Scaling behavior in corrosion and growth of a passive film

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We study a simple model for metal corrosion controlled by the reaction rate of the metal with an anionic species and the diffusion of that species in the growing passive film between the solution and the metal. A crossover from the reaction-controlled to the diffusion-controlled growth regime with different roughening properties is observed. Scaling arguments provide estimates of the crossover time and film thickness as functions of the reaction and diffusion rates and the concentration of anionic species in the film-solution interface, including a nontrivial square-root dependence on that concentration. At short times, the metal-film interface exhibits Kardar-Parisi-Zhang (KPZ) scaling, which crosses over to a diffusion-limited erosion (Laplacian growth) regime at long times. The roughness of the metal-film interface at long times is obtained as a function of the rates of reaction and diffusion and of the KPZ growth exponent. The predictions have been confirmed by simulations of a lattice version of the model in two dimensions. Relations with other erosion and corrosion models and possible applications are discussed.

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I. INTRODUCTION

When a metallic surface is in contact with an aggressive solution, a passive layer containing the metal oxide or hydroxide is formed immediately after the corrosion of the topmost layer. The passive film protects the surface from the attack of the solution. This leads to a slowdown of the corrosion rate. Further corrosion takes place through the diffusion of cations and anions through the passive layer, as illustrated in Fig. 1. Ions are produced at the metal/film (MF) and film/solution (FS) interfaces. They can react in the film, which consequently grows, and cations can be dissolved at the FS interface (see, e.g., Refs. [1–4] for a more complete review of modeling and applications). All these processes are affected by physicochemical conditions such as temperature, the electric field in the insulating film, the pH of the solution, etc. Besides changing the global corrosion rate, these mechanisms must also affect the morphological properties of the MF and FS interfaces in a nontrivial way.

When one aims at modeling specific corrosion problems, it is essential to take into account all those possible mechanisms. Studies along these lines usually focus on the growth velocities of the MF and FS interfaces. On the other hand, some effort is directed to searching for universal behavior of a larger number of apparently different systems. If the focus is interface morphology, previous experience with surface growth models shows that a small number of key features (symmetries) are sufficient to determine scaling laws, for instance, those of surface roughness [5,6].

Following this reasoning, the aim of this work is to study the evolution of the growth rate and of the surface roughness of the MF interface in a simple model that represents some mechanisms of Fig. 1 that may be dominant under certain conditions. First, since it is recognized that the anion transportation is largely responsible for the passive layer growth on different metals (see, e.g., Ref. [7], and references therein), we will take into account only the diffusion of this chemical species through the film. We will also assume that

there is no bias in this diffusion process. Moreover, we will consider a simple first-order reaction mechanism when this species encounters the metallic surface. The short- and long-time growth rates are predicted through a scaling theory, while symmetry arguments are used to predict the roughness scaling. A lattice version of the model is also presented, and simulation results in two dimensions give support to the theoretical predictions.

Although this model adopts a simplified view of corrosion systems, it contains some features that may be interesting for experimental investigation. For instance, the long-time diffusive $(t^{1/2})$ growth of the MF interface displacement is accompanied by a nontrivial dependence on the square root of the anion concentration at the FS interface. The universal surface roughness scaling, which is in the class of diffusion-limited erosion (DLE), should also persist in cases of slower passive layer growth, including those with the usual logarithmic laws [8–10]. We also obtain a relation between the MF interface roughness at long times and the rates of corrosion and diffusion, which involves a roughening exponent of the short-time dynamics. Thus, we believe that this work suggests interesting phenomena to be investigated in real corrosion problems. From this point of view, the simulation work is also interesting to illustrate the difficulties in observing all the dynamical aspects of the model in a single experiment.

From the theoretical point of view, this model is interesting from the perspective of application of competitive sur-

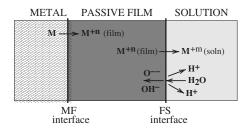


FIG. 1. Scheme of the main processes during corrosion with a passive film growth.

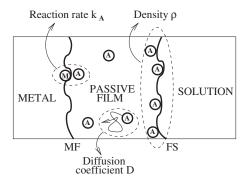


FIG. 2. Scheme of our model, with A representing the anions and M representing the metal.

face growth dynamics, a subject that has attracted some interest in recent years [11–16]. It also advances over a previous model which showed a similar crossover [17,18], because here we consider less restrictive assumptions based on current interpretation of corrosion phenomena. Indeed, in the following we will make clear the different interpretation of that model.

The rest of this work is organized as follows. In Sec. II, we define the model and discuss the scaling behavior of the growth rate of the MF interface. In Sec. III, we discuss the crossover in interface roughness scaling. In Sec. IV, we present a two-dimensional lattice model and results of simulations which give additional support to the previous theoretical analysis. In Sec. V we present our conclusions.

II. THE CORROSION MODEL AND SCALING OF PASSIVE FILM GROWTH

Following Ref. [7], we assume the existence of anionic species which are produced in electrochemical water decomposition at the interface with a solution (Fig. 1). They can immediately react with the metal surface or enter and diffuse through the already formed passive layer until reaching the metal surface and subsequently reacting with it. The diffusion coefficient for the anions is D and the reaction rate with the metal is k_A . We also assume that the concentration of these anions at the metal-solution interface, ρ , is constant during the passive layer growth. It properly represents the balance of electrochemical equilibria at the solid interface with the solution. The products of the reaction of anions with the metal form a passive layer at the same position as the consumed material, thus moving the MF interface to the metal side. An atomistic picture of the process is shown in Fig. 2.

The above model is very simple when compared to related ones discussed in the literature, which account for other important mechanisms, such as the presence of an electric field inside the passive film and energy barriers for metal corrosion [7-10]. Thus, although now we proceed to present its solution, we will address the question of its reliability at the end of this section.

The model corresponds to a diffusion problem with a moving boundary, which is the MF interface. However, it is possible to find the short- and long-time behavior of this system using a scaling approach, with the advantage of providing a clear picture of these regimes and the crossover between them. The starting point of this analysis is to observe that there are two relevant characteristic times in this process: a time for the surface reaction of the metal (dissolution), $\tau_{dis} \sim 1/(\rho k_A)$, and a diffusion time $\tau_{dif} \sim h^2/D$, where h is the height of the passive film (distance between the MF and FS interfaces).

At short times the process is reaction limited, since the global corrosion rate is determined by the rate of reaction without significant limitations due to the slow diffusion of the reactants (the anions). In other words, τ_{dif} is negligible when compared to τ_{dis} . Thus, the MF interface moves with velocity

$$v_I \approx \rho a k_A,$$
 (1)

where a is a characteristic length. The average height of the interface linearly increases in time t as

$$h \approx \rho a k_A t$$
 (2)

(for simplicity, the analysis of this section assumes that the MF interface roughness is negligible, thus no effect of fluctuations of this average height will be taken into account).

At long times, the passive layer is large and the process becomes diffusion limited since the anions need a long time to reach the metal. In this regime it is reasonable to assume that the whole passive layer has an average concentration of anions of order ρ (although the exact value is certainly smaller than ρ). These anions reach the MF surface after a time τ_{dif} , leading to an increase ρh in the height of the passive film. Thus, the MF interface moves with velocity

$$v_F = \frac{dh}{dt} \approx \rho h / \tau_{dif},$$
 (3)

which can be integrated to give a diffusive growth of the passive layer as

$$h \approx \sqrt{\rho Dt}.\tag{4}$$

A crossover between these regimes takes place at a characteristic time where τ_{dif} and the time of dissolution of $\rho h/a$ layers are of the same order:

$$t_c \sim \frac{D}{\rho a^2 k_A^2}.$$
(5)

The same result is obtained by matching the expressions for the height of the passive layer in the initial and final regimes [Eqs. (2) and (4)]. The height at the crossover time is

$$h_c \sim \frac{D}{ak_A}. (6)$$

It is thus reasonable to expect that the average height of the passive layer obeys a scaling relation in the form

$$h/h_c = f(t/t_c), (7)$$

where f is a scaling function such that $f(x) \sim x$ for small x and $f(x) \sim x^{1/2}$ for large x.

Although the long-time dependence of the growth rate is somewhat expected from the model rules, one remarkable feature is its increase with the square root of the concentration, which contrasts with the initial linear dependence. It follows from the assumption of next-to-equilibrium conditions at the FS interface with no pumping of anions from the solution to the solid. This assumption sounds reasonable in corrosion processes in contact with an aggressive environment (e.g., the atmosphere). We are also not aware of any previous work showing this square-root law (on concentration or pressure) in real corrosion processes, but it is certainly an important point to be experimentally investigated.

The $t^{1/2}$ law (also known in the literature as the parabolic law) for growth of a passive film has been observed in some real systems, such as iron oxidation in dry air or in oxygen at high temperatures [19–21]. It was also found in more recent works on iron and iron nitride oxidation, but in this case the rate-limiting process was diffusion of iron cations [22,23].

Models including other physically important mechanisms [7] usually lead to logarithmic laws, which imply that the global corrosion rates decrease in time as 1/t or $1/t^2$. This is usually a consequence of further energy barriers for the diffusion of the ions inside that layer or of its dissolution, which may eventually lead to a steady state where the thickness is constant. Anyway, the overall corrosion is usually much slower than the present $t^{1/2}$ law. There are also cases in which the passive layer grows linearly in time during a large time region, such as in a recent work on tungsten corrosion in stationary conditions [24]. This represents a much faster corrosion than in our model.

Concerning the crossover from a linear to a diffusive growth law, it was recently observed in a numerical model of dry metal oxidation which aims at describing corrosion of nuclear waste systems [25]. That model provides a set of equations for the diffusion of cationic and anionic vacancies inside the oxide and for the evolution of the metal/oxide and the oxide/solution interfaces [25,26]. Comparison with our model mechanisms suggests that the conclusion of a universal crossover is also valid in that model, but further numerical work would certainly be interesting to confirm this proposal.

It is also interesting to discuss the differences between the present results and those of a recently studied corrosion model with porous passive layer formation and relaxation after oxide or hydroxide formation [17,18]. That model was not related to the generally accepted mechanisms illustrated in Fig. 1, and it was defined in a lattice, in contrast with the present one. It assumed that the volume excess of reaction products could suppress the access of the solution to the metal surface, but the access was restored by a diffusion mechanism. The MF interface growth depended on one particular rule of the model, as shown in Ref. [17]. For instance, if a single site was blocked after a corrosion event ($\phi=1$ in the notation of Ref. [17]), then the global corrosion rate was always constant, i.e., no crossover to a diffusive law was observed. On the other hand, diffusive growth was obtained in the case of two blocked sites (ϕ =2). This differs from the present model, in which the crossover is universal, in the sense that it occurs for any set of model parameters. Consequently, although the scaling approach used to explain the previous model's behavior with $\phi=2$ is similar to the above one [18], the models involve very different physicochemical mechanisms.

III. SCALING OF SURFACE ROUGHNESS

The noise induced by random collisions of the anions with the metal surface and by their diffusion leads to roughening of the MF interface. This does not invalidate the previous scaling approach, because this interface is expected to be flat at very large length scales (roughness exponent smaller than 1) [5,6]. On the other hand, understanding the expected roughness scaling may be useful for comparisons with morphological data from real systems. Moreover, the presence of the passive film suggests the possibility of a crossover in the roughness scaling, as observed in other systems, such as the deposition model with a diffusive layer of Ref. [27]. Indeed, the short- and long-time regimes of our model show different roughness scaling, which is equivalent to previously studied (and apparently not related) etching models.

At short times, all points of the MF interface are equally subject to corrosion due to the rapid diffusion of the anions, the reactions being just limited by the dissolution rate k_A . This condition is equivalent to those of a lattice etching model proposed by Reverberi and Scalas (RS) [28], in which all sites in contact with the solution have equal probability to be removed at each time step. The scaling properties of that model are equivalent to those of the Eden model [29,30], in which all neighbor sites of the growing cluster have equal probability to become part of the cluster at each time step. Indeed, except for the behavior of isolated islands (which do not affect roughness scaling), the RS model is the inverse of the Eden model [28].

The surfaces of Eden aggregates and of RS-etched solids are known to evolve according to the Kardar-Parisi-Zhang (KPZ) equation [31]

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 + \eta(\vec{x}, t), \tag{8}$$

where h is the height at the position \vec{x} in a d-dimensional substrate at time t, ν and λ are constants, and η is a Gaussian noise. Thus we expect that the roughness of the MF interface of our model also has KPZ scaling at short times. In the realistic case of d=2 (three-dimensional solid), the global roughness of the interface increases as $\xi \sim t^{\beta}$, with $\beta \approx 0.23$ [32] and the time t typically measured as a number of (grown or eroded) monolayers. The local roughness averaged over windows of size r scales as $w \sim (r/a)^{\alpha}$, with $\alpha \approx 0.39$ [32]. In Sec. IV, we will present simulation results of a square lattice version of our model (d=1 interface), where exponent estimates must be compared with $\beta = 1/3$ and $\alpha = 1/2$ [5,6,31].

However, while RS etching shows KPZ scaling at long times, this is not the case for our corrosion model. Here, the restrictions for the access of the anions to the metal lead to different effective corrosion rates at different points of the rough MF interface. In this regime, the surface peaks are more probably eroded by a small anion concentration than the surface valleys. This slows the roughening process when compared to initial KPZ erosion.

This long-time regime is equivalent to the diffusionlimited erosion model [33]. DLE is a lattice model in which eroding particles are randomly left at points very distant from the solid surface; they are allowed to diffuse and, when they reach the surface, they are annihilated together with an atom of the solid. This is exactly our case when the passive film is large, since there is a rarefied anion gas near the MF surface.

In the continuous limit, the DLE interface is driven by the gradient of a Laplacian field [34]. The field ϕ satisfies $\nabla^2 \phi = 0$ for z < h, vanishes for z > h, and is continuous at the interface (z=h). The normal interface velocity is proportional to the normal field gradient, so that [34]

$$\frac{\partial h}{\partial t} = -D \left(\frac{\partial \phi}{\partial z} \vec{\nabla}_{\parallel} \phi \cdot \vec{\nabla}_{\parallel} h \right)_{z=h}, \tag{9}$$

where D is the diffusion coefficient. In the original DLE model, h linearly increases in time, but this leads only to a trivial transformation $t \rightarrow \sqrt{t}$ for the present diffusive case [Eq. (4)]. A recent discussion of various models of transport-limited dissolution can be found in Ref. [35].

In three dimensions, the global interface roughness of DLE saturates as both $t \rightarrow \infty$ and $L \rightarrow \infty$. The correlations in the interface height have a power-law decay corresponding to a negative roughness exponent $\alpha = -1/2$. This means a very flat interface even at small length scales. In two dimensions (d=1) interface, the squared global roughness increases logarithmically as $\xi_{DLE}^2 \approx B \ln(4\pi h)$, where B is a constant associated with the noise. Thus, even in this case, the interface at long times has a very slowly increasing roughness whose order of magnitude is determined mainly by the KPZ evolution at short times. This feature will also be confirmed in the lattice model of Sec. IV.

The crossover between the different roughening regimes (KPZ and DLE) is also expected to take place at the crossover time t_c [Eq. (5)]. Since the height of the interface is h_c at the crossover [Eq. (6)], we expect that the crossover roughness will be of order

$$\xi_c \sim (h_c/a)^\beta \sim \left(\frac{D}{ak_A}\right)^\beta,$$
 (10)

where β is the KPZ exponent. The roughness of the MF interface is expected to obey a scaling relation involving the crossover time t_c and this crossover roughness:

$$\xi/\xi_c = g(t/t_c),\tag{11}$$

where g is a scaling function.

Equation (10) gives the order of magnitude of the saturation roughness in the three-dimensional DLE regime, and also a rough estimate of the roughness in a large time window in two dimensions (due to the slow logarithmic growth). These results may also be interesting for experimental investigations on corrosion processes with growth of passive layers, although the direct determination of some quantities, such as the ratio D/k_A , is certainly difficult. However, it is remarkable that simple scaling arguments and the model symmetries are able to predict a relation between the interface roughness and the rates of reaction and diffusion.

Dissolution models with similar mechanisms were also considered by Kim and Yoon [36] and by Reverberi *et al.* [37]. In the cases where the movement of the eroding par-

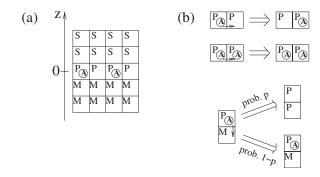


FIG. 3. (a) Initial configuration of the lattice model. (b) Examples of possible movements of a particle *A* to a neighboring site and the subsequent configurations.

ticles was biased toward the surface, an Edwards-Wilkinson [EW; Eq. (8) with λ =0] [38] growth was observed at long times. On the other hand, DLE scaling was found in no-bias conditions [36], which suggests the existence of a DLE-EW crossover in the weak bias case. The KPZ-DLE crossover was also observed in the model of Refs. [17,18], but again we stress that different mechanisms were responsible for that behavior. For instance, the long-time DLE behavior in that case is observed only for the parameter ϕ =2.

IV. LATTICE MODEL AND NUMERICAL RESULTS

Now we consider a square lattice model with the main mechanisms of our corrosion model. The lattice sites may have three different states: M (metal), S (solution), or P (passive). Each state represents the dominant chemical species inside a mesoscopic region. Any P site and the S sites at the bottom layer (to be defined below) may be occupied by an A particle, which represents a diffusing anion.

In the beginning of the process, all sites above a certain row of the lattice are labeled S, all sites below that row are labeled M, and the sites at that row (z=0) are labeled P (a very thin passive layer). The row z=0 is permanently occupied by a fraction ρ of A particles; thus one A particle is added or removed from it at each time this row loses or gains another A particle by diffusion. The lattice at t=0 is illustrated in Fig. 3(a).

At each time step of this system evolution, each A particle executes D random steps to nearest-neighbor sites. No movement to an S site is accepted. If the target is a P site, then the movement is allowed only if there is no A particle there. Otherwise, the movement is rejected. If the target site is an M site then the reaction $A+M \rightarrow P$ occurs with probability p, i.e., the M site is turned into a P site. Otherwise (probability 1-p), the movement is rejected. It represents the reaction of the anion with a metal ion and the formation of the oxide or hydroxide. Thus p is proportional to k_A . These processes are illustrated in Fig. 3(b).

We simulated this model using several values of p and ρ and with D=1: $p=10^{-3}-1$, $\rho=1/64-1/4$. The lateral size of the lattice was L=512 in most cases, but the possibility of finite-size effects was also checked in simulations in L=1024. The height h of the passive layer (position of the MF interface) is the average absolute position of the lowest P

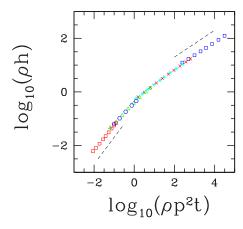


FIG. 4. (Color online) Scaled height of the passive layer as a function of scaled time for the lattice model with D=1 and $\rho=1/16,\ p=1$ (squares, right side); $\rho=1/16,\ p=0.1$ (crosses); $\rho=1/16,\ p=0.01$ (triangles); $\rho=1/16,\ p=0.001$ (squares, left side); $\rho=1/32,\ p=0.1$ (asterisks); $\rho=1/8,\ p=0.1$ (hexagons). The dashed lines with slopes 1/2 (right side) and 1 (left side) indicate the short-time and long-time behavior.

particle at each column of the lattice. Average results were taken typically from 100–1000 realizations.

The scaling analysis of Sec. II suggests that $t_c \sim 1/(\rho p^2)$ and $h_c \sim 1/p$ [Eqs. (5) and (6)]. The scaling relation (7) is tested by plotting ph ($\sim h/h_c$) versus $\rho p^2 t$ ($\sim t/t_c$) in Fig. 4, where data for different values of p and ρ are shown. In all cases, only data for an average height h larger than 10 monolayers were presented. Figure 4 confirms the predicted scaling of the height of the passive layer, and clearly shows a linear time increase for $t \ll t_c$, crossing over to a diffusive growth for $t \gg t_c$.

The roughness scaling suggested in Eq. (11) is tested in the plot of Fig. 5, where we show $\log_{10} \xi p^{\beta}$ versus $\log_{10} \rho p^2 t$ for three different values of p and using the KPZ exponent in d=1, $\beta=1/3$ [5,31]. Good data collapse is also obtained with other values of β , in the range $0.31 \le \beta \le 0.35$. This may be

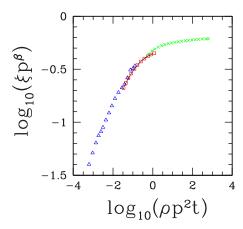


FIG. 5. (Color online) Scaled roughness of the passive layer as a function of scaled time for the lattice model with D=1, $\rho=1/16$, and p=0.001 (triangles), 0.01 (squares), 0.1 (crosses). Results for L=1024, p=0.01, and the same values of D and ρ (solid line) illustrate the absence of significant finite-size effects. The exponent $\beta=1/3$ of the KPZ model in 1+1 dimensions was used here.

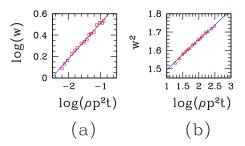


FIG. 6. (Color online) (a) Short-time scaling of the surface roughness of the lattice model with ρ =1/16, p=0.001, and D=1. The solid line is a linear fit with slope 0.34. (b) Long-time scaling of the squared surface roughness of the lattice model with ρ =1/16, p=0.1, and D=1. The solid line is a linear fit.

viewed as evidence of the predicted KPZ scaling for short-time behavior of the model. Finite-size effects are negligible, as illustrated by the data for L=1024; thus small deviations from data collapse in Fig. 5 are probably related to corrections to the relation (11) in p, ρ , or t. Anyway, they seem to be weaker than the finite-size corrections which frequently make it difficult to estimate exponents of discrete KPZ models [28,30,32].

Let us stress that the slow increase of ξ for $\rho p^2 t > 1$ in Fig. 5 does not correspond to roughness saturation due to finite size of the lattice, as we have verified by changing the simulation box size. Instead, it is a slow but continuous increase of the roughness.

From Figs. 4 and 5, the short-time regime is represented by $\rho p^2 t < 1/10$. On the other hand, in order to observe any sort of roughness scaling, it is necessary that several layers of the metal have been eroded. This is possible only if the condition $\rho pt \gg 1$ is also satisfied. In order to match the above conditions simultaneously, we need to analyze very small values of p and very long times t, since p is typically restricted to values of order 0.1. This is possible with p = 0.001 and p = 1/16, so that in Fig. 6(a) we present the time evolution of the roughness for those parameters, with a linear fit that gives p = 0.34. The fits of different regions of that plot give $p = 0.36 \approx 0.36$, which is consistent with the KPZ value p = 1/3. The uncertainty in this estimate is close to those found in models such as ballistic deposition (see, e.g., Ref. [39]).

Unfortunately, with larger values of p (e.g., p=0.01), it is not possible to satisfy the above conditions simultaneously. On the other hand, for smaller p (e.g., p=0.0001), the simulation times necessary to get accurate results are extremely large. Thus, further tests of KPZ scaling with the available data are not possible. However, it is important to recall that the interpretation of the above numerical results as evidence of KPZ scaling (instead of another dynamics which may have a similar value of β) is mainly guided by the symmetries of the model. In other words, it is based on the fact that our model with small p is effectively equivalent to the RS model (equal corrosion probability for all surface points), and this model was also shown to be in the KPZ class, similarly to the Eden model [28]. A detailed discussion of the association of a universality class with a given set of growth rules is found in Ref. [40].

The long-time scaling of the roughness is expected for any set of model parameters. However, accurate simulation results at sufficiently long times ($\rho p^2 t > 100$; see Figs. 4 and 5) can be obtained only for large values of p, which also restricts the useful range of p. In Fig. 6(b) we show the long-time roughness for p = 0.1 and a linear fit which suggests logarithmic increase of the squared roughness. This is characteristic of DLE scaling. The alternative possibility of a power-law increase with a small exponent cannot be completely ruled out, but again the growth rules can be used to justify the claim of DLE scaling: at long times the corrosion is performed by a very rarefied gas of A particles; thus it effectively corresponds to the conditions of the original DLE model [33,34].

As explained above, it is difficult to obtain an illustration of the KPZ-DLE crossover for a single set of model parameters, although the system dynamics justify the claim that it is a universal feature. This suggests that it will also be difficult to observe that crossover in experiments. Depending on the real system features, only a clear KPZ regime or only a clear DLE regime will be easily observed, similarly to our findings.

V. CONCLUSION

We studied the time evolution of the displacement and of the surface roughness of the interface between a metallic surface and a growing passive layer in a model that represents some of the dominant mechanisms of certain corrosion processes. Metal is corroded in a first-order reaction with anionic species created at the solution front, so that their concentration at this front, ρ , remains constant. They are then transported to the metal surface with the diffusion coefficient D in the passive layer. The growth rate predicted by scaling theory crosses over from a linear time increase to a $t^{1/2}$ law. Besides the expected dependence of those rates on k_A and D, there is a nontrivial $\rho^{1/2}$ dependence at long times. Symmetry arguments are used to predict the evolution of the roughness of the metal-film interface, which shows a crossover from KPZ to DLE scaling. An estimate of the roughness in the long-time regime is obtained in terms of the rates of the process and a KPZ exponent. A lattice version of the model is also presented, and simulation results in two dimensions give support to the theoretical predictions.

The present model advances over previous ones by assuming a set of hypotheses which are consistent with the currently accepted mechanisms for corrosion and passivation, and by defining a model from a continuous (mesoscopic) point of view, and not from a particular lattice realization. Despite the absence of other important mechanisms in the description of the passive layer growth, an important feature of this model is to relate the properties on the MF interface to the decreasing flux of aggressive species toward that surface. Indeed, this is the fundamental ingredient that provides preferential corrosion at the interface tips and, from universality grounds, leads to the DLE dynamics. We expect that our results will motivate experimental investigations as well as theoretical works along the same lines, but focusing on specific applications.

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