A cellular automaton model for predicting intergranular corrosion

S.V. Lishchuk, R. Akida, K. Worden, J. Michalski

1. Introduction

A significant advantage of aluminium based alloys is their strength-to-weight ratio, which is valuable for construction, transport, architecture, and many other applications [1]. While aluminium alloys are highly resistant to uniform (generalised) corrosion, they are much more susceptible to different forms of localised corrosion, especially intergranular corrosion; this being a localised attack along the grain boundaries while the grains remain mostly unaffected. Aluminium alloys become sensitive to intergranular corrosion if there are phases along grain boundaries that are anodic to the aluminium matrix. Intergranular corrosion is especially important for aluminium alloys with a high content of copper because of the presence of intermetallic particles and depleted/enriched zones of copper along the grain boundaries.

To theoretically describe intergranular corrosion is a complicated problem. The macroscopic modelling of electrochemical reactions in the mean-field approximation is suboptimal; this is manifested, for example, in the roughness of the corroded surface, or in random initiation of pitting corrosion. This means that some of the information important to engineers is not readily available from the mean-field method. Our proposed probabilistic method allows the accumulation of higher-order statistics (variance, skewness) via the possibility of multiple runs.

In order to numerically simulate local corrosion attack on aluminium alloys, it is necessary to consider the complex microstructure of the alloy, which includes a high number of structural inhomogeneities. Therefore it is necessary to simulate a complex system of inhomogeneous processes and reactions that occur at different scales, especially those electrochemical reactions that trigger the onset of localised corrosion and control the corrosion propagation rate.

A promising approach is to model the progression of intergranular corrosion using cellular automata models. Cellular automata (CA), originally proposed by von Neumann [2], are discrete dynamical systems, yet can exhibit many properties of continuous dynamical systems, while being simpler to implement. This property makes them a powerful tool for modelling physical, chemical, and biological systems. In particular, CAs have recently been exploited to model the progression of uniform corrosion [3–22] and corrosion of a metal with crystalline defects [23].

Córdoba-Torres and colleagues developed a very detailed CA model of a corrosion process that mimics several cathodic and anodic events and allows the effect of different reaction kinetic parameters to be investigated [7]. Their results include forecasting the roughness of the corroding interface from the kinetic parameters [8], simulation of the reactions which are described by fractional-order kinetics rather than mean field approximation [9], and a study of the process of spatial segregation of surface reactants in the corrosion process [10].

On the other hand, Vautrin-Ul et al. [13] have demonstrated that several features of a corrosion process can be recovered by using a CA model which uses only one parameter. This rather simple model has allowed the complicated behaviour of the system to be simulated and quantitative prediction of the roughness of the system.

To study corrosion pit growth, Malki and Baroux [15] considered the metal–film–electrolyte system as a probabilistic cellular automaton with specific transition rules, which showed that the dissolution probability strongly influences both pit morphology.
and pit growth kinetics. Pidaparti et al. [16] used a CA model to study the effects of pH, the potential difference between the metal surface and the solution, and solution concentration upon corrosion pit growth.

The authors of Refs [11,12,17] modified the CA models by allowing random walks of a corrosion product. This has allowed modelling of the diffusion of species, leading to more accurate description of corrosion processes.

The object of the current paper is to apply the CA methodology to the case of intergranular corrosion. The main focus is the simulation of preferential corrosion propagation along grain boundaries after the onset of local dissolution. Preliminary results on the CA modelling of intergranular corrosion on the “brick-wall” model system were reported previously [24,25]. The present paper extends these results in two important aspects. Firstly, a realistic three-dimensional structure of a sample, obtained by electron backscattered diffraction (EBSD), is used in simulations. Secondly, the optimal values of the parameters of the model, corresponding to the experimental data, are determined in a systematic way using a differential evolution technique.

The paper is organised as follows. The CA model is described in Section 2, and the role of different parameters of the model upon the corrosion kinetics is investigated in Section 3. The differential evolution optimisation algorithm is summarised in Section 4. Section 5 describes the details of the experiment, which provides data to calibrate the CA model with the real structure of the sample, and to obtain the main results of this work which are presented in Section 6.

2. Model

This paper presents a probabilistic cellular automaton (CA) model that allows the simulation of intergranular corrosion. The probabilistic approach is chosen because it enables a convenient simulation of the complex interactions between the chemical reactions in the electrolyte domain and the propagation of the corrosion path in the metal domain. The main focus is the simulation of preferential corrosion propagation along grain boundaries after the onset of local dissolution.

The goal is to describe the propagation of intergranular corrosion, and therefore make a number of simplifying assumptions which allow us to predict the rate.

A substantial simplification can be achieved when the difference in time scales of different processes that take place during intergranular corrosion is taken into account. For example, dissolution of aluminium in chloride solution can undergo several stages, e.g. [26–30]

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \\
\text{Al}^{3+} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}^{2+} + \text{H}^+ \\
\text{Al(OH)}^{2+} + \text{Cl}^- & \rightarrow \text{Al(OH)Cl}^- \\
\text{Al(OH)}^{2+} + \text{Cl}^- + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_2\text{Cl}^- + \text{H}^+ \\
\text{Al(OH)}_2\text{Cl}^- + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + \text{H}^+ + \text{Cl}^-
\end{align*}
\]

(1) (2) (3) (4) (5)

each stage having different forward and backward reaction rate, and correspondingly different time scales. If the characteristic time of a reaction is large compared to the characteristic time of the modelling, such reactions can be ignored, being regarded as too slow. On the other hand, reactions which are fast compared to the simulation time, can be thought of as spontaneous, and such stages can be combined with the slower reactions.

The separation of time scales allows simplification of the modelling of other processes in the system. If, for example, there is diffusion of species in the system, having a typical time (determined by the corresponding diffusion constant) large or small compared to the characteristic time of the main process, the diffusion of species can be treated in a simplified model as immovable in the former case, or acquiring an equilibrium concentration in the latter case.

In view of the above, we describe the processes that we want to simulate as follows. The metal is a set of grains separated by grain boundaries; the surface of a metal is separated from the electrolyte solution with a protective layer. When any of the three species (grains, grain boundaries, protective layer) is in contact with solution, a reaction occurs which results in some corrosion product (thus a number of electrochemical reactions are replaced by the principal one); the corrosion product is able to diffuse into the solution.

We assume the rate of corrosion of the grains to be negligible compared to the corresponding rate for the grain boundaries, and the rate of corrosion of the grain boundaries to be dependent upon whether the boundary sites are adjacent to the grains, and if they are, to be different for each grain.

Depending on the assumed diffusion rate, the corrosion product either dissolves within the solution immediately, or diffuses within the solution.

We simulate the intergranular corrosion with the help of a 3D cellular automaton model. It consists of an i by j by k uniform rectangular partitioning with the planar boundaries; i, j, and k initially define the size of the system. Boundary conditions on the right and left of the array are taken to be periodic.

As we are dealing with a mesoscopic description, cells are not to be directly associated with the individual atoms, anions or cations, but to some limit-resolution scale below which we consider the system as unstructured, atomic size effects are thus not accounted for.

Each cell can assume N possible occupation states: E (empty), S (electrolyte), G (metal grain), B (grain boundary), P (corrosion product), and L (surface layer). The model has three parameters: \(P_{\text{grain}}, P_{\text{bound}}, P_{\text{layer}}\). Of those, \(P_{\text{grain}}\) defines the probability for the grain boundary B to corrode if it is in contact with a grain, G, \(P_{\text{bound}}\) is a probability for the grain boundary B, not in contact with grain G, to corrode, and \(P_{\text{layer}}\) is a probability for the corrosion of a surface layer L.

Initially, the lattice is subdivided into a metal domain and solution domain (see Fig. 1). The metal domain consists of a number of grains G separated by boundaries B. The metal domain is bounded by a thin surface layer L and a thin solution layer S. Remaining sites in the solution domain are marked as empty E.

There are different ways to define which cells are defined as the neighbours of the given cell. The most widespread are Moore and von Neumann neighbourhoods, as depicted in Fig. 2. We have chosen to define the neighbours as those which belong to the Moore neighbourhood of range 1 (Fig. 2a). At each discrete time step there are the following CA rules:

1. If \(B\) is in contact with at least one \(S\) and one \(G\), it changes to \(S\) with probability \(P_{\text{grain}}\) corresponding to the \(G\) site.
2. If \(B\) is in contact with at least one \(S\) but not in contact with \(G\), it changes to \(S\) with probability \(P_{\text{bound}}\).
3. If \(L\) is in contact with at least one \(S\), it changes to \(S\) with probability \(P_{\text{layer}}\).

Note, that in the model without diffusion, sites of type \(E, S, G\) remain intact, and sites of type \(P\) are absent.

In the case of diffusion, the CA rules are the following:

1. If \(B\) is in contact with at least one \(S\) and one \(G\), it changes to \(P\) with probability \(P_{\text{grain}}\) corresponding to the \(G\) site.
2. If \(B\) is in contact with at least one \(S\) but not in contact with \(G\), it changes to \(P\) with probability \(P_{\text{bound}}\).
3. If \( L \) is in contact with at least one \( S \) or \( P \), it changes to \( S \) with probability \( p_{\text{layer}} \).

The only difference in these rules compared to the case without diffusion is that \( S \) in rules (1) and (2) is changed to \( P \), i.e. metal changes to the corrosion product instead of transforming directly to the electrolyte solution.

After applying CA rules, diffusion is modelled by a random walk process. Potential walkers are the corrosion product sites (\( P \)), which are allowed to walk into neighbouring sites either occupied by electrolyte (\( S \)) or being empty (\( E \)).

The sites are chosen in random order. If the selected site is of type \( P \), a random neighbour is selected. Then the options are as follows:

1. If the selected neighbour is \( S \), then it becomes \( P \), and the current \( P \) site becomes \( S \).
2. If the selected neighbour is \( E \), it remains unaltered, and the current \( P \) site becomes \( S \).
3. If the selected neighbour is neither \( S \) nor \( E \), no changes are made.

The number of random walk attempts is equal to the number of cells, this ensures that the parameters do not change with the change in the system size. The value of the effective diffusion coefficient is controlled through the simulation time scale, which is the real time corresponding to one CA time step. This time scale is, in addition to the CA probabilities, another parameter of the model.

The result mimics the diffusion of \( P \) species in the electrolyte \( S \). The precise meaning of the concentration of \( P \) depends upon the parameters of the real system, for example, the concentration of any given diffusing species.

It is important to discuss the nature of the CA model in order to explain why it represents a powerful approach to the problem. One can generally divide process models into three classes: white-box, grey-box, and black-box. White-box models are constructed on the basis of a detailed understanding of the underlying physical laws and process; a good example in the context of the corrosion problem would be a mass-transport model formulated in terms of partial differential equations [31]. In contrast, a black-box model is constructed simply to reproduce the input–output behaviour of the system of interest and makes no recourse to physics or chemistry. A model class is chosen which is sufficiently powerful to represent a general function or functional and then a number of tunable parameters are learnt from observed data; a standard example here is the neural network model and these have been used in the past in the context of corrosion problems [32].

White-box models present problems in that the underlying physics may be imperfectly understood; black-box models present problems because they are generally dependent on large training data sets and the resulting parameters will generally have no physical meaning. The CA of this paper belongs to a middle ground in this terminology for models – it is a grey-box model. This means that a parametric model is proposed and the parameters are learned from data; however, as distinct from a black-box model, the para-
The symmetric model is motivated by basic physical ideas instead of simply being selected from a class of universal approximators. The advantage of the grey-box model in general is that it will usually be characterised by much smaller parameter sets and the parameters themselves will yield some physical insight into the problem. In the context of the corrosion problem here, where experimental data are very sparse, the grey-box approach is clearly indicated. The CAs used here have 4 or 5 parameters; a neural network approach would generally have a much larger set of tunable parameters and would demand the existence of large experimental data sets for training.

3. Role of model parameters

In this section, the CA model is applied to the simplified model of the grain structure of the alloy, which we denote the “brick-wall” model. In this model the grains are represented as rectangles (in two dimensions) or cuboids (in three dimensions), as depicted in Fig. 1a. The brick-wall model is able to represent correct average grain sizes of the sample, but not their dispersion or actual shape. Nevertheless, it allows the investigation of the behaviour of the proposed CA model with different parameters.

To investigate the role of the diffusion processes, modelled by random walks, on the time dependence of the average corrosion depth, we perform modelling of the two-dimensional brick-wall model with and without diffusion. The simulation is performed on a $640 \times 320$ lattice which has $8 \times 16 = 128$ rectangular grains, each having size $76 \times 16$ cells, and the width of the grain boundary is set to 4 cells. We use the following values of probabilities: $P_{\text{grain}} = 1.0$, $P_{\text{bound}} = 10^{-2}$, $P_{\text{layer}} = 10^{-4}$.

The average depth of corrosion as a function of time is plotted in Fig. 3. The time dependence is manifestly different without and with the effect of diffusion, tending to linear at long time durations in the former case, while changing to $\sim t^{1/2}$ dependence, which is characteristic to diffusion, in the latter case.

To investigate the effect of different parameters of the CA model upon the corrosion kinetics, we undertake the three-dimensional simulation on a $240 \times 280 \times 240$ lattice. Initially, there are $12 \times 2 \times 4 = 96$ cuboid grains, each having size $20 \times 140 \times 160$ cells. The width of the grain boundary is set to 4 cells, as in the previous case.

The effect of different parameters upon the corrosion kinetics is presented in Fig. 4. In this different probability values have been assigned and the resulting depth versus time profiles have been determined. It can be seen that when $P_{\text{bound}}$ is low the rate of IGC propagation is low (line 3 in Fig. 4), leading to least damage. When the value of $P_{\text{layer}}$ is set at a very low value, the onset of IGC is delayed (line 4 in Fig. 4). Further, when $P_{\text{grain}}$ is set to unity, the rate of IGC is highest.

4. Optimisation by differential evolution

The values of the model parameters described in Section 2 determine the time evolution of intergranular corrosion. Ideally, their values should be determined from first principles. Alternatively, they can be obtained by fitting the simulation results to the data obtained by other means, such as a mass transport model, or directly from experiment. In the latter case the mean square deviation of the simulation results from the experimental data provides a measure of fitness.

When viewed from an optimisation standpoint, the model possesses a complicated error surface in the parameter space which may have many local minima which in turn might attract the solution into one of them depending on the starting position. Non-linearity also makes it necessary to use iterative schemes, which collect local gradient information or a Hessian matrix. However, in cases of discontinuous types of non-linearity or/and unobservable states, estimation of the gradients or the Hessian matrix is not feasible.

In such cases a different approach should be sought that does not require any derivative calculations. These methods can be classified as heuristic or direct search since they rely on the objective function evaluations only. In the literature, there are many such methods available such as the Nelder and Mead downhill simplex
[33], genetic algorithms and simulated annealing [34]. The Nelder and Mead method performs well locally but is trapped in local minima easily. When simulated annealing is incorporated in the Nelder and Mead method on similar optimisation tasks as those in this paper, however, it does not improve significantly [35]. Genetic algorithms are designed to work on a discrete parameter space [36]. In this case, any attempt to discretise parameters can only increase the complexity of the problem.

Hence, for this study an optimisation algorithm was sought which is capable of utilising concepts borrowed from genetic algorithms and the Nelder and Mead method and exploits their strengths. This is found in the differential evolution algorithm [35,37], which uses the concept of the Nelder and Mead method of acquiring information from within a vector population combined with evolutionary methods similar to those of genetic algorithms [36]. A more detailed description of differential evolution follows.

Differential evolution (DE) [35] shares similar concepts with genetic algorithms (GA), except that it is for real-valued optimisation, while GA is for binary value optimisation [38]. For each generation, G, in DE, there is an m-dimensional population vector containing n individuals. The number of individuals, n, does not change over the generations. Each of the m-dimensional population represents the m parameters that is of interest to the user. Like all other inherently parallel search techniques, the initial populations are generated randomly and should give a good coverage of the entire parameter space. For each m-dimensional target vector in the current generation, a mutated vector is generated. The total number in the population, n, must be more than 4 in order to have the mutation take effect [35]. A crossover process is introduced to increase the diversity of the perturbed parameter vectors, leading to a trial vector, which will then be compared with the target vector \( x_i \) in order to decide if it is fit enough to become a member of the next generation. If the trial vector gives a smaller error than the target vector, the original target vector \( x_{i+1} \) is replaced by trial vector \( u_{i+1} \); otherwise \( x_{i+1} \) will remain in the population. The above-mentioned procedures are repeated until all the individuals of the current generation have been chosen as a target vector, then the algorithm restarts with the next generation. The algorithm is terminated when the fitness or error converges to the predefined threshold, or the maximum number of generations is reached.

We use a differential evolution algorithm to determine the values of the CA probabilities which globally minimise the mean square error between the CA model prediction and the experimental data. Time dependence of several quantities can be both measured in experiment and acquired from the model, most common examples being the average corrosion depth, the maximum corrosion depth, the total corrosion path length, and the number of initiation sites. We have chosen the total corrosion path length as a quantity that most adequately represents the degree of corrosion damage. Hence the DE objective function used in our study is the mean square error between experimental and predicted total corrosion path length.

The dimension of the population vector is equal to the number of probabilities to be determined. There are three probabilities in our model, namely \( P_{\text{grain}} \), \( P_{\text{bound}} \), and \( P_{\text{layer}} \). If diffusion is not included in the model, rescaling all probabilities by the same factor changes the time scale of the CA model (the real time which corresponds to one CA time step). Maximum computational efficiency is achieved by setting the maximum possible value of the time step. This corresponds to rescaling all the probabilities by the factor which fixes the value of the maximum probability (\( P_{\text{bound}} \) in our case) to one. In the model with diffusion, the probabilities cannot be rescaled because the CA time scale implicitly sets the value of the diffusion constant. Hence \( m = 2 \) in the model without diffusion, and \( m = 3 \) in the model with diffusion. We have chosen the population size \( n = 10 \) to ensure a good balance between span of the parameter space and computational efficiency.

5. Experiment

5.1. Materials

The experimental material was a commercial aluminium alloy AA2024-T3 having a typical composition as shown in Table 1. A plate of thickness 50 mm was cut into sections in preparation for immersion in sodium chloride and hydrogen peroxide solution according to ASTM Standard G 110-92.

5.2. Coupon testing

IGC tests were performed at six different timescales (8, 24, 48, 72, 96, and 144 h). Following immersion the cut surfaces were polished and etched with Keller’s reagent prior to observation in the scanning electron microscope (Phillips XL40 Series). Using the images gathered during SEM analysis, the measurement of IG ingress was performed using the ‘trace’ function within SigmaScan 3.0 (Systat Software Inc., London, UK) image analysis software. The software was calibrated using the SEM image scale bar.

5.3. Results

Fig. 5 shows typical scanning electron microscope images at selected immersion times. It is observed that intergranular corrosion follows the rolling direction and the preferred path of attack is along the grain boundary parallel to the rolling direction. Table 2 presents the maximum depth of intergranular attack and path length at the different immersion times.

6. Results and comparison with experiment

In this section, we apply the CA model described in Section 2 in conjunction with the DE algorithm described in Section 4 to simulate the kinetics of intergranular corrosion using the real grain structure of the sample. The 3D EBSD data (see Fig. 6) is used to set the initial state of the model. The differential evolution is used to fit the parameters of the CA model to the experimental data on the IGC growth rate obtained as described in Section 5.

There are different experimental outputs that characterise the corrosion propagation, such as maximum corrosion depth, average corrosion depth, number of corrosion initiation sites, etc. We first chose the total corrosion path length as the main characteristic of the corrosion damage, and used our model to correlate the experimental data on the corrosion path length with the corresponding simulation data.

| Table 1 Chemical composition of 2024-T351 in wt.% based on EDX measurements. |
|---------------------|---------------------|
| **Alloy**           | **AA2024-T3**       |
| **Min**             | **Max**             |
| Si                  | –                   | 0.50                |
| Fe                  | –                   | 0.50                |
| Cu                  | 3.8                 | 4.9                 |
| Mn                  | 0.30                | 0.90                |
| Mg                  | 1.2                 | 1.8                 |
| Cr                  | –                   | 0.10                |
| Zn                  | –                   | 0.25                |
| Ti                  | –                   | 0.15                |
| Zr                  | –                   | –                   |
| Al                  | Balance             |

Chemical composition of 2024-T351 in wt.% based on EDX measurements.
The three-dimensional simulation is undertaken on a 512 x 256 x 256 lattice, and mirror-periodic boundary conditions are used in the directions parallel to the surface of the sample to ensure the continuity of the grain boundaries.

Table 2

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Maximum depth (µm)</th>
<th>Path length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>104</td>
<td>1.141</td>
</tr>
<tr>
<td>24</td>
<td>147</td>
<td>3.547</td>
</tr>
<tr>
<td>48</td>
<td>197</td>
<td>4.912</td>
</tr>
<tr>
<td>72</td>
<td>257</td>
<td>5.698</td>
</tr>
<tr>
<td>96</td>
<td>290</td>
<td>7.373</td>
</tr>
<tr>
<td>144</td>
<td>314</td>
<td>9.943</td>
</tr>
</tbody>
</table>

Fig. 6. 3D Reconstruction of the material microstructure of the sample as obtained from scanning electron microscopy operating in electron backscatter detection mode. SD. Note. x, y, and z scales are 1 mm.

Fig. 7. Plots of (a) corrosion path length and (b) maximum corrosion depth as a function of immersion time. Points correspond to the experimental data, solid line corresponds to the model without diffusion. Note. Upper and lower lines in (b) denote standard deviation.

Fig. 5. Experimental observation of IGC development over a period of 96 h. Solution conditions according to ASTM G110-92.
The CA probabilities and time scale were adjusted using the differential evolution technique to obtain the best agreement of the predicted time dependence of the corrosion path length with corresponding experimental data. The best agreement with experimental data is achieved for the following values of probabilities:

\[ P_{\text{grain}} = 1, \quad P_{\text{bound}} = 1.22 \times 10^{-4}, \quad P_{\text{layer}} = 6.14 \times 10^{-3}. \]

One time step corresponds to 0.865 h. Fig. 7a presents the calculated corrosion path length as a function of time, together with the corresponding experimental points. The plot demonstrates satisfactory quantitative and qualitative agreement of experimental and simulation results, and the ability of the model to predict the advance of intergranular corrosion at longer times.

The comparison with experiment here demands further discussion. Essentially the problem considered here is one of machine learning. In order to bring the CA model into correspondence with experiment, the data is used in order to learn ‘optimal’ parameters. In any machine learning problem, the issue of generalisation arises. The critical question is: has the model learned how to represent the underlying physics of interest or has it simply ‘rote-learned’ the experimental data? If the latter, the model will be unable to generalise to any new experimental data which was not part of the learning process. The critical issue for generalisation is that there should be a ‘large’ set of training data points compared to the number of adjustable model parameters. In the current problem, there are two adjustable parameters and six data points and this would often be considered acceptable (certainly in the context of linear regression). However, an often-used rule-of-thumb in the neural network community is that there should be ten training patterns for each adjustable parameter to ensure proper generalisation [39]. The model should also be tested on an independent data set; this is not possible here given the scarcity of data; however, there is another means we can use here to assess generalisation. If the CA model has indeed learned the underlying physics of the corrosion process, it should be able to make predictions of other observable quantities – like maximum corrosion depth – which were not used in the learning process.

In order to apply this test, the CA model trained to reproduce path length was used to predict maximum corrosion depth and the results are shown in Fig. 7b. In fact, the CA model was run eight times with different random initial conditions for grain properties and the mean predicted depth is shown in the figure, together with the one-sigma confidence interval. It is immediately clear that the data points are outside the confidence interval for predictions. This does not immediately mean that there is too little data and that the model cannot generalise; an alternative explanation is that, in order to represent the path length, it has been sufficient for the model to learn a ‘subset’ of the underlying physics which is not rich enough to represent the different observable. This can be explained in other terms; suppose that the predictions of path length are more robust to uncertainty in the parameters than the predictions of maximum depth. In this case, the optimisation process using path length for comparison purposes will terminate at parameters which are adequate to allow predictions of path length, but not precise enough to allow a match of maximum depth. If one optimises on maximum depth however, the process will terminate on parameters which are precise enough for prediction of maximum depth, but also adequate for prediction of path length as that variable allows a range of acceptable parameters. To investigate

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**Fig. 8.** Plots of (a) maximum corrosion depth and (b) corrosion path length as a function of immersion time. Points correspond to the experimental data, solid line corresponds to the model with diffusion.

**Fig. 9.** Plots of (a) maximum corrosion depth and (b) corrosion path length as a function of immersion time. Points correspond to the experimental data, solid line corresponds to the model without diffusion.
this possibility, the process carried out previously was inverted; the model was trained to predict the maximum corrosion depth and then validated on the path length, and the results are shown in Fig. 8. The new results also differ from the previous ones in that diffusion is included in the predictive model; this means that the calibration using differential evolution needs to establish three parameters.

With diffusion in our model, the best agreement with experimental data is achieved for the following values of probabilities: $P_{\text{grain}} = 1$, $P_{\text{bound}} = 8.56 \times 10^{-4}$, $P_{\text{layer}} = 0.248$. One time step corresponds to 0.0411 h. Fig. 8 shows time dependence of maximum corrosion depth and total corrosion path length, correspondingly. In this case, the cross-validation predictions show a good correspondence with the observed data. This provides evidence that the model is appropriately validated and that the underlying physics is represented with enough fidelity to make predictions on different observables than those taking part in the learning process. In order to be completely principled about the validation process, it is necessary to try both training data sets both with and without diffusion. The results of the additional runs needed here are shown in Figs. 9 and 10. In Fig. 9, the results of fitting to depth and validating on path length for the model without diffusion are shown. The results are acceptable; however the predictions on path length are qualitatively different from those in Fig. 8 for the model with diffusion. Without diffusion, the predictions show an initial steep rise followed by a slower growth which is not uniformly monotonic. As one would expect monotonicity, the evidence here would appear to show more support for the model with diffusion. To be completely confident about these conclusions though, one would ideally wish for more data. Finally in Fig. 10, the results for training on path length and validating on depth for the model with diffusion; the results are poor, suggesting that the model with diffusion trained on path length does not generalise adequately. For completeness, the parameters of the additional runs are: $P_{\text{grain}} = 1$, $P_{\text{bound}} = 0.0000273$, $P_{\text{layer}} = 0.640$, time step = 0.349 h (corresponding to Fig. 9) and $P_{\text{grain}} = 1$, $P_{\text{bound}} = 0.001136$, $P_{\text{layer}} = 0.0577$, time step = 2.06 h (corresponding to Fig. 10).

7. Conclusion

We have developed a cellular automaton model for intergranular corrosion. The model is based on a set of CA rules in conjunction with a random walk process, and has four adjustable parameters (probabilities). The adjustable parameters of the model have been calibrated using the differential evolution algorithm to match a specific experiment, which has allowed a prediction of the propagation of the corrosion front for given conditions. 3D simulations show that the computations give good qualitative behaviour and can be computed in reasonable times. The simulation results show qualitative and quantitative agreement with experimental data on the advance of the corrosion front.

The set of CA rules can be modified to include a wider range of electrochemical phenomena occurring in the process of intergranular corrosion in given materials.

Acknowledgements

The authors acknowledge the EU under the auspices of a FP6 programme SICOM proposal #30804 for providing funds for the project and to Mr. S. Dodds for his support in obtaining the experimental data.

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