ILLUSTRATING PIT INITIATION AND EVOLUTION IN ALUMINUM ALLOYS ACCORDING TO A 3-DIMENSIONAL CELLULAR AUTOMATA BASED MODEL

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Kathryn Marie Stalker

August, 2016
ILLUSTRATING PIT INITIATION AND EVOLUTION IN ALUMINUM ALLOYS ACCORDING TO A 3-DIMENSIONAL CELLULAR AUTOMATA BASED MODEL

Kathryn Marie Stalker

Thesis

Approved: 

Advisor
Dr. Nao Mimoto

Accepted: 

Dean of the College
Dr. John Green

Faculty Reader
Dr. Curtis Clemons

Dean of the Graduate School
Dr. Chand Midha

Faculty Reader
Dr. Kevin Kreider

Date

Department Chair
Dr. Timothy Norfolk
ABSTRACT

The objective of this work is to develop a cellular automata based model of pitting initiation and subsequent three-dimensional evolution of pit shapes. Here, a cellular automaton is a collection of cells, each of which may be in one of two states, metallic or electrolyte, arranged over a grid. Pit initiation is implemented over a 2-dimensional grid representative of the metal surface while pit propagation is resolved over a 3-dimensional grid which describes a subsection of the bulk metal. The size of the bulk metal will be on the order of millimeters, and a layer of electrolyte, in which chloride will act as the aggressive anion, will cover the bulk metal. A cell within the automaton may change its state each fixed time interval based on a set of rules, called transition rules. The rules are based upon corrosion mechanisms and are implemented stochastically. Further, parametric analyses are performed to simulate pit damage evolution for a metal electrode in various environments. Results from the model are representative of aluminum alloys relevant to aircraft structures. The initiation scheme is capable of reproducing the number of (meta)stable pitting events per area found in the literature for Aluminum Alloy 7075, and the propagation scheme simulates pit shapes seen in nature, such as subsurface and undercutting pits.
Foremost, I would like to thank my thesis advisers, Dr. Young, Dr. Clemons, Dr. Kreider, and Dr. Mimoto, for guiding me throughout the process of this thesis and throughout my pursuit of this degree. The knowledge, skills, and support they offered me were invaluable, and, for that, I express my sincere gratitude. I would also like to thank my parents, Greg and Lisa Stalker, for all of their love and support; I could not have done this without them. Finally, I would like to thank Colin Groh for always being there for me whenever I needed him. His love and encouragement propelled me through the most difficult of times and inspired me to achieve my goals.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
</tbody>
</table>

CHAPTER

I. INTRODUCTION ................................................. 1

1.1 Pitting Corrosion ........................................ 1

1.2 Cellular Automata ........................................ 11

II. MODEL DESCRIPTION ........................................... 20

2.1 The Initiation Scheme ...................................... 22

2.2 Stable Pit Propagation Scheme ......................... 28

III. MODEL IMPLEMENTATION ....................................... 33

3.1 Algorithm for the Metastable Pit Initiation Scheme 33

3.2 Algorithm for the Stable Pit Propagation Scheme .... 34

IV. RESULTS ......................................................... 35

4.1 Metastable Pit Initiation Scheme ....................... 35

4.2 Stable Pit Propagation Scheme ............................ 57

V. CONCLUSION .................................................... 67

BIBLIOGRAPHY ..................................................... 70
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Constant parameters for all initiation studies.</td>
<td>36</td>
</tr>
<tr>
<td>4.2</td>
<td>Environmental effects and projected number of events for base initiation study.</td>
<td>37</td>
</tr>
<tr>
<td>4.3</td>
<td>Results of the Base Study. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.</td>
<td>39</td>
</tr>
<tr>
<td>4.4</td>
<td>Environmental effects and projected number of events for initiation Case 1.</td>
<td>40</td>
</tr>
<tr>
<td>4.5</td>
<td>Results of initiation Case 1: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.</td>
<td>41</td>
</tr>
<tr>
<td>4.6</td>
<td>Results of initiation Case 1: Scenario 2. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.</td>
<td>41</td>
</tr>
<tr>
<td>4.7</td>
<td>Environmental effects and values of $\beta_E$ and $h_E$ in (4.1) for initiation Case 2.</td>
<td>44</td>
</tr>
<tr>
<td>4.8</td>
<td>Results of initiation Case 2: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.</td>
<td>44</td>
</tr>
<tr>
<td>4.9</td>
<td>Results of initiation Case 2: Scenario 2. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.</td>
<td>45</td>
</tr>
<tr>
<td>4.10</td>
<td>Environmental effects and values of $\beta_{CI}$ and $h_{CI}$ in (4.2) for initiation Case 3.</td>
<td>52</td>
</tr>
</tbody>
</table>
4.11 Results of initiation Case 3: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

4.12 Results of initiation Case 3: Scenario 2. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

4.13 Environmental effects and values of $\beta_T$ and $h_T$ in (4.3) for initiation Case 4.

4.14 Results of initiation Case 4: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

4.15 The values of $\alpha_1$, $\alpha_2$, and $\zeta$ in (2.5) used in propagation Case 1.

4.16 The values of $\alpha_1$, $\alpha_2$, and $\zeta$ in (2.5) used in propagation Case 2.

4.17 The values of $\alpha_1$, $\alpha_2$, and $\zeta$ in (2.5) used in propagation Case 3.
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Indexing of cells in a 2-D (a) and 3-D (b) CA.</td>
<td>12</td>
</tr>
<tr>
<td>1.2</td>
<td>2-D (a) and 3-D (b) Von Neumann neighborhood of a cell $c_i$ (dark gray).</td>
<td>14</td>
</tr>
<tr>
<td>1.3</td>
<td>2-D (a) and 3-D (b) Moore neighborhood of a cell $c_i$ (dark gray).</td>
<td>14</td>
</tr>
<tr>
<td>2.1</td>
<td>An illustration of the total grid $G$. The grid is segmented into two</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>schemes: (meta)stable pit initiation and stable pit propagation. The</td>
<td></td>
</tr>
<tr>
<td></td>
<td>layer of $G$ which represents the bulk solution is not used in the grids</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for the initiation or propagation schemes; however, it is included in $G$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>to assert the consideration of the bulk solution in each stage of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the model.</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic illustration of the neighborhood $N_{pits}$, with radius $R$,</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>of a cell $c_{1,j,k}$ (gray). The neighborhood is used to determine the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sites of stable pits.</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Example of the implementation of $N_{pits}$ and $N_{exclusion}$. In this</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>example, $R$ is one cell and $M_n = 3$ metastable pits. The grid on the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>left shows metastable pits (light gray and black) formed at the current</td>
<td></td>
</tr>
<tr>
<td></td>
<td>time step, where the neighborhood $N_{pits}$ of the cell being evaluated</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(black) is outlined. Because at least 3 metastable pits that formed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at the current time step lie within $N_{pits}$, a stable pit is assumed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>to exist within the neighborhood. In the grid on the right, the cells</td>
<td></td>
</tr>
<tr>
<td></td>
<td>protected from further pitting events (dark gray) are identified using $N_</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>exclusion</em>.</td>
<td></td>
</tr>
</tbody>
</table>
4.1 Affected metal surface for base study after 2000 seconds. The scheme produces 610 metastable pits (small white blocks) and 3 stable pits (large white blocks) on the 1 mm$^2$ grid. The size of the stable pits represented in the figure is not intended to convey the true size of the pit; rather, it is assumed that the stable pit lies somewhere within the region. The axes $j$ and $k$ are the indices of cell $c_{1,j,k}$.

4.2 The general shape of the distribution of environmental influences across the surface metal. The $z$-axis corresponds to potential, chloride concentration, and temperature in Cases 2, 3, and 4 respectively.

4.3 Affected surface in Case 2: Scenario 1. In this example, 165 metastable pits and zero stable pits formed in the 2000 second simulation on the 1 mm$^2$ grid.

4.4 Contour plot indicating the value of the applied potential at cell $c_{1,j,k}$ for all $j$ and $k$ in initiation Case 2: Scenario 1.

4.5 Contour plot indicating the value of $P_{\text{init}}$ at cell $c_{1,j,k}$ for all $j$ and $k$ in initiation Case 2: Scenario 1.

4.6 Contour plot indicating the value of the applied potential at cell $c_{1,j,k}$ for all $j$ and $k$ in initiation Case 2: Scenario 2.

4.7 Plot of $P_{\text{init}}$ versus chloride concentration for initiation Case 3. Here, $E_{1,j,k} = -0.750 \text{ V}_{\text{SCE}}$ and $T_{1,j,k} = 25 \text{ °C}$ for all $j$ and $k$.

4.8 Affected surface in Case 3: Scenario 1. In this example, 296 metastable pits and one stable pit formed in the 2000 second simulation on the 1 mm$^2$ grid.

4.9 3-D (a) and 2-D (b) depictions of simulated pit in propagation Case 1 after 3 hours of growth. The pit is approximately 6.7 $\mu m$ in depth and 114 $\mu m$ in diameter at its largest.

4.10 3-D (a) and 2-D (b) depictions of simulated pit in propagation Case 2 after 3 hours of growth. The pit is approximately 11 $\mu m$ in depth and 250 $\mu m$ in diameter.

4.11 3-D (a) and 2-D (b) depictions of simulated pit in propagation Case 3 after 3 hours of growth. The pit is approximately 6 $\mu m$ in depth and 265 $\mu m$ in diameter. Nearly $2.45 \times 10^5 \text{ $\mu m^3$}$ of the affected sample is dissolved due to uniform corrosion and is not included in determining the depth or diameter of the resulting pit.
CHAPTER I
INTRODUCTION

1.1 Pitting Corrosion

Pitting corrosion is the process by which metals experience a localized dissolution of material as a result of the disintegration of their protective passive film [1]. Owing to the difficulty associated with its detection, this insidious variety of corrosion may result in fatigue cracking and/or perforation of the affected structure. The vulnerability of economically important materials, such as stainless steels and aluminum alloys, to pitting corrosion is due in part to the heterogeneity of their microstructure, which is also where these materials derive much of their strength. Aluminum alloys, in particular, exhibit a great number of intermetallic particles and, as such, are extremely vulnerable to localized corrosion under the right environmental conditions. The model presented in this work aims to simulate the realistic evolution of pits in aluminum alloys that are subjected to various environmental conditions. Because of their relevance to aircraft structures, Aluminum Alloy 1050 (AA1050) and 7075 (AA7075) are the specific alloys under investigation. The results of this model hold great value in the study of pit morphologies and, subsequently, the conditions under which pits induce system failures.
1.1.1 Pit Initiation and Stages of Growth

The process of pitting corrosion can be organized into three general stages: pit initiation caused by the breakdown of the metal’s oxide film, metastable growth, and stable growth. Despite the considerable knowledge developed over recent years in the field of pitting corrosion, the process by which pits initiate on passive metals is still unascertained. However, it is accepted that pitting almost always begins at some structural defect in the metal’s oxide film which allows for the subsequent infiltration of water and aggressive species. Once the aggressive species reaches the metal/oxide interface, localized dissolution occurs [2]. In high-purity aluminum, pits are believed to initiate at flaws, i.e. thinner regions or scratches caused by mechanical processing, and grain boundaries in the oxide layer [1, 2, 3]. Such sites are susceptible to pit nucleation in aluminum alloys as well, but the preferred locations are at intermetallic particles, above which the oxide film may be weakened and the local chemistry of the film altered [1]. In AA7075, high numbers of intermetallic particles, including \( \text{Al}_7\text{Cu}_2\text{Fe}, \text{Al}_{23}\text{CuFe}_4, \) and \( \text{Al}_2\text{CuMg}, \) are found [4, 5]; likewise, 1xxx alloys contain \( \text{Al}_6\text{Fe} \) and \( \text{Al}_3\text{Fe} \) [6]. These particles exhibit electrochemical behaviors different from that of the aluminum matrix and are suggested to act as local cathodes in the pitting process [4, 6].

Perhaps the most explored aspect of the process of pit initiation is the pitting potential \( E_{\text{pit}} \) and its dependence on environmental factors such as temperature, pH, and aggressive anion concentration. It is generally accepted that metals with higher values of \( E_{\text{pit}} \) are less susceptible to pitting; however, in some systems, repeated
measurements of $E_{\text{pit}}$ via potentiodynamic testing can result in wide experimental scatter, and, as such, its reliability in determining the resistance of a metal to pitting is a debated proposition [1]. Nevertheless, $E_{\text{pit}}$ has been shown experimentally to mark the onset of stable pitting. Explanations for this correlation include the increase in current density, a minimum amount of which pits must support prior to stabilization, associated with increasing potential [1]. In aluminum alloys, intermetallic particles, specifically those composed of copper, decrease the value of the pitting potential, thereby supporting the proliferation of stable pits [1, 4].

Pitting corrosion cannot occur in the absence of an aggressive anionic species. This species is almost always chloride, since many metal cations exhibit considerable solubility in chloride solutions and the species has been demonstrated to interfere with passivation of metals [1]. Several theories, involving film penetration, film breaking, and absorption, have been presented to explain the breakdown of the oxide layer by chloride ions [1]. For example, experiments have shown that in neutral solutions, the oxide film of aluminum is positively charged, an effect that causes the absorption of negatively charged chloride ions to be favored [2]. The chloride ions may then penetrate the interior of the oxide film and assist in metal dissolution [2]. The influence of chloride concentration on pit initiation is further supported by its effect on the pitting potential of the metal; it is widely accepted that $E_{\text{pit}}$ decreases with concentration according to

$$E_{\text{pit}} = A - B \log[Cl^-],$$

(1.1)

where $A$ and $B$ are constants [7].
Temperature plays a significant role in pit initiation; for some materials, there is a critical pitting temperature (CPT) above which pitting occurs regardless of other environmental factors [1]. However, aluminum alloys do not exhibit a CPT in chloride solutions [1]. Rather, in agreement with other experiments, a study by Soltis et al. [8] found that the pitting potential of high-purity aluminum in a moderate chloride solution varies with temperature according to

\[ E_{\text{pit}} = a_{\text{pit}} - b_{\text{pit}} T, \]  

where \( a_{\text{pit}} \) and \( b_{\text{pit}} \) are constants depending on the temperature (K) range. Soltis et al. noted that \( E_{\text{pit}} \) decreases very slowly with increasing temperature from 1 to 30°C after which \( E_{\text{pit}} \) is observed to decrease much faster [8]. Soltis attributes the temperature dependence of \( E_{\text{pit}} \) to the variation of activation energy for the anodic reaction in the pit, and it is speculated that the transition at 30°C is due to some kind of change in the pit’s dissolution mechanism [8].

Aluminum and its alloys are amphoteric materials, i.e. they are soluble in both acidic and alkaline solutions [9]. Empirically, however, the effect of pH on pit initiation in these metals has been determined to be insignificant. A study by Zaid et al. [9] on Aluminum Alloy 6061 found that pH has no impact on the pitting potential of the metal; Zaid attributes the metal’s loss of passivity to the presence of OH\(^-\), which facilitates the degradation of the oxide film on aluminum. Indeed, results by Cavanaugh [10] show that pH has no appreciable impact on the initiation of pits in Aluminum Alloy 7075. However absent its effect on initiation, pH has
been demonstrated to be an influential factor for pit growth in AA7075. Cavanaugh [10] found pH, along with temperature, to have the most significant effect on pit morphology, with alkaline conditions being the most destructive.

Following initiation, a pit may repassivate immediately, grow for a short time and then repassivate, or continue to grow indefinitely. The two former phenomena are known as metastable pitting, while the latter refers to stable pitting. Metastable pits have lifetimes on the order of seconds or less and grow to around a micrometer in depth [1, 11]. The onset of such pits is experimentally marked by a sudden increase in current, followed shortly by the repassivation of the pit when the current decreases to the background passive current [12]. In many materials, these spikes in current are often observed at potentials far below $E_{pit}$ indicating that other environmental factors control the induction of metastable pitting events. It is noted here that the ohmic potential drop surrounding the surface of a newly formed pit creates a kind of barrier which suppresses further local pitting events. A study by Reuter and Heusler [13] on the pitting of passive iron found that the width of this barrier, called the “exclusion zone,” varies with the chloride concentration and pH of the solution, as these factors promote further nucleation.

During their growth, metastable pits are covered by a cap, which is composed of remnants of the oxide film [1, 12]. Beneath the cap, dissolved metal ions hydrolyze, producing an acidic environment and inspiring the migration of chloride ions to maintain electroneutrality [2]. The cap itself prevents the bulk solution from diluting the aggressive pit environment while allowing some exchange of chloride and metal ions
and providing the resistance necessary to sustain growth [1, 12]. Eventually, the pressure associated with the growing hydrogen population and a large dissolution current within the pit leads to a rupture of the cap [2, 12]. For metastable pits, this marks the end of growth.

Pits may survive the violent rupture of their covers and continue to grow in a stable fashion. The conditions under which metastable pits transition to stable pits have been explored extensively. It has been observed that during metastable growth, some pits experience the precipitation of a salt film at their surface, a film which is thought to provide the necessary resistance that the pit cap provided prior to rupturing [1, 12]. Galvele [7] claimed that pit stability relies upon a critical level of acidification within the local pit environment, a level which is associated with a critical value $x \cdot i \text{ A/cm}$ where $x$ is the pit depth and $i$ is the pit current density. Pride et al. [11] found that a critical value of $I_{\text{pit}} / r_{\text{pit}}$, where $I_{\text{pit}}$ is the peak pit current and $r_{\text{pit}}$ is the apparent radius of the pit at peak current, must be realized before pit stabilization, specifically in aluminum, occurs. Each of these assertions suggest that a metastable pit must support a minimum amount of current before stabilization is induced. Indeed, metastable growth has been identified as an ohmic controlled process, meaning that potential $V$, resistance $R$, and current density $i$ obey Ohm’s law: $V = iR$. Thus, metastable pits with reasonably large current densities require less resistance to achieve the pitting potential and enter stable growth.

During stable growth, pits undergo a diffusion controlled corrosion process, meaning that the rate of dissolution at the metal/electrolyte interface is equal to
the rate with which metal ions diffuse from the surface [14]. The potential in the 
local pit environment has been noted to decrease over the course of the diffusion 
controlled regime; this can be observed in anodic polarization curves as the region 
where current density appears somewhat constant [6, 15]. Pits that display such a 
decrease in potential tend to repassivate, or cease growth, as the potential eventually 
decreases below a threshold known as the repassivation potential $E_{RP}$.

Results by Okada [16] indicate that repassivation ensues following the ex-
tension of an oxide film over the actively corroding pit bottom. For the oxide layer 
to form, a critical potential, one that Okada claims to be different from but closely 
related to $E_{RP}$, must be realized, and the rate of oxide formation must be greater 
than that of oxide dissolution [16]. The growth of the oxide layer diminishes the 
anodic current density in the pit, causing the dissolution of metal to cease [16]. As 
repassivation is dependent upon the resistance associated with the oxide layer, the 
repassivation stage of pit growth is ohmic controlled.

As it relates to the development of the model presented in this thesis, a brief 
survey of existing stochastic models for metastable and stable pit formation is given 
in the following section.

1.1.2 Stochastic Approaches to Modeling Pitting Corrosion

Pit initiation has been described as stochastic in nature [1]; therefore, much work has 
been put into establishing probabilities of occurrence [3, 10, 17, 18, 19, 20, 21]. For 
instance, Williams et al. [17] derived an expression for the nucleation frequency $\Lambda$
(s\(^{-1}\)) of stable pits in stainless steels:

\[ \Lambda = a \lambda \exp(-\mu \tau_c), \]  

(1.3)

where \(a\) (cm\(^2\)) is the sample area, \(\lambda\) (cm\(^{-2}\) s\(^{-1}\)) is the frequency with which metastable pits were determined to form, \(\mu\) (cm\(^{-2}\) s\(^{-1}\)) is the probability of pit death, and \(\tau_c\) (s) is the critical age at which a metastable pit becomes stable. The development of this relationship was important because it suggested that the susceptibility of a material to the formation of stable pits can be learned by examining the frequency of more abundant metastable pits [1].

Applying a neural networking approach, Cavanaugh [10] confirmed the dependence of metastable pit initiation rates upon several environmental variables in AA7075. With considerable accuracy, the model asserts that pit initiation rates increase exponentially with temperature and logarithmically with chloride concentration, while solution pH has little impact [10]. Further, Cavanaugh discovered that decreasing the number density of intermetallic particles also decreases the pit initiation rate, leading to the assumption that alloy microstructure determines where pits initiate while environmental factors determine the severity of attack [10]. In her study, Cavanaugh also explored the impact of temperature, pH, and chloride concentration on pit growth. She found that temperature and pH had the greatest effect on pit diameter and depth, while varying chloride concentration showed no appreciable difference in pit shape. In particular, Cavanaugh noted that pit depth and diameter increases with pH and temperature, where 12.5 pH and 60\(^{\circ}\)C created the largest pits.
Organ et al. [21] developed a model for the generation rate of metastable pits in a homogeneous metal surface to demonstrate the correlation between pitting events; that is, to show that the formation of pits will increase the likelihood of subsequent events. In this model, the generation rate $w$ is determined by the concentration $C$ of aggressive species at the surface of the pit, the potential drop $\Phi$ in the solution, and the film damage $F$. The combined effect of these quantities is denoted $M$, the memory function

$$M = \alpha_C C + \alpha_F F - \alpha_\Phi \Phi,$$

(1.4)

where $\alpha_C$, $\alpha_F$, and $\alpha_\Phi$ are constants. Then, the generation rate (event per unit area per unit time) is

$$w = \frac{w_0}{1 + \exp((M_0 - M)/H)},$$

(1.5)

where $w_0$ is the maximum generation rate, which simulates the aggressiveness of the solution, and $M_0$ and $H$ are constant parameters that simulate the corrosion resistance of a material. Organ found that under sufficiently aggressive conditions and, therefore, high generation rates, metastable pits indeed promote the formation of subsequent pits in the area [21]. Moreover, the clustering of metastable pits causes an increase in the susceptibility of the region to stable pitting [21].

Following the lead of Organ et al., Colwell [22] created a model for the stable pit density in AA1050 as a function of time and environmental effects. Using a form similar to (1.5), Colwell establishes the metastable pit generation rate

$$w(t) = \frac{W_{\max}}{1 + \exp\left(C_P + C_E \max\{0, E_{\text{pit}} - E\} + \sum_{n=2}^{m} C_n J_n(t)\right)}$$

(1.6)
where $E$ is the applied potential, $C_P$ and $C_E$ are parameters which relate to the pitting potential, and $C_n$ for $n = 2, \ldots, m$ are the weights of functions $J_n(t)$ that correspond to environmental effects such as time of wetness, chloride concentration, and pollutant concentration. Given a starting time $t = 0$, the times of metastable events are calculated using a combination of a nonhomogeneous Poisson process and the kinetic Monte Carlo method, where the nonhomogeneous Poisson process is used at a rate $w(t)$ to create the cumulative distribution function for the waiting times between events. The current caused by each metastable event is calculated using the current function developed by Organ et al.

$$I(t) = \begin{cases} 
0 & t < u \\
I_0 \exp \left( -\frac{t-u}{\tau} \right) & t \geq u,
\end{cases}$$

where $I_0$ is the magnitude of the current spike caused by one metastable pitting event, $u$ is initiation time of the pit, and $\tau$ is the time constant for the current decay. The current function is then plotted using the set of initiation times, and the number of current spikes exceeding a particular value, established using the Galvele criterion for stable pitting, are counted as stable pits. The results of Colwell’s model proved acceptable in many case studies, with the model successfully recreating the (meta)stable pit densities of several sets of field data. However, Colwell concedes that the model is limited in that the maximum number of pits, $W_{\text{max}}$, for a given metal ought to decrease over time due to the increasing number of pits on the metal surface. Nevertheless, Colwell’s metastable pit generation rate is modified and used in this work to determine the probability of metastable pit initiation.
1.2 Cellular Automata

A cellular automaton (CA) is a modeling method involving the spatially discrete arrangement of cells, which are assigned a discrete state and the movements (or state changes) of which are governed by a set of transition rules. The rules are based on the state of the cell as well as the states of the neighboring cells and are implemented iteratively for the desired number of time steps. The academic popularity of CA models stems from their ability to simulate complex behaviors and outcomes from a set of simple local reactions. Perhaps the most famous implementation of CA is Conway’s Game of Life [23], which provides a simple example of the capability of CA’s to produce emergent behaviors and self-organization [24]. However, the name most synonymous with CA’s is Stephen Wolfram, whose comprehensive studies [25, 26, 27] yielded novel insight into the dynamics of CA models. In recent years, CA’s have been applied with varying success to many fields, including traffic flow [28], tumor growth [29], and abnormal grain growth in austenite [30].

1.2.1 Defining a Cellular Automaton

A cellular automaton is characterized by its grid, the states of the cells which comprise the grid, the neighborhoods of each cell, and the transition function. For reasons of clarity, these concepts, as well as model boundary conditions and updating methods, are now elaborated upon.
The Grid. For practical purposes, the grid $G$ over which a CA is executed is a lattice of cells that fill some subset of the Euclidean space $\mathbb{R}^n$, where $n \in \{1, 2, 3\}$. For one-dimensional CA’s, $G$ is typically a line of rectangular cells, while the grid of two- and three-dimensional CA’s may be any shape and are most often comprised of polygon/polyhedron cells [31]. In general, the grid, cell shapes, and dimensions are decided by the configuration of the system being modeled. An example of the indexing of cells in two- and three-dimensional CA’s is given in Figures 1.1a and 1.1b.

![Indexing of cells in a 2-D (a) and 3-D (b) CA.](image)

Figure 1.1: Indexing of cells in a 2-D (a) and 3-D (b) CA.

States. Each cell $c_i$ in $G$ may take on one of $h$ possible states, which are usually represented as integer values so that $h = |S|$ where $S \subset \mathbb{N}$ is the list of possible states. The state of a cell $c_i$ at time step $t$ is denoted throughout this work as $s(c_i, t)$. The states of all cells in $G$ at time step $t = 0$ define the initial condition for the CA. For
most CA’s, each value in $S$ has a unique color assignment and/or is representative of some physical entity in the system. The “elementary cellular automaton,” for example, is a binary, one-dimensional CA, where the states $S = \{0, 1\}$ are represented by the colors white (0) and black (1).

**Neighborhoods.** The neighborhood $N$ of a cell $c_i$, denoted $N(c_i)$, is usually some combination of cells that share at least a vertex with $c_i$ (called radius one neighborhoods). In one-dimensional CA’s, the radius one neighborhood of $c_i$ is defined by the two adjacent cells. The radius one neighborhood of two- and three-dimensional CA’s varies with the chosen shape of the cells, but, as rectangular cells suffice for most modeling purposes, the von Neumann (Figures 1.2a and 1.2b) or Moore (Figures 1.3a and 1.3b) neighborhoods are among those commonly used.

**The Transition Function.** The rules which govern the evolution of a CA make up the transition function $\phi$. The transition function of a cell $c_i$ usually depends on the states of the cells in the neighborhood of $c_i$ at the current time step, as well as the state of $c_i$ itself, and yields the state of $c_i$ for the next time step. For deterministic cellular automaton, every cell at each time step may change state. However, another option is to apply a probability to the implementation of $\phi$ so that the transition function is not applied to some cells at each time step. CA’s which use this approach are called stochastic cellular automata, and the model presented in this work may be defined as such. The complexity of $\phi$ in any case varies according to the model’s
Figure 1.2: 2-D (a) and 3-D (b) Von Neumann neighborhood of a cell $c_i$ (dark gray).

Figure 1.3: 2-D (a) and 3-D (b) Moore neighborhood of a cell $c_i$ (dark gray).
purpose, but logical rules or probabilities are among common examples of transition functions as they adhere to the simplicity associated with CA’s.

**Boundary Conditions.** Due to the finite nature of \(G\), boundary conditions are required for CA’s. There are several options for boundary conditions, however, fixed and periodic boundaries are most commonly implemented. Intuitively, fixed boundaries imply that cells have no neighbors past the border, while periodic boundaries ensure that all cells have the same number of neighbors. In one-dimensional CA’s, fixed boundary conditions have induced less complex and more predictable outcomes than periodic boundary conditions [32], but, of course, the choice of boundary conditions is contingent on the system being modeled.

**Updating Methods.** The implementation of the transition function \(\phi\) is either synchronous or asynchronous; synchronous updating is adherent to the classical definition of CA’s, while asynchronous updating has been introduced to negate the somewhat artificial outcomes apparent in deterministic CA’s using synchronous updating [33]. Synchronous updating entails that \(\phi\) is implemented for each cell in \(G\) and all cells change state at the same time. Problems can arise when synchronous updating is used in CA models of (bio)chemical processes, as mass may be lost when two diffusing cells attempt to move to the same position during the same time step [31]. However, adjustments, which are described later in the following section, can be made in order to comply with mass conservation. Asynchronous updating methods cause cells to be evaluated according to \(\phi\) sequentially, where the order of evaluation depends on
the asynchronous method employed. In deterministic models, qualitatively different
dynamical behavior has been observed between a model using synchronous and asyn-
chronous updating methods. For example, asynchronous methods appear favorable in
simulations of (bio)chemical processes [33]. Stochastic CA’s, on the other hand, show
qualitatively similar results across updating methods, as stochasticity may provide
comparable outcomes no matter the implementation method [33].

1.2.2 Cellular Automata in Corrosion Science

As for the application of CA’s in the field of corrosion, several different models have
been presented [34, 35, 36, 37, 38, 39, 40]. For instance, Stafiej et al. [35] created a
two-dimensional CA model for the growth of a localized pit formed in a painted metal
initially damaged at some point on the surface. In their model, the grid is a square
lattice with square cells that may be found in one of six states: bulk metal $M$, reactive
$R$ and passive $P$ metal sites, and neutral $E$, acidic $A$, and basic $B$ electrolyte sites.
The transition function of the model is based upon the notion that pit propagation
is sustained by acidification of the local environment through the anodic dissolution
process within the pit, while pit passivation is reached through the basification of
the local electrolyte caused by cathodic processes. The model proves capable of re-
producing pit morphologies seen in nature, such as peninsula type morphologies, as
well as phenomena such as the chunk effect, which is observed upon the merging of
several pits and the subsequent detachment of corroded peninsulas.
The existing model most influential to this thesis is that of Van der Weeën
et al. [34], which aims to simulate the initiation and progression of pitting corrosion
in AISI 1040 stainless steel. The model makes use of a three-dimensional grid with
cells that may take on one of the following states: water, chloride, or metal. At
initiation, the cells of the top layer are electrolyte, i.e. both water and chloride,
while the rest of the layers are comprised of metal. The transition function is broken
into three sub-functions which account for pit initiation, the diffusion of chloride
through the electrolyte, and pit propagation. Pit initiation is dependent upon the
location of cells in state chloride in the electrolyte layer; a metal cell below a given
chloride may become the site of pit nucleation (the cell’s state changes from metal
to electrolyte) according to a constant probability \( P_p \in [0, 1] \) determined by bench
marking the model output to the results of preliminary experiments. The diffusion
function acts on all chloride cells within the grid. To mimic the concentration and
potential gradients observed after pits initiate, Van der Weeën introduces a suction
probability \( \iota \in [0, 1] \) which determines if a chloride cell exchanges position with a
water cell in the lowest possible position within the neighborhood or if it does so at
random. As synchronous updating is employed, if two chloride cells attempt to move
to the same position, neither is allowed to move during that time step. Finally, the pit
propagation function determines where an existing pit will grow further. This function
requires a chloride cell to be present within an existing pit; upon validation of this
condition, the dissolution probability \( P_d \in [0, 1] \) for a metal cell in the neighborhood
of such a chloride is calculated according to

\[
P_d = P_{d0} \left( 1 - \frac{\zeta d}{d_m} \right),
\]

where \( P_{d0} \in [0, 1] \) is the dissolution probability at the metal surface, \( \zeta \in [0, 1] \) is the IR-factor, \( d \) is the depth of the metal cell eligible for dissolution, and \( d_m \) is the total depth of the metal. The form of \( P_d \) conveys the tendency for pits to grow horizontally as pit depth increases due to the increasing IR drop.

The model presented in this paper seeks to improve upon Van der Weeën’s method, specifically by revising the transition function \( \phi \) to perhaps dissuade the accuracy issues present in Van der Weeën’s model. For example, Van der Weeën admits that the model is limited by the random manner with which pits initiate on the surface [34]. The model presented in this work is segmented into two schemes: metastable pit initiation and stable pit propagation. The transition function of the initiation scheme is governed by a probability derived from Colwell’s metastable pit generation rate, while the transition function of the propagation scheme utilizes a modified version of Van der Weeën’s \( P_d \) which takes into account both the chemistry of the pit electrolyte and the effects of the potential drop in the pit demonstrated in the work of McKinnon [41]. Several cases studies are performed in order to project the influence of environmental factors, such as chloride concentration, pH, temperature, and applied potential, on pit occurrence and morphology. Congruent with the model of Van der Weeën, the model proposed in this thesis is mesoscopic, meaning that cells are to be associated with homogeneous groupings of atoms or molecules rather
than individual atoms or molecules [34]. The remainder of this thesis is organized as follows:

- The development of the transition function, as well as explanations for the choices of grid/cell shapes, states, neighborhoods, and updating methods, for each scheme of the model is described in Chapter II.

- The implementation process of each scheme is illustrated in Chapter III.

- Chapter IV divulges the results of the model as a whole, and discussions about the significance of the results and limitations of the model are given.
CHAPTER II

MODEL DESCRIPTION

As a whole, the model presented in this work is intended to simulate the evolution of pits over a rectangular prism of aluminum alloy 7075, covered by a layer of chloride containing solution. The grid $G$ is then chosen to be a rectangular lattice of cubes, as rectangular shaped cells maintain the simplicity of the model while providing a sufficient number of neighbors for cell interactions. Each cell may take on only one of two states: chloride-containing solution or metal. Unlike Van der Weeën’s model, the state chloride is not employed because the chloride concentration of the solution is prescribed by means of a space dependent function, and, in this way, details such as the true chloride concentration of the solution may be controlled.

The model is segmented into two schemes; the first is responsible for metastable pit initiation, while the second describes stable pit propagation. The chosen design of the pit initiation model, which is described in the following section, demands a much larger time scale than the propagation stage. Therefore, in order to retain simplicity and properly simulate each process, the two schemes are implemented separately over different grids. In the following sections, the specifications for each scheme are given, and the technique of integrating the two schemes is described. In each scheme, synchronous updating is employed, as the implementation of stochastic transition
functions allows for this simplification. Figure 2.1 gives a schematic depiction of the grid. A cell within the grid $G$ is further denoted $c_{i,j,k}$.

Figure 2.1: An illustration of the total grid $G$. The grid is segmented into two schemes: (meta)stable pit initiation and stable pit propagation. The layer of $G$ which represents the bulk solution is not used in the grids for the initiation or propagation schemes; however, it is included in $G$ to assert the consideration of the bulk solution in each stage of the model.
2.1 The Initiation Scheme

The initial condition for this stage of the model is defined by all cells which comprise the surface metal along with environmental factors affecting the surface such as the potential distribution $E$, the chloride concentration $[Cl^-]$ of the solution, and the temperature distribution $T$. Each of these factors are considered functions of space and time, as various case studies are performed to determine the influence of each effect on (meta)stable pit generation. It is to be noted here that, because the concentration of the solution across the surface is prescribed by the function $[Cl^-]$, there is no need to include the layer of solution within the grid of the model; metal cells that are “dissolved” are simply replaced by solution, as though solution from the bulk had filled the new pit.

The grid of the initiation stage, $G_{init}$, is then simply a two-dimensional lattice of square cells; however, cells in this scheme are still denoted $c_{1,j,k}$ in order to retain the idea that this scheme acts on the first layer of the total grid $G$. Along the $j$- and $k$-axes of the grid, periodic boundary conditions are applied in order to simulate the open metal surfaces pitting corrosion is known to affect. Alternatively, the $i$-axis is subject to fixed boundaries since the purpose of this stage is simply to initiate pits.

2.1.1 Metastable Pit Initiation

In this scheme, all cells within $G_{init}$ are considered possible initiation sites for metastable pits, as the prescribed environmental effects control nucleation. The transition function $\phi_{init}$ is characterized by a probability of initiation $P_{init}$, which depends on the
environmental factors affecting each cell. As mentioned in Chapter I, this probability is derived from the metastable pit generation rate $w(t)$ (pits/cm²/day) developed by Colwell [22] because of the successful implementation of the rate in modeling the stable pit density in AA1050, AA1060, and AA7075. The general form of Colwell’s generation rate is given in (1.6); however, Colwell’s work includes several forms of (1.6) that vary based on the given data set. Because the results of Cavanaugh’s experiments [10] on AA7075 are referenced throughout this work, Colwell’s $w(t)$ derived from Cavanaugh’s data is used. The rate takes the form

$$w(t) = \frac{W_{max}}{1 + \exp \left( C_p + C_E \max(0, E_{pit} - E) + C_1 J_{Cl}(t) + C_2 (J_T(t) - 25) \right)}, \quad (2.1)$$

where the time $t$ is given in days, $W_{max}$ is the maximum generation rate, $J_{Cl}(t)$ is the chloride concentration (M), and $J_T(t)$ is the temperature (°C). Colwell notes that the purpose of $(J_T(t) - 25)$ in (2.1) is for convenience, since many of Cavanaugh’s experiments are conducted at the fixed temperature 25°C in order to study the effects of potential and chloride concentration on initiation. The weights $C_1$ and $C_2$, corresponding to the effects of chloride concentration and temperature respectively, are negative and their magnitudes vary based on the significance of each effect. Then, due to the structure of $w(t)$, these effects increase the generation rate of metastable pits, a result that is supported throughout literature [1, 2, 8, 10].

Although metastable pits may form at potentials far below $E_{pit}$, the potential $E$ of the system influences the frequency of metastable pitting events [6, 10]. The expression $\max(0, E_{pit} - E)$ in (2.1) is used to convey the influence of potential $E$ on pit
initiation. When \( E < E_{\text{pit}} \), the expression holds a positive value, which is magnified by the positive weight \( C_E \) and reduces the generation rate. Conversely, when the potential is close to or exceeds \( E_{\text{pit}} \), the generation rate is considerably greater. The weight \( C_P \) is used to describe situations when the potential of the system is greater than or equal to \( E_{\text{pit}} \); however, even though \( C_P \) is small in magnitude, it is not neglected when \( E < E_{\text{pit}} \).

In (2.1), the pitting potential \( E_{\text{pit}} \) is written as a function of chloride concentration according to the empirically [7] defined relationship

\[
E_{\text{pit}} = A - B \log[C{l^-}],
\]  

(2.2)

where \( A \) and \( B \) are constants. By allowing \( E_{\text{pit}} \) to vary with chloride concentration, the rate captures the significant role of chloride ions in providing a conducive environment for pitting.

In order to adapt (2.1) into a probability of initiation, several changes are made. Because the initiation scheme is implemented on a time scale of seconds, the time units of \( w(t) \) are converted by multiplying by \( \left( \frac{\text{day}}{86400 \text{ seconds}} \right) \). Further, since \( P_{\text{init}} \) is applied at each discrete time step, the rate is multiplied by the time \( \delta t \) associated with one time step in order to define the probability of a pit forming over \( \delta t \) seconds.

Because the value of \( W_{\text{max}} \) is calibrated for a 1 cm\(^2\) coupon of AA7075 and because \( P_{\text{init}} \) is calculated and implemented for each cell, the rate is scaled down by multiplying by the area of the surface of one cell, \( A_s \) (cm\(^2\)). It is to be noted here that the dimensions of each cell are chosen to reflect the average metastable pit radius at
the peak pit current recorded by Pride et al. [11]. In this way, $P_{\text{init}}$ describes the probability of a cell becoming the site of a metastable pit over $\delta t$ seconds.

Hence, the probability of metastable pit initiation is given by

$$P_{\text{init}} = \frac{A_s \delta t W_{\text{max}}}{86400 (1 + \exp(C_P + C_E \max(0, E_{\text{pit}} - E_{1,j,k}) + C_1[Cl^-]_{1,j,k} + C_2(T_{1,j,k} - 25))},$$

(2.3)

where $X_{1,j,k}$ represents the value of each environmental effect at cell $c_{1,j,k}$.

Due to the small magnitude of $A_s$, $P_{\text{init}} \in [0, 1]$ as needed. In fact, $\max(P_{\text{init}}) << 1$, making pit nucleation difficult, but not impossible, in regions of the surface with low potential, chloride concentration, or temperature. In this way, the preference for pits to form in regions where the potential exceeds the pitting potential is reflected, while the ability of metastable pits to form in regions subject to potential lower than $E_{\text{pit}}$ is still supported.

It is important to note that Colwell’s rate $w(t)$ takes on a sigmoidal profile when plotted against independent environmental influences [22]. As such, the probability of initiation $P_{\text{init}}$ retains a similar behavior. For example, if the applied potential $E$ across the surface is varied while chloride concentration and temperature remains fixed, $P_{\text{init}}$ is close to zero when $E$ is significantly less that $E_{\text{pit}}$, and $P_{\text{init}}$ increases drastically as $E$ approaches $E_{\text{pit}}$. When $E$ is greater than or equal to $E_{\text{pit}}$, $P_{\text{init}}$ is at its greatest and is a near constant value. Because $P_{\text{init}}$ is a sigmoid function of each independent environmental influence, the surface is more or less dichotomized into regions where pitting occurs and where is does not based on the distribution of the environmental influence.
In addition to generating metastable pits, the initiation stage of this model identifies where stable pits have formed. The following discussion outlines the development of this procedure.

2.1.2 Identifying Stable Pits

As metastable pits form, the local environment changes. The production of metal cations can induce hydrolysis reactions, which decrease the pH inside and around the pit. The quantity of cations in the area also inspires the migration of chloride ions, increasing the aggressiveness of the local solution. Thus, within the vicinity of metastable pits, the environment is conducive to subsequent metastable events. Organ et al. [21] found that a high number of metastable pits within a small radius make this region favorable for stable pit formation. Indeed, the current spikes caused by metastable events compound when events occur within a small radius and time frame, yielding the appropriate current density required for stable growth. This phenomenon is taken into consideration when determining where and when stable pits are formed within the initiation scheme; when a sufficient number $M_n$ of metastable pits form within a certain distance, which is established using the neighborhood $N_{pits}$, at time step $t_n$, it is assumed that a stable pit has formed somewhere within $N_{pits}$. The neighborhood, shown in Figure 2.2, is chosen to be a two-dimensional Moore neighborhood of radius $R$, where $R$ is determined through a base study described in Chapter IV.
Figure 2.2: Schematic illustration of the neighborhood $N_{\text{pits}}$, with radius $R$, of a cell $c_{1,j,k}$ (gray). The neighborhood is used to determine the sites of stable pits.

It has been observed [13] that a protected zone is created around an active stable pit; for this reason, the neighborhood $N_{\text{exclusion}}$ of a cell which is the site of a stable pit is employed to identify cells that are protected from further pitting events. The size of this neighborhood is chosen to match that of $N_{\text{pits}}$, although it is to be noted that the width of the exclusion zone may vary across chloride and pH levels of the solution. Figure 2.3 depicts the implementation of $N_{\text{pits}}$ and $N_{\text{exclusion}}$ for a cell $c_{1,j,k}$.

The method of identifying stable pits in this model is not unlike the method used by Colwell [22]. As described in Chapter I, Colwell establishes a threshold current that must be exceeded in order for a stable pit to form, i.e.

$$\text{threshold} \geq \text{critical value} \cdot 2\pi r_{\text{pit}}, \quad \text{(2.4)}$$
Figure 2.3: Example of the implementation of $N_{pits}$ and $N_{exclusion}$. In this example, $R$ is one cell and $M_n = 3$ metastable pits. The grid on the left shows metastable pits (light gray and black) formed at the current time step, where the neighborhood $N_{pits}$ of the cell being evaluated (black) is outlined. Because at least 3 metastable pits that formed at the current time step lie within $N_{pits}$, a stable pit is assumed to exist within the neighborhood. In the grid on the right, the cells protected from further pitting events (dark gray) are identified using $N_{exclusion}$.

where the critical value is determined through experiments and $r_{pit}$ is the pit radius. This threshold is based on the findings of both Galvele [7] and Pride et al. [11] which relate pit radius and current to an environment conducive to stable growth. In order for the threshold to be reached at any given time, multiple metastable pits must form within a few seconds, causing the current spikes of each event to accumulate.

2.2 Stable Pit Propagation Scheme

Upon validating the existence of a stable pit, the propagation model is implemented. The initial condition for this scheme consists of all cells comprising a subsection of
the bulk metal, where, at the surface, one stable pit is placed. As such, the cell which
defines the location of the stable pit is given state solution, while all other cells within
the grid of the propagation scheme, \( G_{\text{prop}} \), are in state metal.

In this scheme, periodic boundary conditions are employed along the \( j \)- and
\( k \)- axes to avoid border effects, while the \( i \)-axis is subject to fixed boundaries. Because
this stage requires interactions amongst cells of different states, defining a neighbor-
hood is imperative. The transition function \( \phi_{\text{prop}} \) is implemented only for cells which
exist along pit edges, and, in order to identify where these cells exist within the grid,
the neighborhood of cells in state solution is used, as cells which belong to the solution
inside a pit are easiest to identify. The neighborhood \( N_{\text{prop}} \) employed for this cause
is a modified three-dimensional radius one Moore neighborhood, where the nine cells
above the center cell are neglected. Defining the neighborhood in this way, metal
cells along the sides of a pit and along the pit bottom may be found.

The transition function \( \phi_{\text{prop}} \) for this stage is governed by a probability \( P_{\text{prop}} \)
of metal cell dissolution, which is an adapted version of Van der Weeën’s dissolution
probability \( P_d \) (1.7). The probability is given by

\[
P_{\text{prop}} = (\alpha_1 d + \alpha_2) \left( 1 - \frac{\zeta d}{d_{\text{max}}} \right),
\]

where \( \alpha_1 \) and \( \alpha_2 \) are parameters that depend on environmental effects, \( \zeta \) is a param-
eter which controls the influence of the potential drop within the pit, \( d_{\text{max}} \) is the total
number of cells in the \( i \) direction of \( G_{\text{prop}} \), and \( d \) is the depth of the metal cell subject
to dissolution.
In Van der Weeën’s dissolution probability (1.7), the probability of dissolution in the vertical direction decreases as pit depth increases, mimicking the effect of the potential drop within the pit. Indeed, the term \( \left( 1 - \frac{\zeta d}{d_{\text{max}}} \right) \) may be thought of as a representation of the Galvele pit stability product

\[ x \cdot i = \kappa, \]  

(2.6)

where \( \kappa \) is the critical value of the product which corresponds to the critical pit acidification required for stable pit growth. By rewriting (2.6) as

\[ (a + d) \cdot i = \kappa, \]  

(2.7)

where \( a \) is some constant, solving for the current density \( i \), and expanding via Taylor Series about the depth \( d = 0 \), the pit stability product may be written in the form

\[ i = \kappa[a^{-1} - a^{-2}d + \cdots], \]  

(2.8)

which, when truncated after the second term, is

\[ i = \kappa(a^{-1} - a^{-2}d). \]  

(2.9)

Thus, the minimum current density required for stable growth is given as a function of depth. The form of (2.9) is further justified by the relationship between current density and pit depth found by McKinnon [41]. In his study of unidirectional pit growth, McKinnon found that current density during the diffusion-controlled stage of growth decreases in a sub-linear fashion with pit depth. Moreover, the current density at the pit mouth is nonzero. Then, if the current density is approximated
by a linear function of depth, the form of (2.9) is once again deduced. Since current
density and potential are related by Ohm’s law, the current density, like potential,
decreases as pit depth increases.

The probability $P_{\text{prop}}$ presented in this model adopts the form of (1.7), but
the constant $P_{d0}$ in equation (1.7) is replaced with a term which is intended to capture
the effect of pH on pit growth, as Cavanaugh [10] notes pH, along with temperature,
hold the greatest influence over pit morphology. Because pH decreases with increasing
pit depth due to the hydrolysis of aluminum ions, which are more abundant deeper
into the pit [41, 42], the form $(\alpha_1 d + \alpha_2)$ is chosen. A linear expression is used to
describe this phenomenon since McKinnon [41] found that, with unidirectional pit
growth, the concentration of metal ions, and, therefore, hydrogen ions, inside the pit
increases linearly with pit depth. Although the model presented in this work considers
three-dimensional growth, the linear model for pH is employed for simplicity. Here, $\alpha_2$
conveys the pH of the bulk solution and $\alpha_1$ describes how the pH of the pit electrolyte
varies with depth. For example, Cavanaugh [10] noticed that both extremely low
and extremely high pH in the bulk solution caused uniform corrosion in AA7075;
then, by choosing $\alpha_2 >> \alpha_1$, $P_{\text{prop}}$ is largely dependent upon the term $\left(1 - \frac{\zeta d}{d_{\text{max}}}\right)$
and is greatest at the metal surface, inducing uniform corrosion. Subsurface and
undercutting pit shapes can be expected when pH is moderately acidic or basic. By
choosing $\alpha_2 << \alpha_1$, $P_{\text{prop}}$ takes on a more pronounced parabolic dependence on pit
depth. In this case, $P_{\text{prop}}$ is smallest at the metal surface and, depending on the
choice of $\zeta$, is greatest somewhere between the surface and the maximum depth of
the metal. Pits formed under these conditions are small at the mouth of the pit and are encouraged to grow larger beneath the surface, where the pit chemistry is sufficiently aggressive.

As mentioned in Chapter I, Cavanaugh [10] showed that chloride concentration induced little to no effect on the evolution of pits in AA7075 and seemed to only influence pit initiation. Of course, the presence of chloride within the pit maintains the aggressiveness and electroneutrality of the solution, allowing for the dissolution process to continue; however, Cavanaugh found that pH and temperature had the greatest effect on pit depth and diameter. As such, the chloride concentration within the pit is not factored into $P_{prop}$. 
CHAPTER III
MODEL IMPLEMENTATION

3.1 Algorithm for the Metastable Pit Initiation Scheme

At initialization, the grid $G_{init}$ is formed by a two-dimensional matrix with all entries having value 1. Applied potential, temperature, and the chloride concentration of the solution are given as functions of matrix index. At time step $t_n$, the following sequence is implemented for each metal cell $c_{1,j,k}$:

1. If $c_{1,j,k}$ is not included in the list of cells under protection by the exclusion zone, steps (2) through (4) are taken. If $c_{1,j,k}$ is a protected cell, steps (2) through (4) are not taken.

2. The probability $P_{init}$ is calculated according to the applied potential $E_{1,j,k}$, as well as the temperature $T_{1,j,k}$, and chloride concentration $[Cl^-]_{1,j,k}$ of the solution covering the metal cell.

3. A random number $x \in [0, 1]$ is generated using Mathematica’s pseudorandom number generator.

4. If $x < P_{init}$, the state of $c_{1,j,k}$ is changed to state solution, i.e.

   
   $$s(c_{1,j,k}, t_{n+1}) = 0,$$

   and the cells within $N_{exclusion}(c_{1,j,k})$ are added to the list of protected cells.
3.2 Algorithm for the Stable Pit Propagation Scheme

At initialization, the grid $G_{prop}$ is formed by a three-dimensional matrix with all entries having value 1 except for entry $\{1, \frac{j_{max}}{2}, \frac{k_{max}}{2}\}$ which has value 0 to represent the initialized stable pit. As such, this scheme isolates the growth of one stable pit.

At time step $t_n$, the following sequence is implemented:

1. The position of all 0’s within the matrix are found, i.e. the positions of all cells in state solution.

2. The neighborhood $N_{prop}$ for each solution cell is determined, and all neighbors in state metal are extracted. This step amounts to finding all metal cells which belong to a pit edge.

3. For each metal cell $c_{i,j,k}$ belonging to a pit edge,
   
   (a) $P_{prop}$ is calculated according to the pH and temperature prescribed.

   (b) A random number $x \in [0, 1]$ is generated using Mathematica’s pseudorandom number generator.

   (c) If $x < P_{prop}$, the state of $c_{i,j,k}$ is changed to state solution, i.e. $s(c_{i,j,k}, t_{n+1}) = 0$. 

CHAPTER IV
RESULTS

The grid $G$, which is the total electrode studied in this paper, is representative of a 1 cm$^3$ sample of AA7075 covered by a thin layer of chloride-containing solution. In each of the two schemes, pitting in only a subsection of the total grid is investigated, as use of the total grid in these schemes is too computationally demanding for the model in its current state.

4.1 Metastable Pit Initiation Scheme

By examining the average pit radius at the peak pit current given by Pride et al. [11], the size of each cell is chosen to be $1.1765 \times 10^{-6}$ m by $1.1765 \times 10^{-6}$ m, with the total grid $G_{init}$ being 850 by 850 cells. As such, $G_{init}$ represents a 1 mm$^2$ sample of AA7075, only one-one hundredth of the surface of the grid $G$. In each of the following studies, seven trials of the scheme are implemented, and the number of (meta)stable pits generated across the trials are presented as an average. The results of each study ought to be interpreted as one-one hundredth of the total number of (meta)stable pits formed on the total grid $G$.

Table 4.1 provides the values of $A_s$, $\delta t$, $W_{max}$, $C_P$, $C_E$, $C_1$, and $C_2$ in (2.3), as well as $A$ and $B$ in (2.2), which remain constant across all studies given in this
section. The number of metastable pits $M_n$ that must form at time step $t_n$ within $N_{pits}$ in order for a stable pit to form is chosen to be 5 for all studies and is also listed in Table 4.1. In this section, a base study is first given and is used to calibrate the size of the neighborhood $N_{pits}$. Several additional studies are performed in order to test the influence of environmental effects on metastable and stable pit generation.

Table 4.1: Constant parameters for all initiation studies.

<table>
<thead>
<tr>
<th>Parameter Values</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s$ ($cm^2$)</td>
<td>$1.3842 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\delta t$ (seconds)</td>
<td>50</td>
</tr>
<tr>
<td>$W_{max}$ ($pits/cm^2/day$)</td>
<td>2,700,000</td>
</tr>
<tr>
<td>$C_P$</td>
<td>0.8539</td>
</tr>
<tr>
<td>$C_E$</td>
<td>264.5690</td>
</tr>
<tr>
<td>$C_1$</td>
<td>-160.6738</td>
</tr>
<tr>
<td>$C_2$</td>
<td>-0.1737</td>
</tr>
<tr>
<td>$A$</td>
<td>-0.7635</td>
</tr>
<tr>
<td>$B$</td>
<td>0.0250</td>
</tr>
<tr>
<td>$M_n$ (metastable pits)</td>
<td>5</td>
</tr>
</tbody>
</table>

4.1.1 Base Study

In order to determine the size of the neighborhood $N_{pits}$, a base study, which references a study given by Colwell [22], is performed. Table 4.2 gives the values of
environmental effects used for this study along with the equation for the projected number of metastable pits per mm\(^2\) over \(t\) seconds determined by Colwell using Cavanagh’s data [10, 22].

Table 4.2: Environmental effects and projected number of events for base initiation study.

<table>
<thead>
<tr>
<th>Base Study</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{1,j,k}(V_{SCE}))</td>
<td>-0.750</td>
</tr>
<tr>
<td>([\text{Cl}^-]_{1,j,k}(M))</td>
<td>0.1</td>
</tr>
<tr>
<td>(T_{1,j,k}(^{\circ}\text{C}))</td>
<td>25</td>
</tr>
<tr>
<td><strong>Metastable Events</strong></td>
<td>(0.3460t^{0.987})</td>
</tr>
</tbody>
</table>

In Colwell’s research, the set of values given in Table 4.2 yields 217 stable pits per cm\(^2\) over 2000 seconds; hence, the neighborhood \(N_{pits}\) is chosen such that the scheme produces an average of two stable pits in the same time frame. After several implementations of the model with various neighborhood dimensions, the radius \(R\) of \(N_{pits}\) is determined to be 90 cells. Figure 4.1 depicts an example of the affected metal surface in the base study.

The base study is conducted seven times for 2000 seconds each, and the average number of metastable and stable pits is determined. Table 4.3 provides the average number of events along with the standard deviations. The results closely
Figure 4.1: Affected metal surface for base study after 2000 seconds. The scheme produces 610 metastable pits (small white blocks) and 3 stable pits (large white blocks) on the 1 mm\(^2\) grid. The size of the stable pits represented in the figure is not intended to convey the true size of the pit; rather, it is assumed that the stable pit lies somewhere within the region. The axes \(j\) and \(k\) are the indices of cell \(c_{1,j,k}\).

match those of Colwell, which predict roughly 627 metastable pits and 2 stable pits in 2000 seconds.
Table 4.3: Results of the Base Study. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm²</td>
<td>630.3</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
<td>21.49</td>
</tr>
<tr>
<td>Average Stable Pits per mm²</td>
<td>2.29</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
<td>0.88</td>
</tr>
</tbody>
</table>

4.1.2 Case Studies

In each of the following case studies, $N_{pits}$, and thus, $N_{exclusion}$, is a radius-90 Moore neighborhood based on the results of the base study.

**Case 1: Constant Potential, Chloride Concentration, and Temperature**

Similar to the base case, this study holds all environmental influences constant across the surface. Two different scenarios are investigated, and the results are compared to those of Colwell [22] that reflect pit generation in the same environments. Table 4.4 provides the environmental data for each scenario, as well as Colwell’s equations for the projected number of metastable pits per mm² over $t$ seconds.

The results of Scenarios 1 and 2 are presented in Tables 4.5 and 4.6, respectively. In the first scenario, Colwell’s model predicts about 272 metastable pits and 5 stable pits. The presented model generates roughly the same number of metastable pits; however, the model does not produce any stable pits in this scenario. The dis-
Table 4.4: Environmental effects and projected number of events for initiation Case 1.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$E_{1,j,k}$ (V$_{SCE}$)</th>
<th>[Cl$^-$<em>1]$</em>{1,j,k}$ (M)</th>
<th>$T_{1,j,k}$ (°C)</th>
<th>Metastable Events</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.765</td>
<td>0.1</td>
<td>25</td>
<td>1.898216$t^{0.653}$</td>
</tr>
<tr>
<td>2</td>
<td>-0.750</td>
<td>0.1</td>
<td>0</td>
<td>0.1$t$</td>
</tr>
</tbody>
</table>

crepancy in the number of stable pits is likely due to the low number of metastable pits formed. Colwell’s model considers only the time at which metastable events occur in order to determine the formation of stable pits; as the presented model considers both the time and the location of metastable events, it is apparent that metastable pits can not form close enough in time and space for stable pit growth to occur. Similarly, for the second scenario, Colwell expects 200 metastable pits and 5 stable pits; the number of metastable pits generated by the presented model coincides with Colwell’s findings, but the number of stable pits does not. The absence of stable pits in both scenarios is plausible due to the low potential across the surface; in the first scenario, the potential $E_{1,j,k}$ is much lower than the pitting potential $E_{pit}$ for all $j$ and $k$, and in the second scenario, the low temperature raises $E_{pit}$ [8], although this phenomenon is not factored into the formulation of $E_{pit}$ explicitly. Since pit initiation is ohmic controlled, the metastable pits formed in both of these scenarios would require large current densities or resistance to achieve the pitting potential and enter stable growth.
Table 4.5: Results of initiation Case 1: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 1: Scenario 1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm²</td>
<td>273.3</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
<td>8.83</td>
</tr>
<tr>
<td>Average Stable Pits per mm²</td>
<td>0</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.6: Results of initiation Case 1: Scenario 2. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 1: Scenario 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm²</td>
<td>210.7</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
<td>13.73</td>
</tr>
<tr>
<td>Average Stable Pits per mm²</td>
<td>0</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
<td>0</td>
</tr>
</tbody>
</table>
Case 2: Varying Potential with Constant Chloride Concentration and Temperature

In this study, the potential distribution across the surface metal is given as a function of space according to

\[ E_{1,j,k} = \beta_E \left( \frac{j - j_{\text{max}}}{2} - \frac{k - k_{\text{max}}}{2} \right) - (E_{\text{pit}} + h_E) \] (4.1)

where \( \beta_E \) and \( h_E \) are parameters. Defining the potential distribution in this way allows for the examination of (meta)stable pit generation across a surface that has regions with potential above and below the pitting potential \( E_{\text{pit}} \). The parameters \( \beta_E \) and \( h_E \) are chosen so that, in the first scenario, most of the surface is assigned potentials below \( E_{\text{pit}} \) and, in the second scenario, most of the surface is assigned potentials above \( E_{\text{pit}} \). In this way, the two scenarios reflect that \( P_{\text{init}} \) is a sigmoidal function of applied potential, a notion that is supported throughout literature [19, 20, 21, 22]. In the first scenario, because most of the surface is assigned potentials below \( E_{\text{pit}} \), (meta)stable pits are expected to form only in the small region of the surface where the applied potential is greater than \( E_{\text{pit}} \). In the second scenario, because most of the surface is assigned potentials above \( E_{\text{pit}} \), (meta)stable pits are expected to form over the majority of the surface.

Table 4.7 presents the values for \( \beta_E \) and \( h_E \) used in each scenario, as well as the chloride concentration and temperature. Because the form of (4.1) is also used in Cases 3 and 4 to describe the distribution of chloride concentration and temperature, Figure 4.2 is provided to illustrate the general shape of the distributions for each
of the cases. The results of Scenarios 1 and 2 are presented in Tables 4.8 and 4.9, respectively.

![Figure 4.2](image)

Figure 4.2: The general shape of the distribution of environmental influences across the surface metal. The $z$-axis corresponds to potential, chloride concentration, and temperature in Cases 2, 3, and 4 respectively.

Due to the dependence of the pitting potential on the chloride concentration of the solution by (2.2), and since both scenarios hold $[\text{Cl}^-] = 0.1 \ M$, $E_{pit} = -0.706 \ V$ in both scenarios. In the first scenario, the maximum potential on the surface is $-0.600 \ V_{SCE}$, but the vast majority of the surface is assigned a potential below $E_{pit}$. Thus, the first scenario exhibits a cluster of pits in a small circular region of the surface, as shown in Figure 4.3. It is apparent from Figure 4.4 that in this region, the potential is greater than $E_{pit} - 0.100 \ V$ and outside of this region, the potential
Table 4.7: Environmental effects and values of $\beta_E$ and $h_E$ in (4.1) for initiation Case 2.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$\beta_E$</th>
<th>$h_E$</th>
<th>$[\text{Cl}^-]_{1,j,k}$ ($M$)</th>
<th>$T_{1,j,k}$ ($^\circ C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-3 \times 10^{-6}$</td>
<td>1.306</td>
<td>0.1</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>$-1.5 \times 10^{-6}$</td>
<td>1.206</td>
<td>0.1</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 4.8: Results of initiation Case 2: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 2: Scenario 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm$^2$</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
</tr>
<tr>
<td>Average Stable Pits per mm$^2$</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
</tr>
</tbody>
</table>
Table 4.9: Results of initiation Case 2: Scenario 2. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 2: Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm$^2$</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
</tr>
<tr>
<td>Average Stable Pits per mm$^2$</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
</tr>
</tbody>
</table>

is less than $E_{pit} - 0.100 \, V$. As mentioned, the surface is dichotomized into regions where pits form and where pits do not form due to the sigmoidal profile of $P_{init}$. A contour plot of $P_{init}$ for this scenario, given in Figure 4.5, demonstrates this sigmoidal profile. In some trials, stable pits appeared near the center of the region; however, few trials exhibited stable pits. Similar to Case 1, the low number of metastable events coupled with the confinement of events to a small area can explain the scarcity of stable pitting in this scenario.

In the second scenario, the maximum potential on the surface is -0.500 $V_{SCE}$, and the potential of the majority of the surface is above $E_{pit}$, as shown in Figure 4.6. Pits in this scenario form in a large circular region, which occupies most of the surface. The potential distribution in this scenario yields results similar to those of the base study, with every trial producing stable pits. However, despite the potential
Figure 4.3: Affected surface in Case 2: Scenario 1. In this example, 165 metastable pits and zero stable pits formed in the 2000 second simulation on the 1 mm$^2$ grid.
Figure 4.4: Contour plot indicating the value of the applied potential at cell $c_{1,j,k}$ for all $j$ and $k$ in initiation Case 2: Scenario 1.
Figure 4.5: Contour plot indicating the value of $P_{\text{init}}$ at cell $c_{1,j,k}$ for all $j$ and $k$ in initiation Case 2: Scenario 1.
exceeding $E_{\text{pit}}$ across much of the surface, fewer pits are observed in this scenario than in the base study, as $P_{\text{init}}$ is relatively the same for potentials very close to $E_{\text{pit}}$, like in the base study, and for potentials exceeding $E_{\text{pit}}$. Moreover, the regions of the surface which are insusceptible to pitting because of low potential decrease the number of pitting events in this scenario; this is supported by the relationship (1.3) found by Williams et al. [17], which implies that the frequency of stable pitting events is proportional to sample area.

**Case 3: Varying Chloride Concentration with Constant Potential and Temperature**

In this study, the distribution of the chloride concentration in the solution covering the metal surface is given as a function of space according to

$$[\text{Cl}^-]_{1,j,k} = \beta_{\text{Cl}} \left( j - \frac{j_{\text{max}}}{2} \right) - \left( k - \frac{k_{\text{max}}}{2} \right) + h_{\text{Cl}}$$

where $\beta_{\text{Cl}}$ and $h_{\text{Cl}}$ are parameters, as in Case 2. The values of $\beta_{\text{Cl}}$ and $h_{\text{Cl}}$ are chosen so that, in the first scenario, the range of concentration is small and is centered around 0.1 $M$, while in the second scenario, the range of concentration is larger, extending up to 0.6 $M$. In this way, the first scenario demonstrates the influence of chloride concentration in (meta)stable pitting, particularly its influence on $E_{\text{pit}}$. Pits formed in this scenario are expected to be located in regions of the surface where the concentration is greater than 0.1 $M$, as $E_{\text{pit}}$ is closer to the applied potential $E$ in these regions. The second scenario is intended to demonstrate the sigmoidal profile of $P_{\text{init}}$, shown in Figure 4.7. The distribution of pits in this scenario is expected to
Figure 4.6: Contour plot indicating the value of the applied potential at cell $c_{1,j,k}$ for all $j$ and $k$ in initiation Case 2: Scenario 2.
be uniform in regions of the surface subjected to chloride concentrations greater than 0.1 \( M \), with very little pitting outside of this region.

Figure 4.7: Plot of \( P_{\text{init}} \) verses chloride concentration for initiation Case 3. Here, \( E_{1,j,k} = -0.750 \ V_{SCE} \) and \( T_{1,j,k} = 25 ^{\circ}C \) for all \( j \) and \( k \).

Table 4.10 presents the values for \( \beta_{Cl} \) and \( h_{Cl} \) used in each scenario, as well as the applied potential and temperature. As mentioned, the general shape of the distribution of chloride concentration is depicted in Figure 4.2. The results of Scenarios 1 and 2 are presented in Tables 4.11 and 4.12, respectively.

The chloride concentration of the solution ranges from 0 \( M \) to 0.15 \( M \) in the first scenario, with much of the solution having a chloride concentration greater than 0.05 \( M \). In this scenario, metastable pits mostly form in regions of the surface where the chloride concentration is greater than 0.1 \( M \). Considering that the
Table 4.10: Environmental effects and values of $\beta_{CI}$ and $h_{CI}$ in (4.2) for initiation Case 3.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$\beta_{CI}$</th>
<th>$h_{CI}$</th>
<th>$E_{1,j,k}$ ($V_{SCE}$)</th>
<th>$T_{1,j,k}$ ($^\circ C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-6.5 \times 10^{-7}$</td>
<td>0.15</td>
<td>-0.750</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>$-3.5 \times 10^{-6}$</td>
<td>0.65</td>
<td>-0.750</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 4.11: Results of initiation Case 3: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 3: Scenario 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm$^2$</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
</tr>
<tr>
<td>Average Stable Pits per mm$^2$</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
</tr>
</tbody>
</table>
Table 4.12: Results of initiation Case 3: Scenario 2. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 3: Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average Metastable Pits per mm$^2$</strong></td>
</tr>
<tr>
<td><strong>Metastable Pit Standard Deviation</strong></td>
</tr>
<tr>
<td><strong>Average Stable Pits per mm$^2$</strong></td>
</tr>
<tr>
<td><strong>Stable Pit Standard Deviation</strong></td>
</tr>
</tbody>
</table>

Pitting potential depends on the chloride concentration, parts of the surface where the concentration is low have relatively high pitting potentials while places where the concentration is high have relatively low pitting potentials. Apparent from Figure 4.7, the difference between $P_{init}$ for 0.1 $M$ chloride concentration and 0.15 $M$ concentration is very small, which explains why the distribution of metastable pits in areas of the surface where $[Cl^-] \geq 0.1$ $M$ is more or less the same. In trials where stable pits formed, the pits appeared closer to the edge of the pitted region, as in Figure 4.8, although this occurrence may be coincidental considering the mostly uniform distribution of metastable pits.

In the second scenario, the chloride concentration ranges from 0 $M$ to 0.6 $M$ where the majority of the surface is subjected to chloride concentration greater than 0.1 $M$. Similar to the results of the first scenario, metastable pits are more or less
uniformly distributed in the region of the surface where \([\text{Cl}^-] \geq 0.1\ M\) due to the structure of (2.3). These results are supported by those of Cavanaugh [10], which report that the relationship between the number of metastable events and time is similar for metal exposed to 0.1 \(M\) NaCl solution and 0.6 \(M\) NaCl solution. Stable pitting in this scenario is expected since the potential of the system is close to or exceeds \(E_{\text{pit}}\) where the molarity of the solution is greater than 0.1 \(M\).

Figure 4.8: Affected surface in Case 3: Scenario 1. In this example, 296 metastable pits and one stable pit formed in the 2000 second simulation on the 1 mm\(^2\) grid.
Case 4: Varying Temperature with Constant Potential and Chloride Concentration

In this study, the distribution of the temperature across the surface metal is given as a function of space according to

\[ T_{1,j,k} = \beta_T \left( \left( j - \frac{j_{\text{max}}}{2} \right) - \left( k - \frac{k_{\text{max}}}{2} \right) \right) + h_T \]  

(4.3)

where \( \beta_T \) and \( h_T \) are parameters chosen so that temperature ranges from 0°C to 40°C across the surface in the one scenario presented in this case. This temperature range is chosen because it captures the majority of the temperature range investigated by Cavanaugh [10]. Pits in this scenario are expected to form across the entire surface, with a noticeable increase in (meta)stable pit density as the temperature increases from 0°C to 40° due to the relationship between temperature and \( E_{\text{pit}} \) described by Soltis et al. [8].

Table 4.13 presents the values for \( \beta_T \) and \( h_T \) used in this scenario, as well as the applied potential and chloride concentration, and Table 4.14 gives the results for average number of (meta)stable pits and standard deviations. As opposed to Cases 2 and 3, in which pitting is sequestered to a region of the surface, pitting is observed across the entire surface in Case 4, but a tiering in the density of metastable pits on the surface is noticeable. Most of the metastable pits form when the temperature is above 20°C, with the density of pitting tapering down as the temperature decreases toward 0°C. Further, stable pits appeared in the regions of the surface with temperature between 20°C and 40°C. These observations agree with those of Soltis et al. [8] that
cite a linearly decreasing relationship between temperature and $E_{pit}$, compelling pits to nucleate where temperature is relatively high. Moreover, these results compare to those of Cavanaugh [10] who found an exponentially increasing relationship between temperature and metastable pit initiation rate.

Table 4.13: Environmental effects and values of $\beta_T$ and $h_T$ in (4.3) for initiation Case 4.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>$\beta_T$</th>
<th>$h_T$</th>
<th>$E_{1,j,k} (V_{SCE})$</th>
<th>$[\text{Cl}^-]_{1,j,k} (M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-2.5 \times 10^{-4}$</td>
<td>40</td>
<td>-0.750</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 4.14: Results of initiation Case 4: Scenario 1. The average number and standard deviation of metastable and stable pits formed in 2000 seconds across seven trials is presented.

<table>
<thead>
<tr>
<th>Case 4: Scenario 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Metastable Pits per mm$^2$</td>
</tr>
<tr>
<td>Metastable Pit Standard Deviation</td>
</tr>
<tr>
<td>Average Stable Pits per mm$^2$</td>
</tr>
<tr>
<td>Stable Pit Standard Deviation</td>
</tr>
</tbody>
</table>
4.1.3 Discussion

The results of the case studies demonstrate that the initiation scheme presented in this work holds promise in simulating the formation of (meta)stable pits in AA7075. In Case 1, the number of metastable pits generated by the model reflects the findings of Colwell [22] and Cavanaugh [10]. Further, in Cases 2, 3, and 4, the results of the model adhere to phenomena supported throughout literature, such as the influence of chloride concentration on pitting occurrence. The model is limited in the manner with which the locations of stable pits are chosen. The number of metastable pits \( M_n \) that must form in \( N_{pits} \) is assumed to be five; however, there exists little evidence in literature of the true number of metastable pits that must form in a given area over a given time for a stable pit to grow. Moreover, because Colwell’s prediction of the number of stable pits in the Base Study and Case 1 are not validated by Cavanaugh’s work, the size of \( N_{pits} \) may be inaccurate as well. The model may be improved by using experimental data for the calibration of \( M_n \) and \( N_{pits} \).

4.2 Stable Pit Propagation Scheme

As in the initiation scheme, \( \Delta j \) and \( \Delta k \) are \( 1.1765 \times 10^{-6} \) m for each cell, while, for this scheme, \( \Delta i \) is chosen to be \( 1.0000 \times 10^{-7} \) m. The grid \( G_{prop} \) is 150 by 200 by 200 cells, representing a subsection of the bulk metal, roughly 15 \( \mu m \) by 350 \( \mu m \) by 350 \( \mu m \), where only one stable pit may grow. Three cases are presented in this section, with each case demonstrating pit shapes produced by different environments. Wherever
possible, results are compared to those of Cavanaugh [10], who reported depths and diameters of pits grown in AA7075 under various environmental conditions.

4.2.1 Case Studies

In each of the following case studies, the magnitudes of $\alpha_1$ and $\alpha_2$ in (2.5) are chosen based on preliminary sensitivity analysis of the propagation scheme, which provided insight into the appropriate order of magnitude for these parameters. Moreover, the temperature of the system in each of the following cases is assumed to be $25^\circ C$ and the time step $\delta t$ is 2 seconds.

Case 1: Undercutting Shape

The undercutting pit shape is expected to develop in bulk solutions where pH is moderately acidic or basic due to the results of Cavanaugh [10], which indicate that no uniform corrosion is evident in this pH range and pits are modestly sized. As mentioned in Chapter II, this pit shape corresponds to $\alpha_2 << \alpha_1$ in (2.5) so that the probability of metal dissolution is smallest at the mouth of the pit, thereby avoiding uniform corrosion. The value of the parameter $\zeta$, which controls the influence of the potential drop in the pit, is chosen based on the expected pit shape. Since pits that display the undercutting shape tend to be smaller in depth than in width, the potential drop within the pit is smaller compared to pits that are more deep than wide. Table 4.15 provides the values of $\alpha_1$, $\alpha_2$, and $\zeta$ used in this case study, and Figures 4.9a and 4.9b depict the pit formed using the model.
Figure 4.9: 3-D (a) and 2-D (b) depictions of simulated pit in propagation Case 1 after 3 hours of growth. The pit is approximately $6.7 \, \mu m$ in depth and $114 \, \mu m$ in diameter at its largest.
Table 4.15: The values of $\alpha_1$, $\alpha_2$, and $\zeta$ in (2.5) used in propagation Case 1.

<table>
<thead>
<tr>
<th>Parameter Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
</tr>
<tr>
<td>$\alpha_2$</td>
</tr>
<tr>
<td>$\zeta$</td>
</tr>
</tbody>
</table>

The pit grown in this simulation displays the general undercutting shape, and is indeed much larger in diameter than in depth, supporting the original assumption about the pit’s dimensions. In her work, Cavanaugh [10] found the following relationship between pH, temperature, time of growth, and maximum pit depth:

$$d = 4.8 t^b,$$

(4.4)

where the depth $d$ is given in $\mu$m, the time $t$ is given in hours, and

$$b = 0.3 - 0.006 T + 0.07 pH + (6 \times 10^{-5}) T^2 - 0.006 pH^2,$$

(4.5)

with the temperature $T$ in $^\circ$C. Using equation (4.4) to solve for the time exponent $b$ with the depth of the simulated pit and then equation (4.5) to determine the pH, the bulk solution in Case 1 is 2 pH or 9 pH assuming the temperature of the system is 25$^\circ$C. These results somewhat coincide with the expectations of the bulk solution pH for this pit shape, although the expected pH was more basic.
Case 2: Subsurface Shape

Similar to the first case, the subsurface pit shape is expected to develop in moderately acidic or basic solutions. As such, $\alpha_1$ is chosen to be greater than $\alpha_2$ so that uniform corrosion is inhibited. The value of the parameter $\zeta$ in this case is selected to be larger than the value of $\zeta$ in the first case, since the diameter of subsurface pits is usually greater than the depth, with both dimensions being rather large. In this way, the potential drop within the pit becomes more significant in determining pit morphology. Table 4.16 gives the values of $\alpha_1$, $\alpha_2$, and $\zeta$ used in this study, and Figures 4.10a and 4.10b depict the simulated pit.

Table 4.16: The values of $\alpha_1$, $\alpha_2$, and $\zeta$ in (2.5) used in propagation Case 2.

<table>
<thead>
<tr>
<th>Parameter Values</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>$-1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The pit grown in this case is spherical in shape, like most subsurface pits, with the diameter of the pit being larger than the depth. However, the time exponent $b$, determined using equation (4.4) with the depth of the simulated pit, does not coincide with any value reported by Cavanaugh. Rather, the closest pH and temperature couple that produces a time exponent close to $b$ for this case is 6 pH and 0°C. This may be attributed to the magnitude of $\alpha_1$, which is most likely too large, causing
Figure 4.10: 3-D (a) and 2-D (b) depictions of simulated pit in propagation Case 2 after 3 hours of growth. The pit is approximately 11 µm in depth and 250 µm in diameter.
the pit to grow fast. Indeed, most pits are presumed to grow at a rate \( t^{1/2} \) during diffusion controlled growth [1], while, in this case, the time exponent is around 0.75.

**Case 3: Uniform Corrosion**

According to the results of Cavanaugh [10], uniform corrosion is evident in environments where the bulk solution has high pH. Then, in this case, \( \alpha_1 \) is chosen to be much smaller than \( \alpha_2 \), which describes the high bulk pH, and \( \zeta \) is chosen to be the same as in Case 2 so that the “pit” corrodes both uniformly across the surface as well as in depth. Table 4.17 gives the values of \( \alpha_1 \), \( \alpha_2 \), and \( \zeta \) used in this study, and Figures 4.11a and 4.11b depict the simulated pit.

Table 4.17: The values of \( \alpha_1 \), \( \alpha_2 \), and \( \zeta \) in (2.5) used in propagation Case 3.

<table>
<thead>
<tr>
<th>Parameter Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 )</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
</tr>
<tr>
<td>( \zeta )</td>
</tr>
</tbody>
</table>

It is apparent that some uniform corrosion occurs within the simulation and that, in addition, a pit also forms. The appearance of this pit beneath the uniform corrosion is most likely due to the structure of \( P_{\text{prop}} \), which, for the values given in Table 4.17, is greatest at the mouth of the pit and decreases with pit depth. This phenomenon, however, is not unlike the results Cavanaugh [10] obtained in her work. For samples of AA7075 exposed to solutions with high pH, Cavanaugh found that
Figure 4.11: 3-D (a) and 2-D (b) depictions of simulated pit in propagation Case 3 after 3 hours of growth. The pit is approximately $6 \, \mu m$ in depth and $265 \, \mu m$ in diameter. Nearly $2.45 \times 10^5 \, \mu m^3$ of the affected sample is dissolved due to uniform corrosion and is not included in determining the depth or diameter of the resulting pit.
severe uniform corrosion occurs so that, although pit depth does not decrease, the surface from which the pit depth is measured recedes with time [10]. In this way, Cavanaugh finds that the value of time exponent $b$ in (4.4) is skewed by the uniform corrosion, causing $b$ to be smaller than it should be. Indeed, using equation (4.4) to solve for the time exponent $b$ with the depth of the simulated pit and then equation (4.5) to determine the pH, the bulk solution in the simulation is 12 pH, coinciding with Cavanaugh’s result that 12.5 pH induces uniform corrosion. If the depth of the uniform corrosion is included in the depth of the pit, equation (4.4) yields that the time exponent is double the value of the time exponent found when only the pit depth was considered. In fact, the time exponent determined using both the depth of the uniform corrosion and the depth of the pit is close to 0.5, which is congruent with most pit growth kinetics reported in the literature.

4.2.2 Discussion

Although the present model is capable of producing pit morphologies seen in nature, there is much room for improvement. Given the lack of experimental data used to calibrate the model, many assumptions are made about the conditions under which pits take on particular shapes. Among the three cases performed in this study, only the conditions under which uniform corrosion occurs are supported by experimental evidence. Hence, further experimental studies would need to be conducted in order to improve the model in this regard. The structure of $P_{prop}$ could also be revised in order to include a dependence on temperature, as Cavanaugh [10] found that temperature
plays a significant role in pit growth. Moreover, the depth \( d \) in (2.3) should be replaced by the actual distance of the cell from the pit mouth. In this way, the pH and potential at the cell’s position is more accurately reflected. Finally, the algorithm of the model must be improved in order to make the simulation practical for use. The model, as it stands, is computationally demanding and requires a significant amount of time (roughly one to four days on a Dell Precision T7910 with an Intel Xeon CPU E5-2687W v3 @ 3.10GHz processor and 64-bit operating system) to simulate growth. With the aforementioned improvements, however, the model would be a useful tool in simulating three-dimensional pits, which may be employed in various academic and industrial studies.
CHAPTER V

CONCLUSION

The model presented in this work seeks to simulate the initiation and propagation of localized pits in AA7075 using a cellular automata approach. The motivation behind the model is the monetary and temporal costs associated with studying the behavior of pitting experimentally, along with the difficulty of testing factors such as the loading required for fatigue crack initiation in small pits. The metal AA7075 is chosen because of its relevance to aircraft structures; the model provides a means of predicting (meta)stable pit generation and growth in this metal.

The approach used in this model to simulate pit initiation and propagation is unique compared to other approaches in the literature. In the initiation model, the grid of the cellular automata is a two-dimensional lattice of square cells in which metastable pits form with a probability \( P_{\text{init}} \) at each time step. The probability \( P_{\text{init}} \) depends on several environmental variables, including applied potential, temperature, and the concentration of chloride in the bulk solution. The formation of stable pits in this scheme is determined by the proximity in time and space of metastable events.

In the propagation scheme, one stable pit is grown over a three-dimensional grid of cells. The stable pit is initiated at time \( t = 0 \), and cells which comprise the pit edges are dissolved with a probability \( P_{\text{prop}} \) at each time step. The probability of dissolution
takes into account the pH of the bulk solution as well as the influence of the potential drop within the pit.

Several different case studies for each of the two schemes are presented in Chapter IV, and the results suggest that the model is capable of reproducing the number of metastable pits formed under different environmental conditions in experimental studies and is able to create several different pit shapes. The model is limited, however, by the lack of experimental data available to calibrate the model. Cavanaugh’s work [10] is relied upon heavily for validation of the model, but many of the case studies performed in this work are not comparable to any of Cavanaugh’s studies, making it difficult to determine the validity of the results presented in Chapter IV. In addition to the lack of experimental validation, the model is limited by:

- the procedure used to determine the locations of stable pits,
- the neglect of temperature in the calculation of $P_{prop}$,
- the choice of the depth $d$ used to calculate $P_{prop}$,
- and the computational inefficiency of the propagation scheme.

Improving the above limitations would drastically increase the value of the presented model. For example, incorporating a temperature dependence in $P_{prop}$ would allow for a more in-depth analysis of pit morphology under different environmental conditions, since Cavanaugh [10] found temperature, along with pH, to be the most influential factor in pit growth. Another important factor in the pitting of aluminum alloys that is neglected in this work for simplicity is the microstructure of the metal; intermetallic...
particles have been shown [10] to play a significant role in pit initiation and, to some extent, in pit growth. Intermetallic particles could be incorporated into the model by introducing a third cell state, which represents these particles and is distributed throughout the bulk metal. Because increasing the number density of intermetallic particles also increases pit initiation rate [10], the transition rule for the initiation scheme could be adjusted so that the probability of initiation is greater at or near these particles.
BIBLIOGRAPHY


APPENDIX

MATHEMATICA CODE

(* Illustrating Pit Initiation and Evolution in Aluminum Alloys
According to a 3-Dimensional Cellular Automata Based Model *)
(* Code for the Initiation Scheme *)

(* Constant Parameters *)
A = -0.7635;
B = 0.0250;
cP = .8539;
cE = 264.5690;
c1 = -160.6738;
c2 = -.1737;
wmax = 2700000(* rate of pits/cm^2/day *);
surfaceArea = 1.5376*^-8 (* cm^2 *);
timestep = 50;(* seconds *)

(* Parameters for Potential (E), Chloride Concentration (Cl),
and Temperature (T) Distributions *)
(* As shown, letting betaX = 0 makes the distribution constant *)
hE = -0.750;
betaE = 0;
hCl = 0.1;
betaCl = 0 ;
hT = 25;
betaT = 0;

(* Duration of experiment *)
time = 2000; (* seconds *)
Nsteps = IntegerPart@Floor@(time/timestep);
(* number of time steps the CA-based model is evaluated for *)

(* Variables needed for creation of CA *)
sizeHorizontal = 850; (* number of rows and columns *)
sizeVertical = 1; (* grid depth *)
searchDistance = 90; (* Radius of N_pits *)

(* Preallocation *)
protectedCells = {};(* list that contains all proteced cells
where no new pit can be initiated *)
pitsCurrentTime = {}; (* list of all cells that have
become the site of a metastable pit at the current time step *)
stablePits = {}; (* list of cells which are the site of a stable pit *)
numberOfPits = {};

(* Neighborhood definitions *)
neighborhoodPits = Tuples[Range[-searchDistance, searchDistance, 1], 2];
(* neighborhood to find nearby pits and create protection *)
neighborhoodIsol = {{0, 1}, {0, -1}, {1, 0}, {-1, 0}};
(* neighborhood to look for metal unattached to the bulk *)
neighborhoodLights = Drop[Tuples[{0, 1, -1}, 2], 1];
(* neighborhood used in creating the 2-D array of affected surface *)
neighborRule = Join[Table[i -> sizeHorizontal + i, {i, -searchDistance + 1, 0}], Table[sizeHorizontal + i -> i, {i, 1, searchDistance}]] (* to implement periodic boundary conditions *)

(* Necessary functions *)
(* Functions to create grid *)
gridInitiation = Function[{sizeH, sizeV},
  matrix = ConstantArray[1, {sizeH, sizeH}]];

(* Determining the neighborhood *)
findNeighbors = Function[{position, sizeH, neighborhood},
  neighbors = (position + #) & /@ neighborhood;
  neighbors = neighbors /. neighborRule];

(* Determine the state of a certain cell *)
cellState = Function[{position},
  matrix[[Sequence @@ position]]];

(* Changes the state of a cell from metal to solution, i.e. the metal is dissolved *)
dissolveMetal = Function[{position},
  matrix[[Sequence @@ position]] = 0];

(* Function that calculates the pitting potential Epit using chloride concentration *)
Epit = Function[{A, B, mols},
  pittingPotential = A - B*Log[mols]];

(* Function that calculates the applied potential at cell c_{1,x,y} *)
potentialDistribution = Function[{x, y, sizeH, Ep, betaE, hE},
  temp = betaE*((x - (sizeH/2))^2 + (y - (sizeH/2))^2) - (Ep - hE);
  appliedPotential = If[temp >= Ep - .2, temp, Ep - .2]];

(* Function that calculates the chloride concentration at cell c_{1,x,y} *)
chlorideDistribution = Function[{x, y, sizeH, betaCl, hCl},
  temp = betaCl*((x - (sizeH/2))^2 + (y - (sizeH/2))^2) - hCl;
  chlorideMolarity = If[temp >= 0, temp, 0];]

(* Function that calculates the temperature at cell c_{1,x,y} *)
tempDistribution = Function[{x, y, sizeH, betaT, hT},
  temp = betaT*((x - (sizeH/2))^2 + (y - (sizeH/2))^2) - hT;
  Temperature = If[temp >= 0, temp, 0];]

(* Function that calculates P_{init} for a cell c_{1,x,y} *)
initiationProbability = Function[{position, sizeH},
  coordinates = Take[position, -2];
  chlorideDistribution[Sequence @@ coordinates, sizeH, betaCl, hCl];
  Epit[A, B, chlorideMolarity];
  potentialDistribution[Sequence @@ coordinates, sizeH, pittingPotential, betaE, hE];
  tempDistribution[Sequence @@ coordinates, sizeH, betaT, hT];
  Pinit = (wmax*surfaceArea* timestep)/(86400*(1 +
    Exp[cP + cE*Max[0, pittingPotential - appliedPotential] +
    c1*chlorideMolarity + c2*(Temperature - 25)]));]

(* Function that creates new metastable pits *)
NewPit = Function[{sizeH},
  posCorrosive = Position[matrix, 1];
  Table[
    initiationProbability[posCorrosive[[i]], sizeH];
    If[RandomReal[] < Pinit,
      pitsCurrentTime = Append[pitsCurrentTime, posCorrosive[[i]]];
      numberOfPits = numberOfPits + 1;
      dissolveMetal[posCorrosive[[i]]];
      , {i, Length@posCorrosive}]];

(* Perform Simulation *)
gridInitiation[sizeHorizontal, sizeVertical];
Monitor[Do[
  (* First initiate new pits *)
  NewPit[sizeHorizontal];
  (* Next check for stable pit formation *)
  Table[
    (* Find N_pits for newly formed metastable pit c_{1,j,k} *)
    temp =
      findNeighbors[pitsCurrentTime[[i]], sizeHorizontal, neighborhoodPits];
    (* Find all neighbors that are the site of a metastable pit *)
    temp2 = Position[(cellState[#] & /@ temp), 0];
    (* Find all neighbors that are protected from pitting *)
    temp3 = Flatten[Complement[(temp[[#]] & /@ temp2),
      protectedCells], 1];
    (* If any neighbors are protected,
    this neighborhood cannot become the site of a stable pit *)
    (* If no neighbors are protected and if at least 5 newly
formed metastable pits are in $N_{\text{pits}}$, the neighborhood $N_{\text{pits}}$
becomes the site of a stable pit *)

```math
\text{temp4} = \text{Table[MemberQ[protectedCells, temp[[i]]],}
\{i, \text{Length[temp]}\};
\text{If[Count[temp4, False] == Length[temp4],}
  \text{closePits = Intersection[temp3, pitsCurrentTime],}
  \text{closePits = 0];}
\text{If[Length[closePits] >= 5,}
  \text{newlyProtected = temp;}
  \text{protectedCells = Join[protectedCells, newlyProtected];}
  \text{stablePits = Append[stablePits, pitsCurrentTime[[i]]], \{i,}
  \text{Length[pitsCurrentTime]\};}
  \text{pitsCurrentTime = {}};}
\text{, \{t, Nsteps\}, t]};
```

(* Generate 2-D array of (meta)stable pits formed in the simulation *)

(* The radius-one Moore neighborhood of each metastable pit is
changed to state solution so that the pits may be more easily viewed *)

```math
\text{Table[matrix[[Sequence @@ protectedCells[[i]]]] = 0, \{i,}
  \text{Length[protectedCells]\};}
\text{temp = Complement[Position[matrix, 0], protectedCells];}
\text{lightup = Flatten[DetermineN[#, sizeHorizontal, neighborhoodLights] & /@ temp,}
  \text{1];}
\text{Table[matrix[[Sequence @@ lightup[[i]]]] = 0, \{i, Length@lightup\};}
\text{ArrayPlot[matrix, FrameTicks -> All,}
  \text{FrameTicksStyle -> Directive[FontSize -> 20, FontFamily -> Times, Black ],}
  \text{FrameLabel -> \{j, k\},}
  \text{LabelStyle -> Directive[FontSize -> 30, FontFamily -> Times, Black ],}
  \text{RotateLabel -> False]}
```

77
(* Illustrating Pit Initiation and Evolution in Aluminum Alloys
According to a 3-Dimensional Cellular Automata Based Model *)
(* Code for the Propagation Scheme *)

(* Model parameters *)
solPercent = 0.51;
zeta = 0.50;
alpha1 = 1.5*^-4;
alpha2 = -1*^-4;

(* Duration of experiment *)
time = 18000; (* seconds *)
timestep = 2; (* seconds *)
Nsteps = IntegerPart@Floor@time/timestep;
(* number of time steps the CA-based model is evaluated for *)

(* Variables needed for creation of CA *)
sizeHorizontal = 200; (* number of rows and columns *)
sizeVertical = 150; (* grid depth *)
boundaryDistance = 4; (* used in periodic boundary conditions *)

(* Preallocation *)
diep = ConstantArray[0, Nsteps + 1]; (* the pit depth at every time step *)

(* Neighborhood definitions *)
neighborhoodProp = 
  Drop[Drop[Tuples[{0, 1, -1}, 3], 1], -9]; (* neighborhood to find pit edges *)
neighborhoodIsol = {{0, 0, 1}, {0, 0, -1}, {0, 1, 0}, {0, -1, 0}};
(* neighborhood to look for islands of metal, i.e. detached from the bulk metal *)
neighborRule = 
  Join[Table[i -> sizeHorizontal + i, {i, -boundaryDistance + 1, 0}],
    Table[sizeHorizontal + i -> i, {i, 1, boundaryDistance}]];
(* to implement periodic boundary conditions *)

(* Necessary functions *)
(* Functions to create grid *)
gridPropagation = Function[{sizeH, sizeV},
  matrix = ConstantArray[1, {sizeV, sizeH, sizeH}]];

(* Determining the neighborhood *)
findNeighbors = Function[{position, sizeH, neighborhood},
  neighbors = (position + #) & /@ neighborhood;
  neighbors = DeleteCases[neighbors, {0, _, _}];
  neighbors = DeleteCases[neighbors, {sizeVertical + 1, _, _}];
  neighbors = neighbors /. neighborRule];
(* Determine the state of a certain cell *)
cellState = Function[{position},
  matrix[[Sequence @@ position]]];

(* Changes the state of a cell from metal to solution, i.e. the metal
is dissolved *)
dissolveMetal = Function[{position},
  matrix[[Sequence @@ position]] = 0];

(* Function that initiates one stable pit *)
startedPits = Function[{sizeV, sizeH},
  matrix[[1, sizeH/2, sizeH/2]] = 0];

(* Identify cells belonging to pit edges *)
identifyProp = Function[{sizeH},
  If[Length@pits > 0,
    temp = Position[matrix, 0];
    numberOfSolutionCells = Round[Length[temp]*solPercent];
    temp = RandomChoice[temp, numberOfSolutionCells];
    temp2 = findNeighbors[#1, sizeH, neighborhoodProp] & /@ temp;
    temp3 = Table[cellState[#1] & /@ temp2[[i]], {i, Length[temp2]}];
    temp4 = Position[temp3, 1];
    temp5 = Table[temp2[[Sequence @@ temp4[[i]]]], {i, Length@temp4}];
    reacSitesProp = Union[temp5]]];

(* Function that calculates the propagation probability *)
propagationProb = 
  Function[{a1, a2, zeta, sizeV, d}, (a1*d + a2)*(1 - zeta/sizeV*d)];

(* Function that dissolves metal at pit edges *)
Reaction = Function[{alpha1, alpha2, zeta, sizeH, sizeV},
  If[Length@reacSitesProp > 0,
    Pprop = 
      Partition[
        propagationProb[alpha1, alpha2, zeta, sizeV, #] & /@ 
          reacSitesProp, 1];
    probabilities = Append[#, 1 - #[[1]]] & /@ Pprop;
    mechanism = RandomChoice[# -> {0, 1}] & /@ probabilities;
    posDisolve = Flatten@Position[mechanism, 0];
    If[Length@posDisolve > 0,
      dissolveMetal[reacSitesProp[[#]]] & /@ posDisolve]];]

(* Remove islands of metal cells *)
RemoveIsolated = Function[{sizeH, sizeV, neighborhood},
  posMetal = Position[matrix[[1 ;; 3, All, All]], 1];
  temp = findNeighbors[#1, sizeH, neighborhood] & /@ posMetal;
  temp = 
    Count[#1, 1] & /@
    Partition[cellState[#1] & /@ Flatten[temp], 3], 4];
  isol = Flatten@Position[temp, 0];
  If[Length@isol > 0,
    dissolveMetal[posMetal[[#]]] & /@ isol];
(* Perform simulation *)
gridPropagation [sizeHorizontal, sizeVertical];
startedPits [sizeVertical, sizeHorizontal];
AbsoluteTiming[Monitor[Do[
    identifyProp[sizeHorizontal];
    Reaction[alpha1, alpha2, zeta, sizeHorizontal, sizeVertical];
    RemoveIsolated[sizeHorizontal, sizeVertical, neighborhoodIsol];
    diep[[t + 1]] =
        First[First[Sort[Position[matrix, 0], #1[[1]] > #2[[1]] &]]];
    , {t, Nsteps}], t];
]

(* Create 3D images of simulated pit *)
electrolyte = Position[matrix, 0];
Graphics3D[
    Table[{Cuboid[electrolyte[[i]], electrolyte[[i]] + 1]}, {i, 
        Length[electrolyte]}], Axes -> True, AxesLabel -> {i, j, k},
    Ticks -> Automatic]