Computer Simulation of Pitting Corrosion of Stainless Steels

by N. J. Laycock, D. P. Krouse, S. C. Hendy, and D. E. Williams

Stainless steels and other corrosion resistant alloys are generally protected from the environment by ultra-thin layers of surface oxides, also called passive films. Unfortunately, these films are not perfect and their Achilles' heel is a propensity to catastrophic local breakdown, which leads to rapid corrosion of the metallic substructure (see Fig. 1). Aside from the safety and environmental hazards associated with these events, the economic impact is enormous.[1] In the oil and gas and petrochemical industries, it is of course usually possible to select from experience a corrosion-resistant alloy that will perform acceptably in a given service environment. This knowledge is to a large extent captured in industry or company-specific standards, such as Norsok M1.[2] However, these selections are typically very conservative because the limits tend to be driven by particular incidents or test results, rather than by fundamental understanding. Decision-making can be very challenging, especially in today's mega-facilities, where the cost of production downtime is often staggeringly large. Thus significant practical benefits could be gained from reliable quantitative models for pitting corrosion of stainless steels. There have been several attempts to develop purely stochastic models of pitting corrosion.[3-6] On the other hand, purely deterministic models[7,8] have also been proposed.

The critical processes involved in pitting corrosion can be clearly separated into those involved in initiation, nucleation of a 'metastable' pit, and propagation or maintenance of the stability of growth of the initially formed defect.[9] Fluctuations in current signal the nucleation, temporary growth, and cessation of growth ('death') of metastable pits. A steadily increasing current signals the formation of a pit whose propagation continues. Analysis of these current fluctuations leads to a simple idea connecting the frequency of initiation of metastable pits, λ, with the frequency of formation of stable pits, Λ

$$\Lambda = \lambda \exp(-\mu \tau_c) \qquad (1)$$

where μ denotes the probability of 'death' of a metastable pit and τ_c is a 'critical age': if the metastable pit continues to propagate for a time longer than τ_c, then it transitions to 'stability'.[9]

Within a pit of any size, the solution conditions are extreme and very different from those outside the pit (Fig. 2). The questions for modeling are therefore (a) for initiation, how are the required extreme gradients developed in the first place, and (b) for propagation, how are they maintained. Development of a reliable predictive model for pitting corrosion in industrial service conditions requires a robust model for both the pit nucleation and pit propagation processes. Moreover, fundamental improvements in the performance of the less-expensive stainless steels are at least as likely to come from manipulation of the nucleation process as from further effects on pit propagation.

Pit Nucleation: Passive Film Formation and Breakdown

The nucleation stage of pitting corrosion involves the breakdown of the protective passivating layer; the establishment of the extreme local gradients that drive propagation and its mechanism is the subject of intense debate.[10-15] Metastable pit nucleation in commercial alloys is dominated by processes at sulfide inclusions.[17] This region adjacent to MnS inclusions has been shown to be an area of high electrochemical activity.[10,18] An unusually high-rate dissolution of MnS inclusions has been shown to lead to a sulfur crust over the inclusion, and it is assumed that the steel passivity then breaks down within the aggressive solution formed underneath this crust as a consequence of dissolution of the inclusion.[19] An Fe(Mn)S layer around the inclusion rim, detected by high-resolution SIMS microscopy, has been proposed as the cause of the initial inclusion dissolution.[16] These observations point to passive film breakdown in a sulfide-chloride solution formed by inclusion dissolution as the critical event. Similarly, the deleterious effect of the sigma phase in duplex stainless steels may also be caused by a locally Cr-depleted zone that is more susceptible to pitting than is the surrounding matrix. Pits will also nucleate on inclusion-free materials[20] and tiny current fluctuations that are assumed to represent possible trigger events (and are not associated with inclusions) have been detected in electrochemical imaging experiments.[21]

For the Fe-Cr alloy system, various experimental results have been interpreted using a passivation model proposed by Sieradzki and Newman,[22-25] which provides a framework for understanding compositional thresholds for passivity and the effect of variations
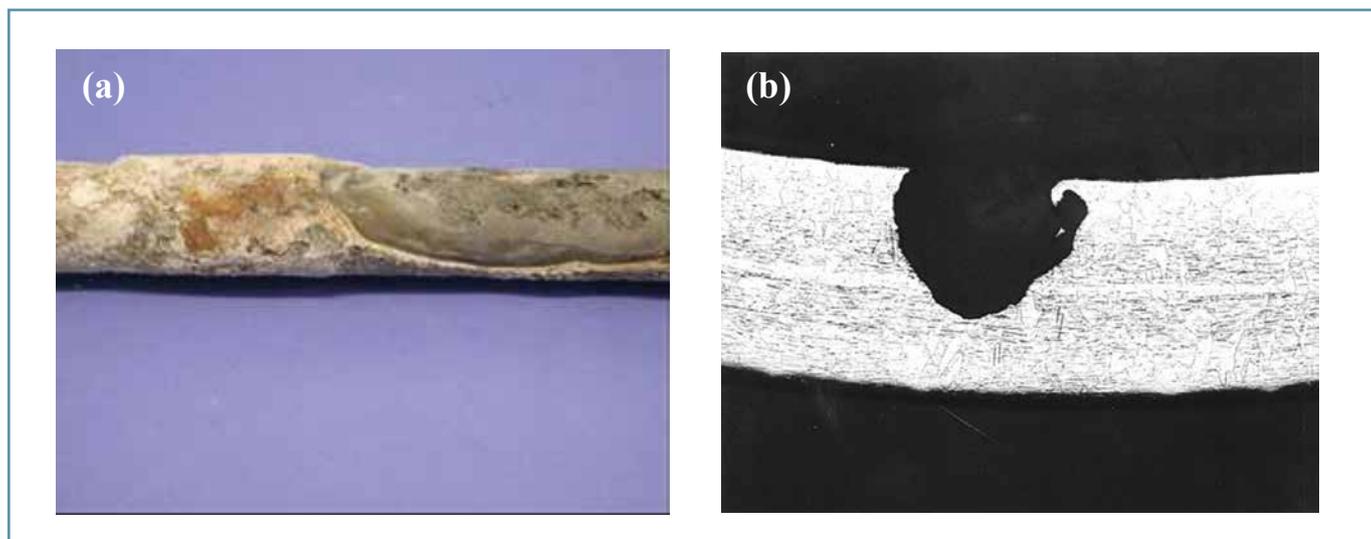
Fig. 1. *(a) Extensive pitting corrosion damage beneath thick deposits on a SAF2205 duplex stainless steel heat exchanger tube with cooling water on the shell side; (b) pitting corrosion in 316 SS heat exchanger tubes unintentionally exposed to high chloride brine in a geothermal power station.*

of Cr content on susceptibility to pitting corrosion. The model is based on the application of percolation theory, which quantifies the connectivity of a "random medium." In this model, the passivation of Fe-Cr alloys in acid solutions is due to formation of solid Cr (hydr)oxide with concurrent selective dissolution of Fe. Further Fe dissolution is eventually blocked by stable (-O-CrOH) chains, the formation of which depends critically on the connectivity of Cr atoms within the alloy lattice. We have carried out simulations of passivation for Fe-Cr (bcc) alloys in ideal situations, and the results are consistent with a variety of experimental results.[26] These ideas have led to a proposal for passive film breakdown that has been explored by computer simulation.[12] Nanoscopic clusters that contain only iron atoms would be randomly distributed throughout the material, therefore occasionally becoming exposed to the electrolyte simply through the slow dissolution of the passive film, and would then rapidly dissolve, to create a nanoscopic cavity with relatively Cr-rich boundaries. The speculation is that the resultant current pulse might create a local environment that might cause further dissolution of the boundaries of the cavity. In this model, the probability of the existence of a critical cluster size is the key factor in determining the likelihood of pitting, and it can be related to the alloy content via a percolation type model. For the binary Fe-Cr (bcc) lattice $P_c(1)$ is 0.25. Hence there are "infinite" chains of Fe atoms in 1st nearest neighbor sites for Fe contents above 25%. However, if we define an Fe cluster as a chain of Fe atoms that have only Fe atoms as 1st nearest neighbors, then Monte Carlo simulations show that these clusters have a P_c of approximately 0.85. Simulations were performed with a bcc lattice containing 3,953,501 atoms arranged in a cube, with lattice points randomly assigned as Fe or Cr atoms in the desired proportions. In each of 1000 simulations, Fe clusters anchored at the top surface were counted for size and depth. Figure 3 shows an example of a large (but not "infinite") cluster. Initial results suggest a surface number density of potential nucleation sites of about 10 to 100 cm^{-2}. This remains 3-4 orders of magnitude lower than the total number of events observed in our experiments with high-purity metal films.[27]

Propagation

Pit nucleation events occur at a very high frequency, even in conditions where stable pits do not form.[10,17,28] The transition from nucleation event to propagating pit depends on the fact that, in chloride solutions, the solution within the incipient pit cavity becomes highly acidic and concentrated in chloride, thus permitting the metal to dissolve actively instead of passivating. The concentration of dissolved metal cations (Fe and Cr) at the metal surface controls the local pH via the following hydrolysis reaction:

$$M^{z+} + y\,H_2O \rightarrow [M(OH)_y]^{(z-y)+} + y\,H^+ \qquad (2)$$
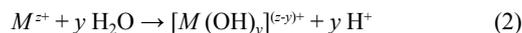
where M represents a metal cation and z can be 1, 2, or 3, with a decreasing equilibrium pH and a decreasing rate of reaction as z increases. Chloride ions also migrate into the corrosion site to balance any excess of metal cations, and there is an additional acidification because the highly concentrated chloride solution has a mean ionic activity coefficient greater than one. At the same time, there are concentration and potential gradients that lead to transport of metal ions out of the pit. Thus, a pit will only initiate (*i.e.*, continue to propagate after a nucleation event) if the metal can dissolve fast enough to maintain the local environment that will sustain this dissolution. The critical solution chemistry for 300 series stainless steels at ambient temperature is about 70% of saturation in metal chloride. This approach derives essentially from the work of J. R. Galvele,[29,30] as described in detail in an earlier edition of *Interface*.[31] We believe that almost all the alloying and environment effects in localized corrosion of stainless steel can be explained using this basic idea.

A model along these lines for propagation of single pits has been presented in detail elsewhere.[32-35] The local chemistry is modeled using the method proposed by Sharland,[36] and then anodic and cathodic reactions in the concentrated pit solutions are modeled on a semi-empirical basis, with parameters for a particular set of conditions determined by comparing the predictions of the model against experimental results from various artificial pit experiments. For metal inside a propagating pit, we assume that anodic dissolution obeys Tafel's Law such that at an applied potential of E_{app}, the anodic current density, i_a, at any point on the pit surface is given by

$$E_{app} = E_{corr} + b_a \log\left(\frac{i_a}{i_{corr}}\right) + \phi_s + \phi_{sf} \qquad (3)$$

where i_a is the anodic current density, b_a is the anodic Tafel slope, E_{corr} and i_{corr} are the open-circuit corrosion potential and corrosion current density (within the local pit environment), ϕ_s is the ohmic potential drop in solution, and ϕ_{sf} is the potential drop across any precipitated salt film on the corroding surface. This equation gives the anodic current density at any surface point within the pit, provided that the solution at that point remains concentrated enough to prevent passivation, and the repassivation process is modeled using the method described in Ref. 35.

In the early work, we assumed that each pit is initially a hollow truncated sphere with an open "mouth" at a perfectly flat metal surface. Later, we introduced surface roughness, as described in Ref. 37. The key results of such simulations are as follows. For a given initiation site, the lifetime of the pit depends on potential. At low potentials, pits cannot be initiated in this particular cavity and the lifetime is effectively zero. Above the first critical potential, E_m, pits can be initiated, but they have only a finite lifetime before spontaneously repassivating. This behavior, known as metastable pitting, is shown by the anodic current transient at the lower applied potential in Fig. 4. Above a second critical potential, E_s, the pits do not repassivate within the time scale of our simulations (also shown in Fig. 4) and are assumed able to propagate indefinitely; *i.e.*, they are considered to be stable pits. The values of E_m and E_s also depend on the initiation site geometry, as discussed in detail elsewhere.[35,37]

Local environment and pitting

Outside the pit
- Current density
  nA cm^{-2}
- Chloride concentration
  mmol dm^{-3}
- pH
  neutral

Inside (pit size is μm-cm)
- Current density
  A cm^{-2} (10^9 greater)
- Chloride concentration
  mol dm^{-3} (10^3 greater)
- pH
  < 0 (>10^7 greater)

Inside the pit, the solution is virtually saturated in stainless steel. There is a critical degree of dilution (ca 80%). If the solution becomes more dilute, the steel passivates. Restriction of diffusion out of the pit maintains the active state. Loss of restriction → pit 'dies'.

Fig. 2. *Comparison of conditions inside and outside a pit, illustrating the extreme gradients that are established.*

Combining Nucleation and Propagation Models

A pragmatic model with predictive capability can be constructed by combining the deterministic model for the propagation of single pits in stainless steel with a stochastic model of pit nucleation. The deterministic model replaces the empirical 'pit death' probability, μ, and 'critical age', τ_c, in Eq. 1. There is assumed to be a fixed initial density of possible nucleation sites and if a pit nucleates at a site (frequency λ), then that site is removed from the simulation. The model can be used to simulate potentiostatic or potentiodynamic experiments using samples on which there are many possible pitting sites, and the results of model simulations show very good quantitative agreement with experimental results for the effects on the pitting potential of molybdenum alloying, surface roughness and potential scan rate,[37] temperature,[34] and solution chloride concentration.[38]

Multiple Pit Interactions

For a stainless steel to be immune from pitting corrosion in a chloride-containing service environment, the maximum open-circuit potential of the passive steel must be lower than its 'pitting potential' in that environment. This understanding has been gained in large part through laboratory measurements of the 'pitting potential', and most of these experiments have been performed using potential-control of small samples. Research in this area has generally focused on the critical factors determining the growth stability of individual pits,[39-42] although more recently there has been increasing interest on the interactions between pits.[43-45] However, real corrosion does not occur under potentiostatic conditions; rather, there is a limited supply of cathodic current that must be shared between all simultaneously propagating pits. This situation is somewhat more closely resembled by experiments under galvanostatic control.[46,47]

A multiple-pit version of the single-pit algorithm has been implemented using the standard parallel processing library, MPI. Propagation of each pit is assigned to a separate process and these processes communicate the information required to update the effective bulk concentration and applied potential at each time step. The pit initiation process at any given initiation site is deemed to create a saturated local chemistry within that pit cavity, and all the applied anodic current must be used by propagating pits. Thus, if only one pit is initiated at the start of a simulation, the first few iterations of the simulation will determine an E_a value that supports propagation of that pit at the selected applied current. If the applied current is too low, no solutions will be found and the simulation will end.
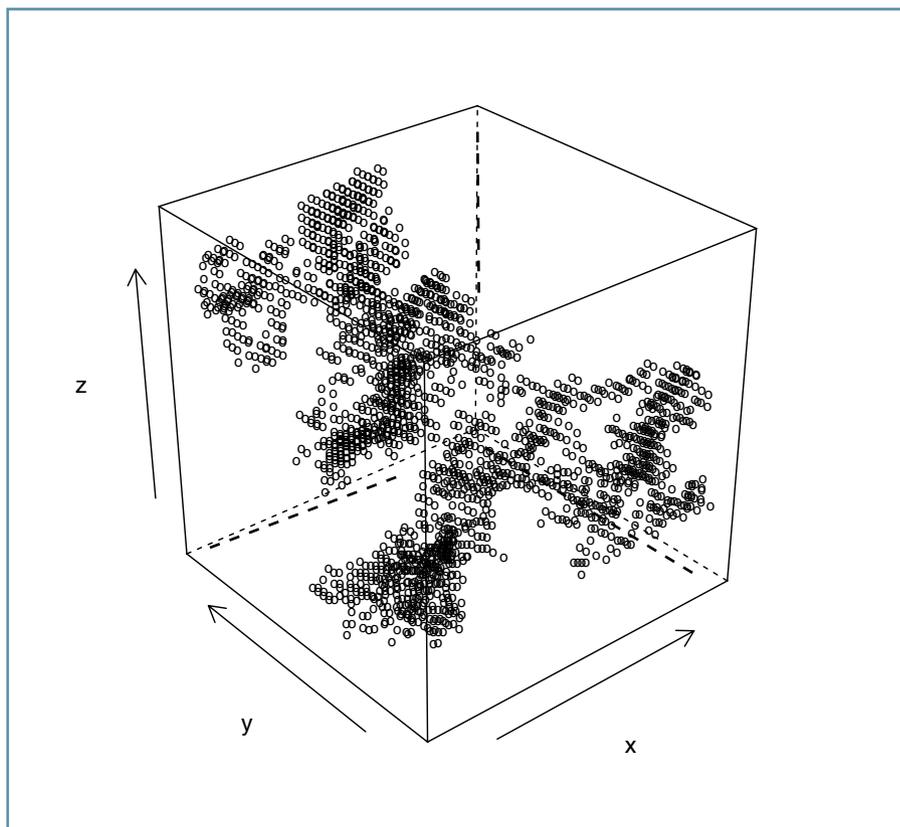
Fig. 3. *Large Fe-cluster in a Fe-Cr 16% alloy. The cube shows the boundary of a bcc lattice of 3,953,501 atoms. Only the Fe atoms within the large cluster are shown in black.*
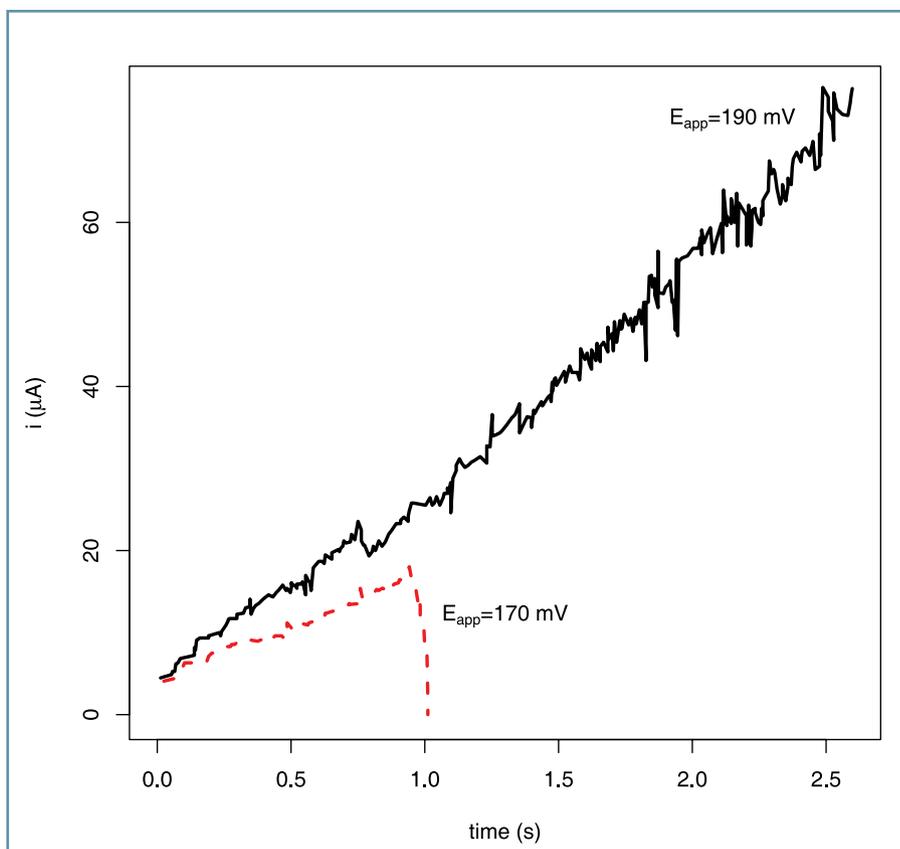
Fig. 4. *Model current transients from a single simulated pit in 316 stainless steel, propagated at 170 mV or 190 mV in 1 M NaCl.*[35]

In this model, there are two ways in which a propagating pit will influence a nearby pit; via a local increase in the chloride concentration, and via changes in the local effective applied potential. Simulations for regular arrays of identical pit initiation sites (Fig. 5) show a negative impact of pit interactions in galvanostatic conditions, with pits having the greatest number of neighboring pits being the first to repassivate. This is due to the depression of the effective applied potential around each propagating pit. Introducing variations in the spatial distribution, geometry and initiation time for each pit results in increasingly complex behavior due to the unique conditions experienced by each pit during the period of the simulation.[48]

Long-Term Predictions

In the atmospheric corrosion of stainless steel, airborne salts are deposited on exposed metal surfaces with a certain deposition density (DD, g/cm^2). Then, depending on the specific composition of the deposited salts and atmospheric relative humidity (RH), the salts absorb moisture from the air to create a thin liquid layer with the equilibrium concentration of dissolved salt. For deposited $MgCl_2$ salts, Tsutsumi *et al.*,[49] found that pitting corrosion of 304 stainless steel under these conditions initiated when the RH was ~ 65%, corresponding to a dissolved chloride concentration of ~ 6M.

To simulate long-term atmospheric exposure of stainless steel, we have coupled the pit propagation model adapted to high chloride conditions[38] with a cathode model similar to that developed by Chen *et al.*[50,51] Our main difficulty has been in extending the time scales of computer simulations from tens of seconds to the much longer times necessary to assess whether a pit has indeed reached a maximum size. We have been able to overcome some of these problems using a method of 'quasi-steady state' simulation in which the pit grows at the current required to maintain a chloride dependent critical concentration of metal ions on the bare metal surface. The results of simulations employing this model indicate that a pit growing under a thin liquid film adapts to the cathodic current limitation by adopting a shallow dish-shaped morphology, in which the current becomes confined to a decreasing lateral area of the pit as the bottom of the pit repassivates, while the lateral surfaces are able to grow. Using relatively aggressive conditions of continuous high DD and high RH to simulate a worst case scenario, the model predicts a maximum depth of pits of the order of 100–300 microns attained over periods of several months, as shown in Fig. 6.[52] Both the time scales and depths predicted by the model are consistent with available field data, although such data are insufficiently time resolved to be able to attempt a rigorous validation of the model. In particular, quantitative data on long-term pit growth for stainless steel under atmospheric conditions show a relatively limited variability in maximum pit depths under similar exposure conditions.
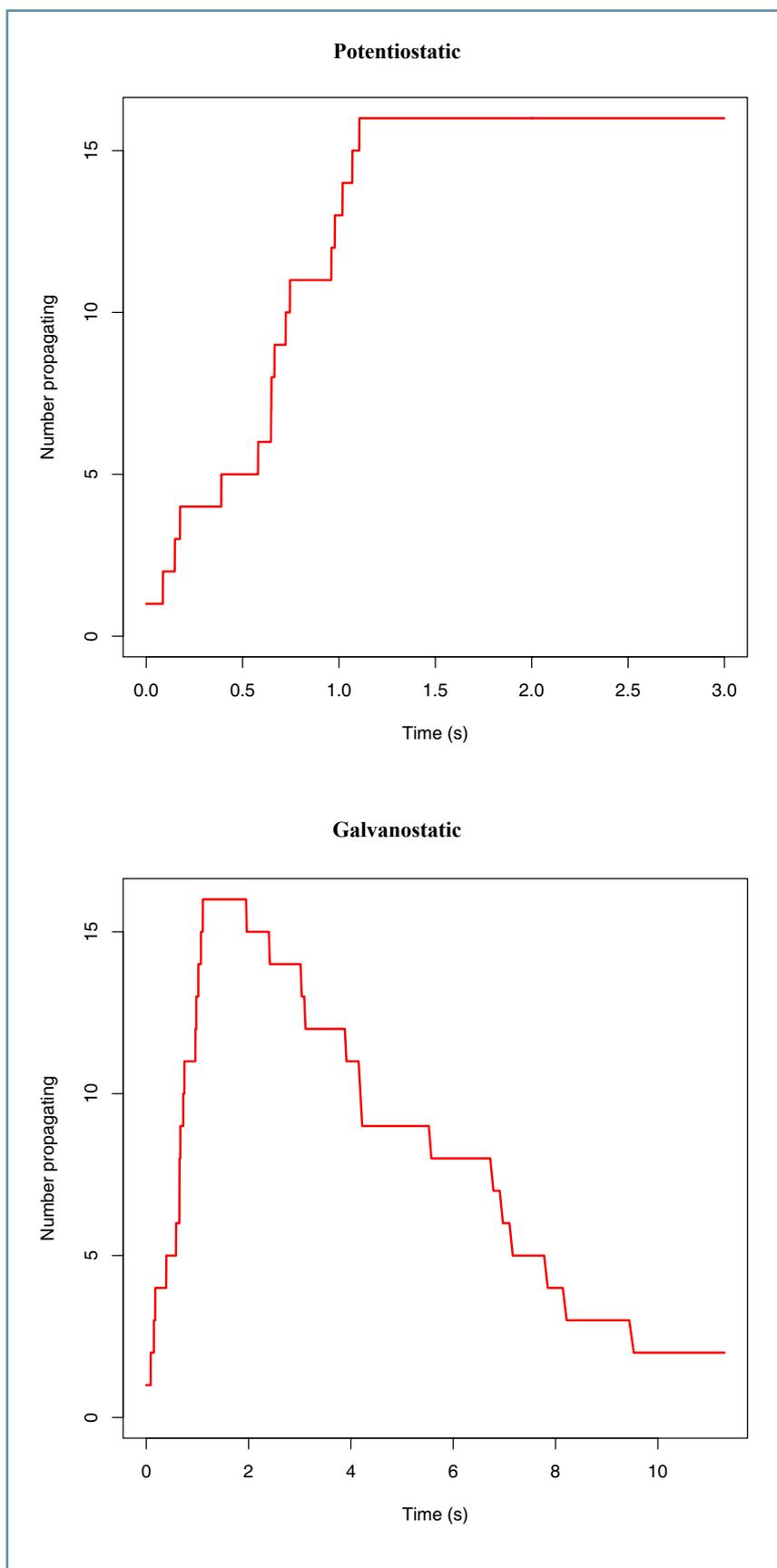
Fɪɢ. 5. *Multiple pit simulations in 1M NaCl.[48] 16 pits with random initial radii between 10 and 40 microns were initiated at random starting times (between 0 and 1s) with one pit started at time zero. Galvanostatic and potentiostatic runs for comparable initial conditions: E_{app} = 0.1 V, I_{app} = 30 µA.*

The Future

A full description of the pitting corrosion of stainless steels will require a multiscale modeling approach that combines fully three-dimensional simulations of the propagation of multiple pits with electrochemically accurate pit nucleation models. The influence of external pits on the propagation of a single pit is currently only treated in two-dimensions, with simulations of individual pits restricted to cylindrical symmetry, and the physical overlap of pits is ignored. Moving to three-dimensions may well alter the type of behavior seen in two-dimensional multi-pit simulations, but such simulations will be highly computational intensive. Hence, the first steps toward simulations of three-dimensional pit propagation will likely need to treat multi-pit interactions using a mean-field or homogenization approach.[53]

Pit nucleation models need to be based on a quantitative understanding of both the kinetics of oxide formation and dissolution[54] and the thermodynamic stability of the nanocrystalline passive film.[55,56] First principles calculations have been used to investigate the thermodynamic stability of the iron-chromium oxides that passivate Fe-Cr alloys in acidic environments.[53] *In situ* X-ray diffraction suggested that these oxide films have a nanocrystalline spinel structure with a stoichiometry of the form $Fe_{3-2x}Cr_{2x}O_4$.[56,57] These films are observed to be enriched in Cr, compared to the bulk Fe-Cr alloys that they passivate, and density functional theory calculations suggest that the observed Cr enrichment in the films[55] are in fact a necessary requirement for passivity. This is consistent with the Sieradzki-Newman model of the passivation of Fe-Cr alloys described above,[22,23] where selective dissolution of Fe would result in a Cr-rich surface layer that oxidizes to form a thermodynamically stable Cr-enriched oxide. This also has implications for our understanding of the breakdown of passivity, as the local depletion of Cr in the oxide would lower the thermodynamic stability of the film in the acidic microenvironments that become established at incipient localized corrosion sites.[58]

While such thermodynamic considerations are suggestive, the kinetic stability of these films is much more difficult to model on an atomistic scale. As a result many models of film kinetics treat the passivating oxide layer as homogeneous,[59] despite its evident nanocrystalline structure and the fact that first principles calculations of ion transport through the passive layer[54] suggest that the nanocrystalline grain boundaries provide the dominant pathway for the passive current. This in turn suggests that the grain boundary structure, which itself will evolve over time, may play an important role in the evolution of local Cr content in the alloy. Indeed, first principles methods have also been used to study the role of extended surface defects, such as step edges, on film stability[60,61] and it should eventually be possible to extend these to grain boundaries.

Bridging the gap between our understanding of the nanoscale structure of passive films and the phenomenological models of pit initiation will also require a multiscale modeling approach.[62] Increases in computational power, new techniques for accelerating atomistic simulation methods, and effective approaches to coupling these atomistic techniques to continuum methods will be needed to resolve the nanoscale heterogeneity of passive films, and capture processes with timescales as widely separated as metal ion dissolution and structural relaxation. Kinetic Monte Carlo (KMC) methods,[63] with transition rates parameterized by the results of first principles calculations, can access much larger time and spatial scales than molecular dynamics methods, while allowing for a degree of chemical accuracy (especially compared to the heuristic approach of the percolation simulations described above). In principle, KMC methods can be coupled to continuum simulations,[64] which would enable a dynamic treatment of the external electrochemical environment, and could handle complex interfacial reactions.[65] ◼

Fig. 6. *Model results for the depth of a single propagating pit in 304 SS growing under atmospheric conditions with varying chloride deposition density (DD) and relative humidity (RH). The fluctuations in calculated depth arise from the errors in the finite element approximation used to implement the model.[52]*

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