive (4) site. If $X' < k_d N_p \delta t$ then one of the N_p passive (4) sites is selected randomly and removed. [The passive (4) site is converted to an empty (1) site].

The passivation rate constant k_p determines the passivation probability:

$$P_p = k_p N_s \delta t , \tag{2}$$

and the depassivation rate constant k_d determines the

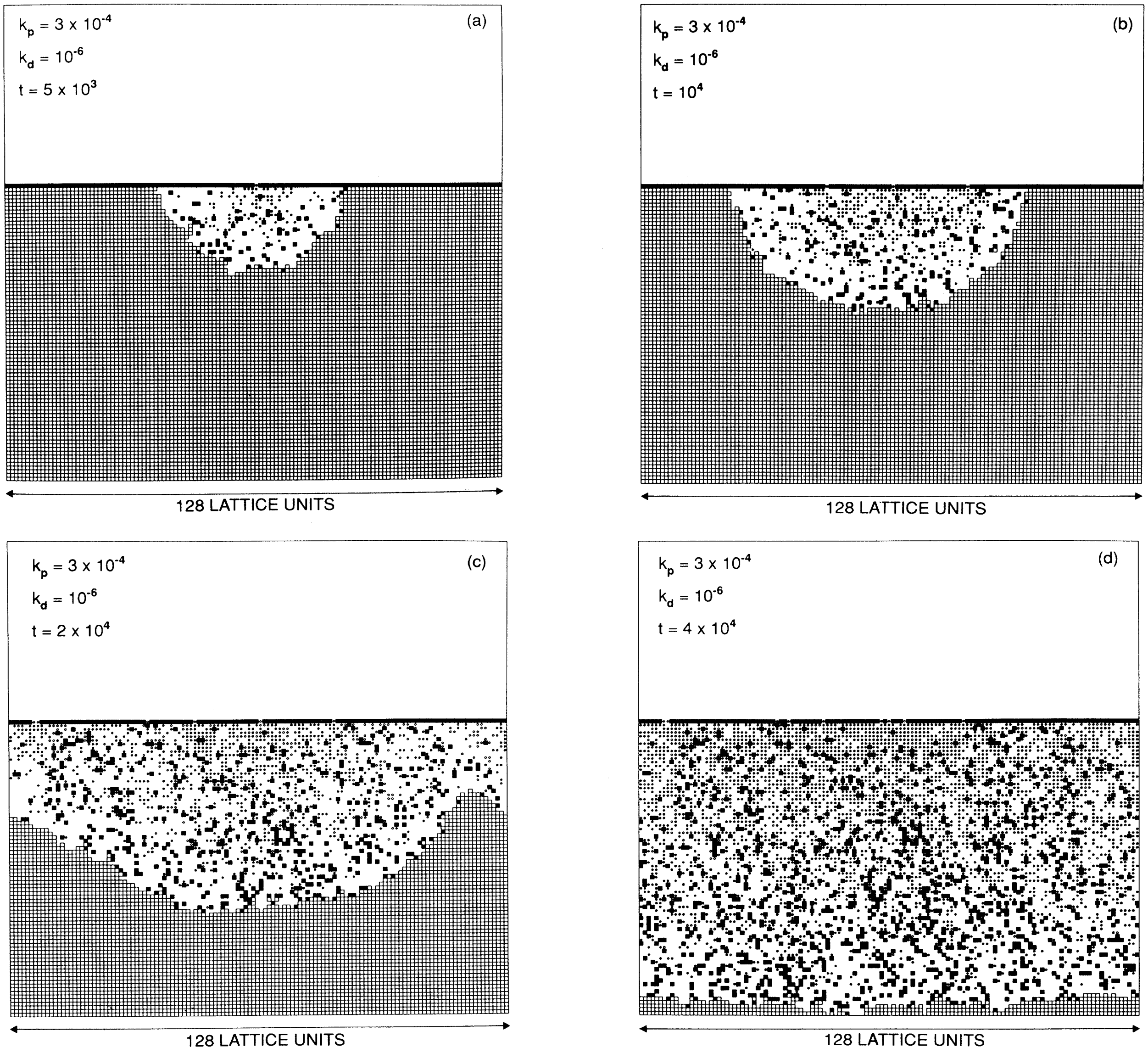

FIG. 3. Results obtained from small-scale simulations carried out using model II in which a constant density ($\rho = 1$) of corrosive particles is maintained in the gaps in the upper surface (the initial layer of passivated sites). The figure shows four stages in a single simulation carried out using the parameters $k_p = 3 \times 10^{-4}$, $k_d = 10^{-6}$.

depassivation probability

$$P_d = k_d N_p \delta t \ . \tag{3}$$

Here P_p and P_d are the probabilities that a passivation or depassivation event will take place during a single time step of length δt. The time increment δt is inversely proportional to the number of corrosive sites since we model a process in which all the corrosive species follow simultaneous Brownian trajectories instead of moving one at a time as in our simulations. Thus in N_c attempts to move a (randomly selected) corrosive site the total time is incremented by unity independent of the number of corrosive sites in the system. Since the probabilities P_d and P_p can be quite small the random numbers X and X' are constructed using two integers from a long-cycle random-number generator that generates integers in the range $0-(2^{31}-1)$. In some of our simulations an alternative procedure of multiplying P_p or P_d by a convenient factor ($Q \gg 1$) and carrying out the appropriate steps, if $X < QP$ and $X' < 1/Q$, was used where P represents P_d or P_p. In this case X and X' were generated using two different random-number generators. In a typical simulation the steps described above are carried out many times.

Figure 1 shows results from a small-scale simulation in which corrosive particles are not allowed to enter or leave the system. In this case the parameters $k_d = 10^{-6}$ and $k_p = 10^{-3}$ were used. These are the only parameters in our model. In some of the simulations a constant concentration ρ of corrosive particles was maintained at the upper boundary. In this case if a corrosive particle moves away from a site adjacent to the upper boundary the vacated site is refilled and the number of corrosive particles is increased by 1. Simulations carried out using this model are shown in Fig. 2 for several combinations of the rate constants k_p and k_d.

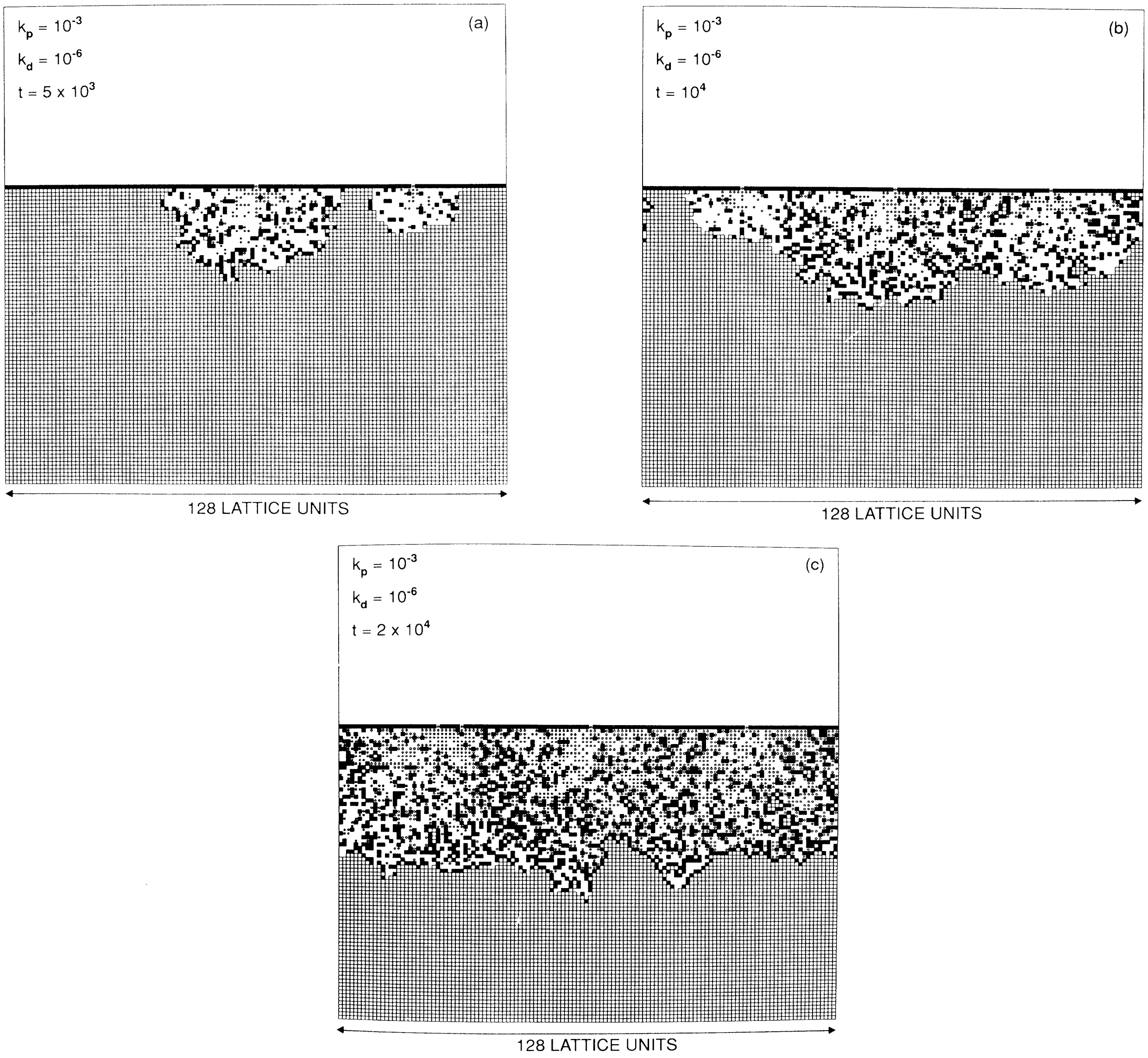

FIG. 4. Three stages in a model II simulation carried out using the parameters $k_p = 10^{-3}$, $k_d = 10^{-6}$.

Most of our simulations were carried out using a slightly different model. In this model the initial gap in the protective layer and any gaps formed by depassivation in that part of the protective layer which was at the flat upper surface at the start are constantly filled with corrosive particles. If a corrosive particle moves away from such a gap in the upper surface it is immediately replaced. The model (model II) is more efficient than model I since the random-walk motion of the corrosive particles in the region above the initial surface of the corroding "material" is not simulated. Simulations carried out using this model are illustrated in Figs. 3 and 4.

Simulations were also carried out using a "single-pit" version of model II (model IIa) in which the depassivation rate constant k_d for the sites representing the original passive layer (the outer surface) was set to zero. Depassivation was allowed (with a rate constant k_d) for those sites at the surface of the single pit that grows via the gap in the outer passive layer. Figure 5 shows several stages in the growth of a two-dimensional pit generated using this model.

Exactly the same models can be used to represent pitting corrosion processes in which the rate of corrosion at the bare metal surface is limited by the diffusion of corrosion products away from the surface. In this version of the model the empty "fluid" sites represent the corrosion product and the filled fluid sites represent product free regions or vacancies that diffuse in the corrosion product.

III. RESULTS

Figures 1–5 illustrate the evolution of corrosion pits for models I and II for several combinations of the parameters k_p (the passivation rate constant) and k_d (the

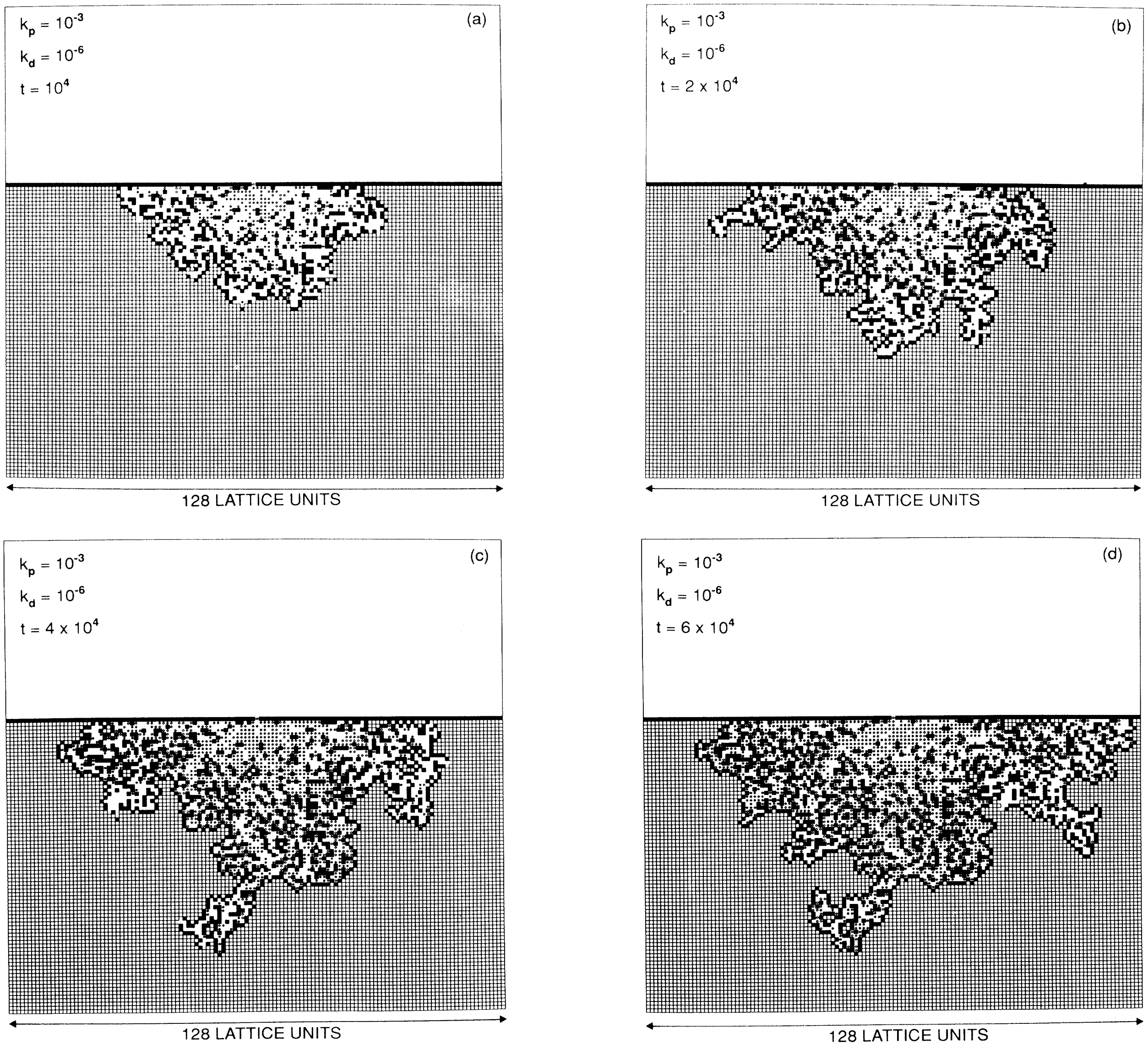

FIG. 5. Several stages in the growth of a pit simulated using the single-pit model with a depassivation rate constant k_d of 10^{-6} and a passivation rate constant k_p of 10^{-3}.

depassivation rate constant). For small values of k_p the pits grow in a stable manner (for the relatively short times explored in these simulations) and have a "hemispherical" shape with smooth surfaces. This result is not surprising. In the limit $k_p \to 0$ the models investigated here become equivalent to a simple diffusion-limited-annihilation model for surface growth [53,54] which leads to the formation of quite smooth surfaces. Pits formed under these conditions can be considered to correspond to "brightening pits" [45] formed under stable pit-growth conditions. For larger values of k_d the surfaces of the pits have a much more irregular structure and if the depassivation rate constant is sufficiently small they stop growing after a finite time. Pits formed under these unstable pit-growth conditions may be considered to correspond to "etching pits" [45].

Large-scale simulations were carried out using model II with systems with a width L_x of 8192 lattice sites. The corrosion current $I(t)$ was determined by measuring the number of sites removed $\delta N(t)$ over the interval $t \to t+100$. The corrosion current $I(t)$ is then given by $I(t)=\delta N(t)/100$. This means that the corrosion current is simply the rate at which metal "atoms" are removed by the corrosion process. Removal of a complete layer of L_x sites from a smooth surface in a time t would correspond to a corrosion current of L_x/t. Figure 6 shows results from some of these simulations.

In Figs. 6(a)–6(c) the corrosion current consists of a sequence of distinct current pulses. The large pulses correspond to the initiation growth and passivation of a new corrosion pit starting with a depassivation event on the outer surface. The smaller pulses may correspond to the same process occurring inside a pit that has been passivated at an earlier stage. Figures 6(b) and 6(c) show that during each current pulse the current falls steadily (apart from fluctuations) with increasing time. All of the large current pulses have approximately the same shape and size (corresponding to the amount of "material" removed during the formation of a single pit). In Fig. 6(d) the passivation rate constant is relatively small and the depassivation rate constant is relatively high. Under these conditions the corrosion current rises quite rapidly

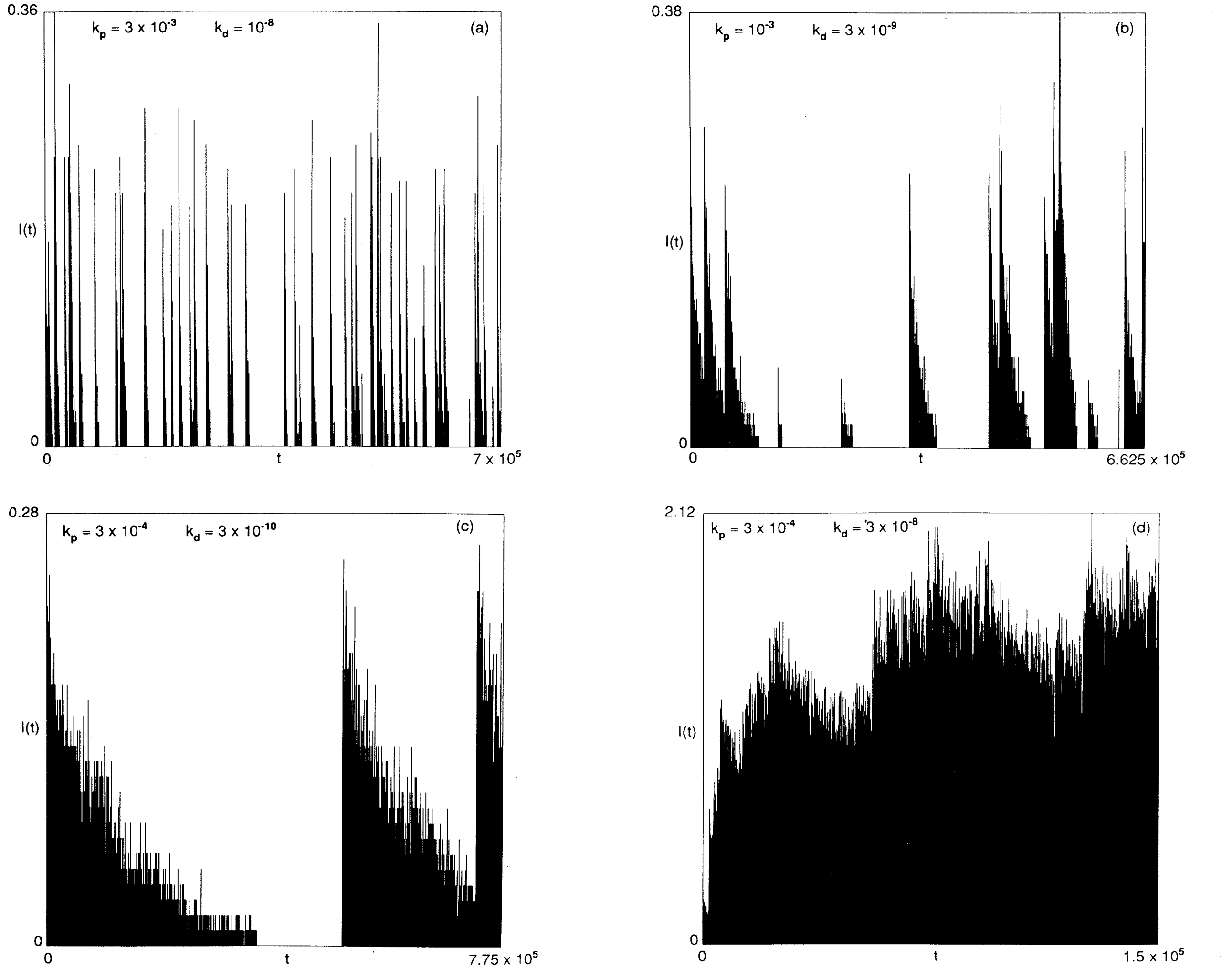

FIG. 6. Typical corrosion current profiles $I(t)$ obtained from simulations carried out using model II with a system width L of 8192 lattice units.

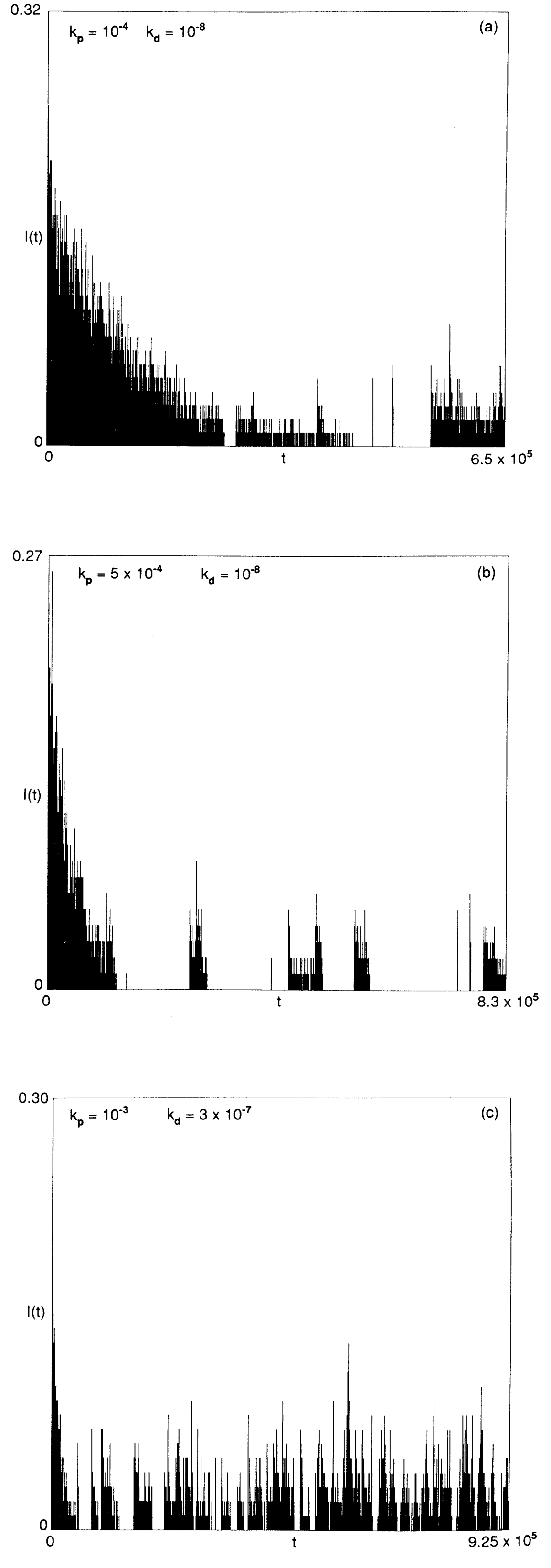

FIG. 7. Representative corrosion current profiles $I(t)$ obtained from model IIa (single-pit) simulations.

and approaches a constant value (with large fluctuations about the value).

To develop a better understanding of the corrosion current profiles additional simulations were carried out using the single-pit model (model IIa) in which only one pit is allowed to grow via a single gap in the outer surface. Figure 7 shows three current profiles $I(t)$ obtained using this model. Figure 7(b) shows quite clearly the initial current pulse and several smaller pulses corresponding to pits growing in the large pit corresponding to the initial current pulse. Figure 7 supports the idea that the small pulses in Figs. 6(a) and 6(b) result from pitting inside pits that have already grown and become passivated. Simulations were carried out to determine the average shape of the initial current transient. Using the single-pit model the current profile $I(t)$ was measured for times t in the range $0 \leq t \leq 10^5$ and the results from a number (up to 1000) simulations were averaged. Figure 8 shows some

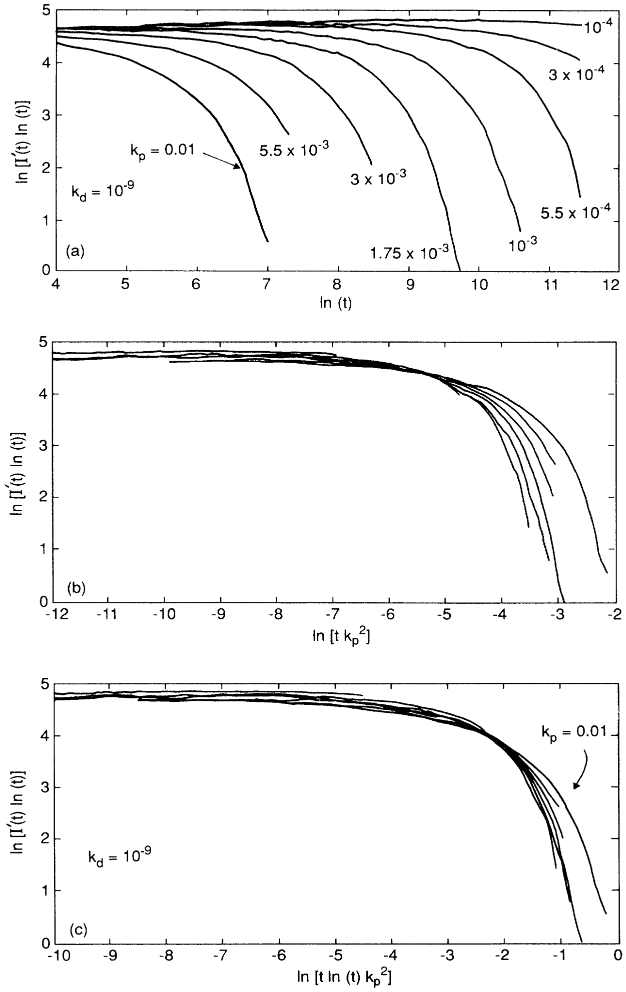

FIG. 8. Part (a) shows mean current profiles $I(t)$ obtained from single-pit model simulations with a very small depassivation rate constant ($k_d = 10^{-9}$). Here $I'(t)$ is $100 \times I(t)$. Part (b) shows the results of an attempt to scale the results shown in part (a) using the scaling form given in Eq. (4) with $t^* \sim k_p^{-2}$. Part (c) shows the data collapse obtained using Eq. (4) with $t^* \ln(t^*) \sim k_p^{-2}$.

results for simulations carried out with a very low depassivation rate constant ($k_d = 10^{-9}$). The simulations indicate that $I(t)$ can be represented quite well by

$$I(t) \sim 1/\ln(t) \; , \tag{4}$$

and this is illustrated in Fig. 8 for simulations carried out using eight different values for the passivation rate constant. Under these circumstances the pit can be represented by a semicircle of radius R and the current $I(R)$ is the probability that a random walker launched from the mouth of the pit will reach this semicircle before returning to the mouth of the pit. From the Einstein relationship between diffusion and conductivity this is proportional to the conductivity across a conducting sheet between the pit mouth and the surface of radius R

$$I(t) \sim 1/(\ln R/r) \; . \tag{5}$$

Here r is the effective radius of the pit mouth. Since the current is related to the pit radius by

$$I(t) \sim R \, dR/dt \; . \tag{6}$$

It follows from Eqs. (5) and (6) that in the asymptotic (long-time) limit $R^2 \ln R \sim t$ and $I(t) \sim 1/\ln(t)$. Under these conditions (essentially no depassivation) the current transient appears to have the form

$$I(t) = f(t/t^*)/\ln(t) \; , \tag{7}$$

where the cutoff function [$f(x)$ in Eq. (7) has the form $f(x) = \text{const}$ for $x \ll 1$ and $f(x)$ decays faster than any power of x for $x \gg l$] [i.e., $t \gg t^*$ where $t^*(k_d)$ is the characteristic depassivation time]. Figures 8(b) and 8(c) show the results of two attempts to scale the current transients shown in Fig. 8(a). The data collapse shown in Fig. 8(c) appears to be better than that shown in Fig. 8(b) and is converging more rapidly as k_p decreases. Figure 8(c) indicates that the characteristic passivation time t^* might be related to the passivation rate constant k_p by

$$t^* \ln(t^*) = k_p^{-2} \; . \tag{8}$$

A series of simulations was carried out using larger values for the depassivation rate constant. Figures 9(a) and 9(b) show the mean current. $I(t)$ (averaged over a number of simulations) for simulations carried out with a constant value for k_d ($k_d = 10^{-6}$) in Fig. 9(a) and a constant value for k_p ($k_p = 10^{-3}$) in Fig. 9(b). In general, the corrosion current $I(t)$ is essentially constant. [$I(t) \sim 1/\ln(t)$] at short times at which passivation is unimportant. At intermediate times passivation becomes important and the corrosion current decreases rapidly as the passive layer covers the pit surface. At later times depassivation becomes important and the corrosion current reaches a minimum value and then increases slowly with increasing time. This slow increase is associated with a slow increase in the pit size which leads to more depassivation events.

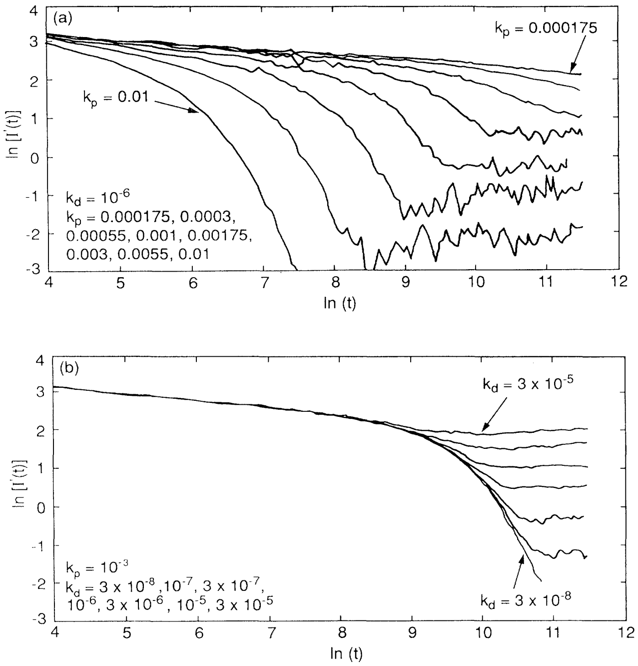

FIG. 9. Mean current profiles $I'(t)$ obtained from the single-pit model. Part (a) shows results obtained with a constant depassivation rate constant ($k_d = 10^{-6}$) and eight different passivation rate constants. Part (b) shows results obtained with a constant passivation rate constant ($k_p = 10^{-3}$) and seven depassivation rate constants. Here I' is $100 I(t)$.

IV. SUMMARY

Despite the simplicity of the two-dimensional models for pitting corrosion explored in this work they appear to be capable of reproducing some of the most characteristic features associated with many pitting corrosion phenomena. Depending on the model parameters (k_d and k_p) both smooth surfaced brightening pits and rough surfaced "etching" pits can be generated. Earlier simulations with a diffusion-limited surface annihilation model [53,54] that can be considered to be a model for electropolishing indicate that the surfaces of the brightening pits would be even more smooth and regular (hemispherical) in a corresponding three-dimensional simulation.

These pitting corrosion models cannot, of course, represent the complex electrochemical environment inside and outside of the pits. To the extent that these environments evolve in time the parameters k_d and k_p should be time-dependent quantities that are continuously updated. The simple models described here generate current fluctuations that resemble those observed in at least some experimental systems. In these models the current fluctuation can be associated with the initiation and growth of individual pits. The corrosion current is largest just after a pit has started to grow and decline (on average) until the pit becomes passified. A similar shape for the current fluctuation has been observed in some experimental studies but in other experiments the current rises to a maximum after the initiation event and then falls abruptly to a very low value. In some cases this behavior has been linked to rupture of the pit cover which brings about a rapid change in the electrolyte composition inside the pit. If the lattice sites in the model are taken to represent individual atoms then the current pulses in these simulations are very small. Larger current pulses could be generated using different parameters in these models and/or the corresponding three-dimensional models.

In real corrosion processes the metal-ion concentration inside the pit increases and this may result in a large osmotic pressure inside the pit. This osmotic pressure may eventually become large enough to rupture the film of passivating material that covers the pit. Because this process depends on the transport and mechanical properties of the pit cover as well as the corrosion process itself the stage at which this process will occur can be expected to be sensitive to the nature of the corroding material and the corrosion conditions. The buildup of corrosion products inside the pit and the increase in osmotic pressure could be included in the passivation and depassivation model (we have carried out simulations in which corrosion products are allowed to diffuse and, in some cases, react with the passivating layer). In the context of the present model the opening of the pit cover would give more ready access of the corrosive fluid particles to the underlying surface and would accelerate the corrosion process. In models in which the corrosion products are themselves corrosive the opposite effect would occur (the corrosive fluids inside the pit would be released when the pit cover was removed). Since the passivation and depassivation model studied in this work does not include pit cover rupture it should be regarded as a model for the early stages of pitting corrosion.

In the limit $k_p \rightarrow 0$ (no passivation) our model is closely related to the diffusion-limited etching model that was developed by Kuiken and co-workers [55–57] to represent etching of a masked surface. In this process and pitting corrosion both diffusion of reactive species towards the reactive surface and diffusion of reaction products away from the surface may play an important role. In practice one of these two processes is often the rate-limiting process. As was noted above, the models described above can be used to simulate either of these two limiting cases. In these models we have implicitly assumed that the corrosion reaction is first order in the concentration of the corrosive species [or depends linearly on $\rho(p)_{\max} - \rho(p)$ where $\rho(p)$ is the corrosion product concentration and $\rho(p)_{\max}$ is the maximum value of $\rho(p)$ for the corrosion product diffusion-limited corrosion model]. In many systems these will be reasonable approximations but in other cases more elaborate models will be needed. Similarly more elaborate models will be needed if both the diffusion of corrosive materials and the diffusion of corrosion products both play an important role in the corrosion process.

Because of topological effects many two-dimensional models do not provide a reliable or realistic representation of three-dimensional phenomena. In this case, however, the formation of loops is not important and the model does not represent a critical phenomenon. Consequently we expect that the qualitative features observed in the two-dimensional simulations would survive in a corresponding three-dimensional model. Consequently we believe that this simple two-dimensional model does provide insight into real (three-dimensional) corrosion phenomena. The logarithmic corrections to the simple power law expressed in Eqs. (4)–(6) are a consequence of the unique characteristics of diffusion and random walks in two-dimensional systems [the number of sites visited by a random walker after n steps on a two-dimensional lattice is proportional to $n/\ln(n)$]. In the corresponding three-dimensional models these logarithmic corrections should disappear leaving only power-law corrections to the asymptotic algebraic behavior.

We believe that the simple models described here provide a basis for the development of more realistic but more complex models that can be used to simulate a broader range of corrosion processes. There are many ways in which the models used in this work could be modified to provide a more realistic representation of specific systems. For example, we could incorporate features from simple dealloying [58–60] and etching [61] models to represent the role played by metallurgical factors. This might be implemented using simple percolation models for the alloy structure or may be based on more detailed models for the morphology such as spinodal decomposition models or models for the growth of grain boundaries. In most systems the passivation and depassivation rate "constant" depend on the electrochemical environment inside the pit. Consequently models that take these interactions into account would have to be developed to obtain results of predictive value for real systems. However, our objective in this work was to develop a simple generic model for pitting corrosion that could be used as a limiting case scenario to help develop a better understanding of a variety of pitting corrosion processes.

Current transients have been studied in simple models for the dealloying and the pitting corrosion of binary alloys [58–60]. In these models current pulses arise in a natural way when a connected region of more reactive atoms (lattice sites) is exposed by the slow removal of less reactive atoms. These fluctuations are most pronounced for large reactivity ratios (dissolution probability ratios) between the two components of the alloy and for more reactive atom concentrations near to the percolation threshold concentration. In the passivation and depassivation model the current transients arise in quite a different way when a hole is generated in the passive layer that protects the underlying reactive metal sites. In this model the rate at which current transients appear depends on the size of the passive layer and the depassivation rate constant that is a parameter in the model.

After this work was completed, an even more simple model for pitting corrosion was introduced by Nagatani [62]. This model is based on the diffusion-limited-aggregation model [63] (each random-walk trajectory is completed before another is started). Both depassivation and corrosion are a result of contacts between the random walkers and the surface. There is no passivation process in Nagatani's model.

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