



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Corrosion Science 47 (2005) 171–182

**CORROSION
SCIENCE**

www.elsevier.com/locate/corsci

Computer simulation of the corrosion pit growth

B. Malki *, B. Baroux

*Institut National Polytechnique de Grenoble, LTPCM/CNRS/GEDAI, 1130, Rue de la piscine,
St. Martin d'Hères, 38402, France*

Received 5 November 2003; accepted 9 May 2004

Available online 20 July 2004

Abstract

Numerical simulations of the corrosion pit growth are performed using both Monte Carlo (MC) and Cellular Automata (CA) techniques. The theoretical framework of these two methods is presented. In the MC technique, a dissolution algorithm is proposed for elementary dissolution events. Varying the repassivation probability at the atomic scale on the pit walls is shown to control the pit growth kinetics (t^n law, with n varying from 1/2 to 2). In the CA technique, the Metal/Film/Electrolyte system is considered as an automaton with some specific transition rules. The dissolution probability is shown to strongly influence both pit morphologies and the t^n law. Last, predominant effect of the IR drop inside the pit is evidenced. These preliminary investigations motivate future works to simulate in more details the pit growth process and the repassivation of metastable pits.

© 2004 Published by Elsevier Ltd.

1. Introduction

Although pitting corrosion has formed the subject of a lot of works in the last decades, modelling of pit growth is still an open question, even when the recent experimental works aiming the microscopic scales promise substantial advancements [1–7]. Pitting involves several convoluted phenomena (mass transport, IR drops, repassivation. . .) operating at different length scales, making modelling the whole pitting process a very complex problem. This complexity is also characterized by a non-linear behaviour [8–13], which has been treated using self-organization and

* Corresponding author. Tel.: +33-4-76-82-67-29; fax: +33-4-76-82-67-67.

E-mail address: brahim.malki@ltpcm.inpg.fr (B. Malki).

chaos theories [14,15] reflecting a strong dependence on the experimental conditions [16]. Extensive works aiming to understand the basic mechanisms by which the observed complexity is produced are currently in progress [17,18]. However, a troublesome point is that the assumptions to be made for modelling at the microscopic scale the reactions, which control this complexity, are still conjectural and that hardly to be verify by laboratory experiments. Then, the idea of the existence of universal patterns of pitting corrosion, which does not necessarily depend on mechanistic details at microscopic scale, could open the possibility of modelling from a different standpoint the pitting dynamics by using simulation approaches at a mesoscopic scale. Actually, using numerical simulations is proved to be convenient and indispensable tools in many fields in materials science [19] and more recently also in corrosion science [20–22].

In this regard, it is intended in this paper to use two numerical simulations approaches (Monte Carlo and Cellular Automata) to deal with pit repassivation: The basic idea is that we shall be able to substitute some of the physical laws of these phenomena especially the dissolution and the repassivation reaction by probabilistic laws (built to take into account the repassivation). The critical point in using these techniques is to well identify not the determining mechanism and the appropriate length. As far as metastable pit is concern, the typical length scale of the dissolution, then the repassivation reaction can range from nanometer (for the earlier stage of the propagation) to micrometer (for events at an inclusion scale), the latter being large enough to use simulation tools based on the mean field approximations. The very few works devoted to this subject, and based on the assumption of a pit growth kinetic controlled by the diffusion of a corrosive agent [21], succeed to discern clearly the steps of metastable and stable pitting. The transition between the two was found to be closely associated to a particular pit geometry. Obviously, the investigations can be extended to a list of other physical variables, such as the applied potential or the parameters of the repassivation reaction. The final purpose of this paper is to investigate a class of mathematical models for the pit propagation stage and to abstract from the obtained results some features of pit growth laws and possibly some expected consequences on metastable-stable pit transition. The consequences of some hypotheses regarding the repassivation conditions on the growth kinetics will be explored throwing light on the possible role of the IR drops on the pit growth stabilization, a key problem in the metastable pitting.

2. The Monte Carlo method

2.1. Simulation procedure

It appears from the works by Reigada [22] that the elementary dissolution events can be modelled in a 2-D space, assuming that the elementary dissolution event is an instantaneous formation of a so called “crystallographic” tunnel, as illustrated in Fig. 1. This method has been previously proposed by Kaesche [23] for the aluminium based alloys where the author stipulates that when a pit initiates an oxidation occurs

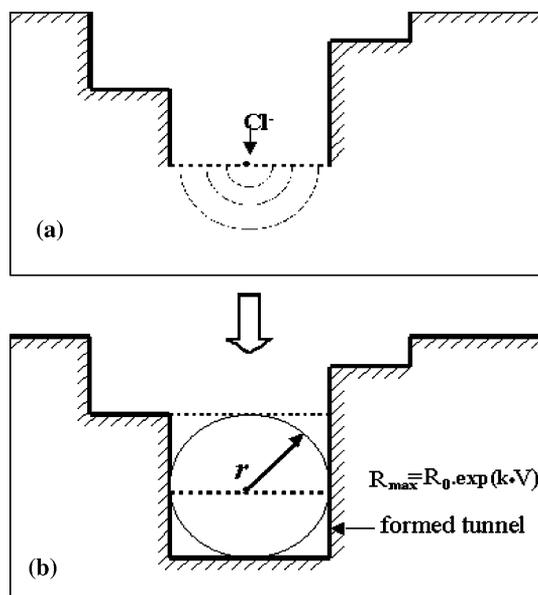


Fig. 1. A schematic picture of the “tunnelling” model: (a) the chloride concentration trigger a sudden oxidation process; (b) a “digging” radius R is randomly selected between 0 and maximum value R_{\max} which is estimated making the assumption of an exponential dependence of R on the “applied” potential (V) at the interface, R_0 and k are two parameters of the system.

followed by a fast propagation while forming a “crystallographic” tunnel. It is assumed the technique can be generalized even when the base mechanism is not of the Al type. So did, a 2D pattern (1024×2048 pixels) is used in which a starting site is put on a perfect horizontal line as shown in Fig. 2. Then a Monte Carlo test is done according to a dissolution probability P , ranging between 0 and 1 and we kept this possibility when writing the simulation programmes, in order to allow further adjustments (particularly the physical time vs. the arbitrary time of the simulation, which is simply represented by the number of iteration steps). However, in the work presented below, we chose $P = 1$, i.e. that all MC tests are positive. Once the test is positive (every time in our case), a randomly value of a “digging” radius R in the metal is selected between 0 and a maximum value $R_{\max} = R_0 \exp(k \cdot V)$, where V counts for the applied electrochemical potential, R_0 reflects the nature of the electrolyte and counts for corrosion activity of the electrolyte and k is a constant. Choosing $V = \text{cst.}$ means that we are dealing with pit propagation in applied potential mode. The case of an open circuit potential mode needs to take into account the cathodic reaction that will be presented in a forthcoming paper.

Afterwards, a square geometry is interpolated starting from a disc of radius R and then a tunnel is built counting for an elementary amount of the dissolved metal. Hence, for each starting step, new surfaces are created behaving like fresh active areas and so on the tests are reiterated several times on each new elementary surface until setting up a macroscopic pit (see Fig. 2). In practical terms, the simulation is

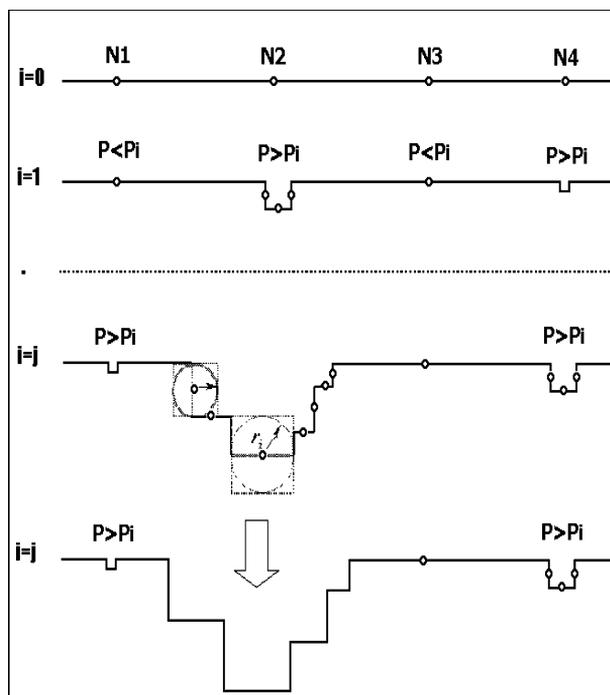


Fig. 2. Implementation procedure of the MC simulation technique: a 2D pattern (1024×2048 pixels) is used in which a starting sites are put on a perfect horizontal line. For all the initial sites, a Monte Carlo test for the dissolution is done. For each site, new surfaces are created and so one the process is reiterated several times. Each iteration represents the unit time scale of the simulation.

performed in two different ways. First, starting from the dissolution setting up procedure presented above, we carried out an extensive parametric study, in order to check the validity of the model assumptions and to understand the role of various physicochemical parameters taken into accounts. Secondly, the repassivation reaction is introduced by fixing at every iteration step the ratio of active/passive surfaces. In practice, one prefers to introduce the probability P_r for the dissolution of a freshly created surface to be prevented. Choosing P_r from 0 to 1 allows controlling the repassivation process.

2.2. Results

For the preliminary tests, done in order to scale the system under consideration, convenient set parameters are found in the range of: ($R_0 = 1$, $V = 2$, $k = 1$). A parametric study of the simulation is then performed, starting from these initial arbitrary conditions. First of all, starting by varying the “applied” potential V , one verifies that the higher the value of V , the higher the dissolution current (Fig. 3). In this figure are represented the current transients corresponding to the removed pixels

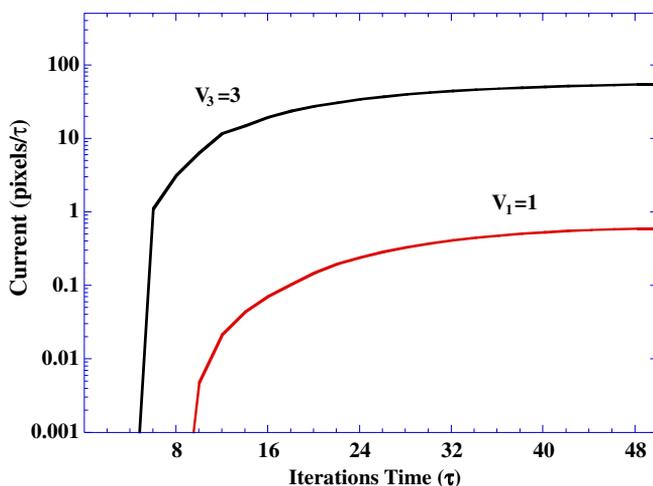


Fig. 3. Corrosion current evolution vs. “arbitrary time” from MC technique. The simulations parameters were $R_0 = 1$, $V =$ variable from 1 to 3 and $k = 1$. The higher the value of the “potential” V , the higher the dissolution current.

for the different value of the “applied” potential V . This effect was expected, since increasing the value of V also increases the mean size of the “digging” radius R and hence the dissolution currents. The corresponding corrosion patterns are shown in Fig. 4, where one can note the isotropic morphology of growing pits whatever the applied potential.

Now varying the repassivation probability P_r from 0 to 1, one finds that the current decreases when P_r increases, which was expected. But, when we have a look to time dependence of this current, the probability of repassivation is shown to induce noticeable changes in the corrosion current vs. time laws ($I \sim t^n$), from $n = 1/2$ to 2, simply by varying P_r in a rather narrow range (Fig. 5). This result is surprising at a first glance, because there is no experimental evidence that demonstrates any role of the repassivation reaction in the pit growth process. We believe that it denotes a particular pit growth mode not reported previously, in which the surface coverage of the inner pit walls is the governing parameter. A precise description of the involved

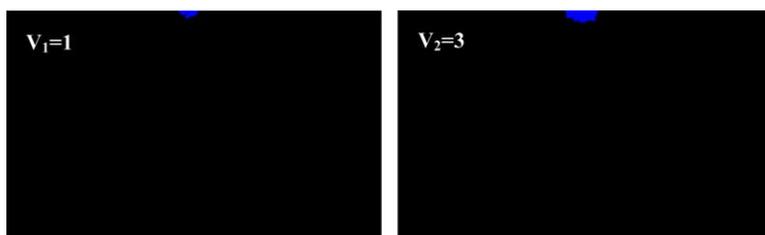


Fig. 4. Corrosion patterns obtained in MC technique after 100 iterations for $R_0 = 1$, $V =$ variable, and $k = 1$.

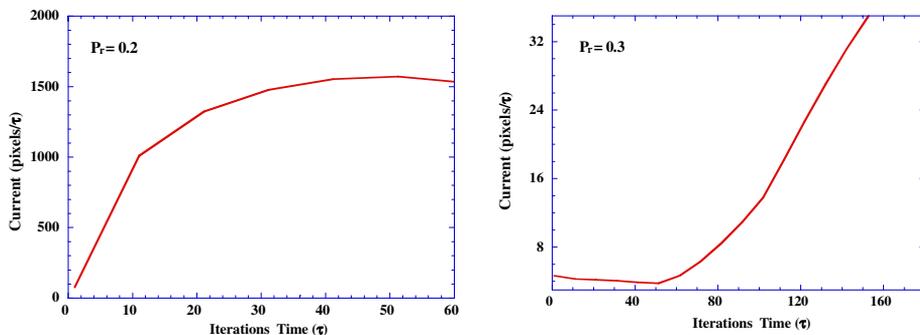


Fig. 5. Current vs. time evolution obtained in MC technique for different P_r values, indicating a strong dependence of the growth law on the local repassivation probability P_r . The simulations parameters were $P_r = \text{variable}$, $R_0 = 1$, $V = 2$, and $k = 1$.

mechanism is not yet possible without considering a repassivation model instead of the schematic one which is used in this work, but this point deserves more attention in future work on the metastable to stable pit transition.

3. Cellular Automata

3.1. The Cellular Automata technique

Models based on CA provide an approach involving discrete coordinates and variables as well as discrete time steps. By virtue of the simplicity of their construction they are susceptible to describe even complex dynamic systems [20]. The basic assumptions of the model are that:

- (a) Pit is supposed to have already initiated;
- (b) The passive film around the pit acts like a perfect barrier regarding to the dissolution;
- (c) The corrosion kinetics are first based on diffusion mechanisms. In a second step, the transport mechanism is extended to a pseudo electro-migration of the charged species in the supposed electrolyte.

Such modelling system can be built using a finite two-dimensional Cellular Automata rectangular lattice, where the system *Metal/Film/Electrolyte* is discretised into regular network of sites (also named “cells”) and where each cell is characterized by a couple $\{x, y\}$, taken from a finite set of states (see Fig. 6) namely the nature of the cells (*A* for a corrosive cell, *B* for a non-corrosive cell, *M* for the metallic substrate cell and *F* represents the passive film cell) and their directions. Then, for the elementary physicochemical processes, such as mass transport, metal dissolution, passivation and repassivation, we assume simple interactions rules between the cells

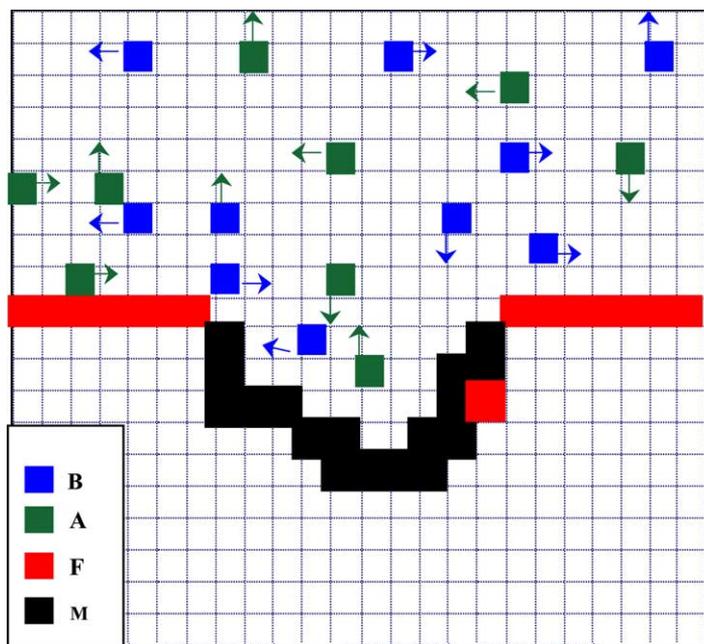


Fig. 6. A schematic representation of the constructed Cellular Automaton for a corrosion pit reactive system. The Automaton is built by discretising the “Metal/Film/Electrolyte” system into regular network of sites (also named “cells”). Each cell is characterized by a couple $\{x, y\}$, taken from a finite set of states: A is a corrosive cell; B a non-corrosive cell, F a passive film cell and M the metallic substrate cell. Each electrolyte cell has an initial row with indicates the diffusion direction.

of the CA as expected with this method. For the details of the simulation elaboration steps, a review is given in Appendix A, with a description of the relevant parameters and the fundamentals used interactions rules. At every step of the simulation procedure, we determine the resulting pit configuration and calculate the number of dissolved metal sites as a function of time, which represents the dissolution current. Note that the simulation time unit is here arbitrary, regarding the nature itself of the method used.

We particularly focus on the effect of the following parameters:

- The electrolyte concentration, by modifying the ratio $c = A/B$ of the concentrations in “corrosive” and “non-corrosive” cells, being randomly distributed in the electrolyte side of the automata;
- The rate of metal dissolution via the dissolution probability d (see Appendix A). The number of removed sites are then computed counting for the dissolved metal and hence for the dissolution current;
- The effect of IR drop: It is true that in real systems the potential distribution obeys to complex laws that matters to know precisely, however we chose for the simplicity of the calculations to introduce a linear gradient of the potential

which consists of relating the dissolution probability d to the pit depth z . In other words, the deeper the pit, the lower the dissolution probability, which amounts to include an IR drop along the metal/electrolyte interface. Thus, one by varying the magnitude of the gradient, i.e. the dissolution probability, one should analyse its influence on the pit growth regime. In this purpose, we use the following law: $d(z) = d_0(1 - \alpha z/z_0)$, where d_0 is the dissolution probability in the absence of potential gradient, z the pith depth, z_0 a scale constant and α counts for the effect of the IR drop.

3.2. Results

In the absence of dissolution gradient (no IR drop, $\alpha = 0$), the pit morphology is found to remain isotropic, whatever the concentration c and the dissolution probability d . As expected, the dissolution current is found to increase with c . The new result is that its time dependence ($I \sim t^n$) depend on the dissolution probability d : for a constant concentration in “corrosive” cells ($c = 0.2$), the law was found linear ($n = 1$) for low dissolution probabilities ($d = 0.2$) but parabolic ($n = 2$) for higher ones ($d = 0.8$). It is worthy to note that in the first case the pit growth is expected to be diffusion-controlled whereas the second one (high dissolution rate) more likely simulates an interface control.

The introduction of an IR drop ($\alpha \neq 0$) leads to perforating pit morphologies, as shown in Fig. 7, and modifies the current time evolution law, as shown in Fig. 8. Starting from a parabolic evolution law (t^2) for high enough dissolution probability and no IR drop ($\alpha = 0$), the introduction of a potential gradient ($\alpha = 1/10$) seems to lead to a linear ($\sim t$) current law. This joins the classical point of view of several authors in the literature, which postulate an indubitable IR-control of the current growth laws [24–28].

Let us finally note that no $t^{1/2}$ law was found in this study, probably due to a lack of numerical experiments in the appropriate range of parameters, and that linear laws are observed both for low dissolution probabilities and large IR drops, whereas

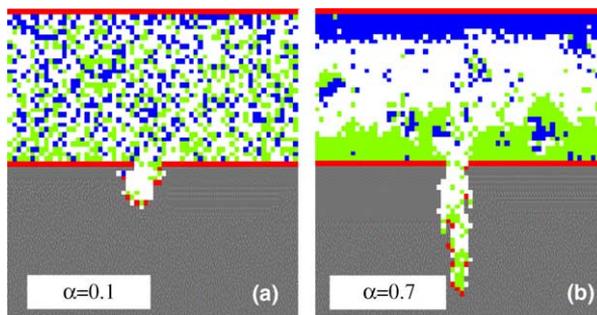


Fig. 7. Corrosion patterns obtained from CA technique, after introducing an IR drop from (a) $\alpha = 0.1$ to (b) $\alpha = 0.7$, ($d_0 = 0.5$ and $z_0 = 100$). Increasing the IR drop leads to perforating pit morphologies.

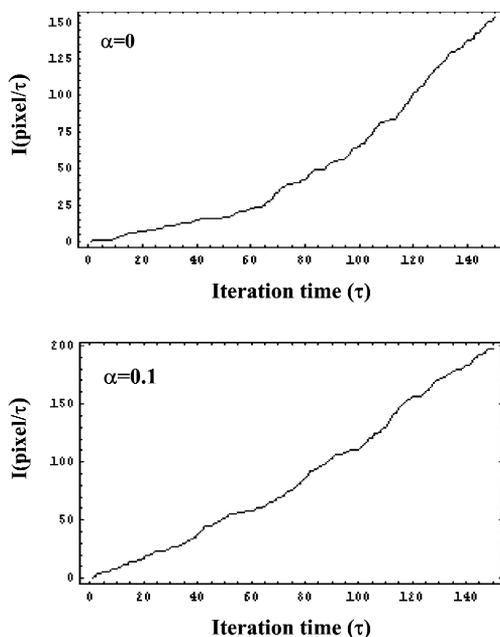


Fig. 8. Corrosion current laws obtained from CA technique, after introducing an IR drop, varied from $\alpha = 0$ (parabolic) to $\alpha = 1/10$ (linear) Other parameters are $d_0 = 0.5$ and $z_0 = 100$.

t^2 laws are found for large dissolution probabilities or low IR drops. It motivates further works to clarify this point.

4. Concluding remarks

It was proposed in this work to use Monte Carlo (MC) and Cellular Automata (CA) as simulation tools to study the corrosion pit growth kinetics. In a first step, these techniques were successfully implemented and a number of the experimental macroscopic effects namely the effect of the potential and the electrolyte concentration were rightly simulated by MC method. Moreover, anodic dissolution as well as mass transport effects are properly simulated using CA method. Noteworthy changes have been revealed in the current growth laws and pit morphologies. However, the most relevant points were (1) the role of the repassivation reaction and (2) the effect of the IR drop inside the pit. These findings ensue two major observations: the first one is that the repassivation probability plays a major role in the growth step. It motivates future work for simulating more precisely the active-passive transition on the pit walls, aiming finally to simulate the repassivation of a whole metastable pit. The second one is that the role of the IR drops so much related in the literature of the pit growth processes has been found again via these approaches. It

also motivates future works for relating the simulated laws to the experimental ones, aiming particularly to distinguish the relative effect of the dissolution reaction and of the mass transport in the growth processes.

Acknowledgement

This work has been supported by CNRS, France (ACI 2000 project “Surfaces, Interfaces et Conception de nouveaux matériaux”, #S13).

Appendix A

A.1. The basic model of the Cellular Automata and simulation procedure

During the time evolution of this automaton, each cell can change its states according to rules known as transition rules which depend only on the its initial states and on a those of the neighbouring cells. As to define the transition rules, we select them in order to reflect a realistic pit growth dynamic. In other words, we assume first a diffusion control of the electrolyte species, a uniform dissolution process at the “metal/electrolyte” interface and disregard any chemical changes in the pit solution. The $\{x, y\}$ set of states for the above pit reactive system is defined as following: x represents the type of a cell where

- (a) M is the metallic substrate cell;
- (b) F is the passive film cell;
- (c) A is a corrosive cell which can dissolve the non-protected metallic cells;
- (d) B is a non-corrosive cell having no interaction with the metallic cells, which allows to modify the electrolyte concentration by fixing the ratio of the cells number A/B .

y is a state number that varies between 0 and 4 which reflects the cell direction:

- (a) 0 the cell of the network is not occupied, a free cell;
- (b) 1 the cell is oriented towards north;
- (c) 2 the cell is oriented towards east;
- (d) 3 the cell is oriented towards south;
- (e) 4 the cell is oriented towards the west.

The automata is being defined, the system evolves over a succession of time steps using a set of rules that take into account the values of the sites and its neighbouring sites. The values of all sites in the lattice are updated synchronously in each step.

A.1.1. Choice of the initial and boundaries conditions

In updating the values of a site in the CA lattice, it is necessary to consider the site value and the values of the sites in its vicinity. Then, a CA neighbourhood is

employed which consists of a set 12 nearest neighbours, a combination of the Von Neumann (four neighbours) and Moore (eight neighbours) models [29,30]. This seems to be useful to model diffusive processes. Generally, the boundary conditions that are used in the CA depend on the specific physics of the system being modelled: periodic, absorbing and reflecting boundaries [30,20]. Traditionally, the neighbourhood of border sites are taken periodic in the case of an infinite system, where border sites have sites on the opposite border. In our computations, we choose to use the periodic boundary the most commonly used in diffusive process. On other hand, in the part of CA lattice devoted to the electrolyte we choose a random distribution of a fixed ratio $c = A/B$ in order to simulate the electrolyte concentration.

A.1.2. Transitions rules

Rules that update the value of a lattice site, based on the values of the sites in the neighbourhood of the site have the following form:

1. When a metal site M is faced by a corrosive site A it becomes a vacancy (dissolution) depending on a fixed dissolution probability d ;
2. Passive film site F is supposed to remain immobile;
3. Any metal site having in the neighbourhood passive film sites F or metal sites remains a site of metal;
4. Any metal site having in its neighbourhood a corrosive site A non-oriented toward or non-corrosive site B remains a metal site.

For the diffusion process and at each time step all of the sites in the electrolyte simultaneously attempt to jump to adjacent sites. When a site attempts to move to the nearest neighbour site it faces, three possible situations will determine the outcome:

1. The adjacent site is occupied by another site, in which case the sites remain in place and randomly chooses a direction to face;
2. The adjacent site is empty and is faced by one or more other particles in which case the particles remains in place and randomly chooses a direction to face;
3. The adjacent site is empty and no other particles face it, in which case the particle abandons its current site and move into the site and randomly choose a direction to face.

To sum up, during a transition, all the cells are moved towards the direction of their initial state, when two or several cells meet, they change their states according to whether a corrosive cell meets or not a metallic cell or a passive film cell. In which case, metallic cells are substituted by free or passive film cells depending on whether we want to simulate the dissolution and/or the repassivation. Therefore, probability laws are built in order to control dissolution and repassivation processes.

References

- [1] B.K. Nash, R.G. Kelly, *J. Electrochem. Soc.* 139 (1992) 147.
- [2] H. Bohni, T. Suter, A. Schreyer, *Electrochim. Acta* 40 (1995) 1361.
- [3] A.J. Aldykiewicz, H.S. Isaacs, *Corros. Sci.* 40 (1998) 1627.
- [4] J.O. Park, C.H. Paik, R.C. Alkire, *J. Electrochem. Soc.* 143 (1996) L174.
- [5] Y. Kobayashi, S. Virtanen, H. Bohni, *J. Electrochem. Soc.* 147 (2000) 155.
- [6] N. Casillas, S.J. Charlebois, W.H. Smyrl, *J. Electrochem. Soc.* 140 (1993) L142.
- [7] J.W. Still, D.O. Wipf, *J. Electrochem. Soc.* 144 (1997) 2657.
- [8] M.R. Barlett, *Trans. Electrochem. Soc.* 67 (1945) 145.
- [9] A. Rius, R. Lizarbe, *Electrochim. Acta* 7 (1962) 513.
- [10] P.P. Rusell, Newman, *J. Electrochem. Soc.* 130 (1983) 547.
- [11] P.P. Rusell, Newman, *J. Electrochem. Soc.* 133 (1986) 2093.
- [12] W. LI, X. Wang, K. Nobe, *J. Electrochem. Soc.* 137 (1990) 1184.
- [13] W. LI, K. Nobe, A.J. Pearlstein, *J. Electrochem. Soc.* 140 (1993) 721.
- [14] A. Legat, V. Dolecek, *J. Electrochem. Soc.* 142 (1995) 1851.
- [15] H. Mayet, B. Baroux, Critical factors in localized corrosion II, in: P.M. Natishan, R.G. Kelly, G.S. Frankel, R. Newman (Eds.), PV 95-15, The Electrochemical Society Proceedings Series, Pennington, NJ, 1995, p. 368.
- [16] J. Stringer, A.J. Markworth, *Corros. Sci.* 35 (1993) 751.
- [17] G. Berthomé, B. Baroux, “Crevice corrosion of stainless steels: electrochemical noise analysis at rest potential” in the 198th Meeting of the Electrochemical Society, Phoenix, October 22–27, 2000.
- [18] B. Malki, D. Gorse, B. Baroux, Instances of chaotic behaviors in several types of localized corrosion in the 200nd Meeting of the Electrochemical Society, Symposium on critical factors in localized corrosion, San Francisco, September 2–7, 2001, 2001.
- [19] Computer Simulation in Materials Science, Nano/Meso/Macroscopic Spaces and Time scales, in: H.O. Kirchner, L. P. Kubin, V. Pontikis (Eds.), Proceedings of the NATO Advanced Study Institute, Kluwer Academic Publishers, 1996.
- [20] S. Wolfram, *Cellular Automata and Complexity*, Addison-Wesley, 1994.
- [21] P. Meakin, *Phys. Rev. E* 48 (1993) 2906.
- [22] R. Reigada, F. Sagues, J.M. Costa, *J. Chem. Phys.* 101 (3) (1994).
- [23] M. Baumgärtner, H. Kaesche, *Corros. Sci.* 29 (2/3) (1989) 363.
- [24] G.T. Burstein, P.C. Pistorius, S.P. Mattin, *Corros. Sci.* 35 (1993) 57.
- [25] S.H. Isaacs, *Corros. Sci.* 29 (1989) 313.
- [26] G.T. Burstein, P.C. Pistorius, *Phil. Trans. R. Soc. Lond. A* 341 (1992) 531.
- [27] T.R., R.C. Alkire, *J. Electrochem. Soc.* 126 (1979) 1662.
- [28] D.E. Williams, C. Westcott, M. Fleischmann, in: A. Turnbull (Ed.), *Corrosion Chemistry within Pits, Crevices and Cracks*, HMSO, London, 1987, p. 61.
- [29] E.F. Moore, Machine Models of self reproduction, in: Proceeding of a symposium on applied Mathematics, 14, 17, 1960, reprinted in *Essays on Cellular Automata*, A.W. Burks (Ed.), University of Illinois, Urbana, 1970.
- [30] J. Von Neumann, in: A.W. Burks (Ed.), *Theory of Self Reproducing Automata*, University of Illinois, Urbana, 1966.