A Computational Diffusion Model to Predict Accelerated Corrosion Propagation

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Aerospace materials are especially subject to corrosion damage when they are exposed to certain environments, such as salt air, salt water, or certain fuels. Furthermore, the extreme conditions in these operating environments may greatly accelerate corrosion rates, specifically pitting corrosion. For these reasons, it is important to understand the impact that a corrosive environment will have on the mechanical integrity of said aerospace materials. This study aims to model the corrosion propagation, or corrosion "diffusion," that is observed during the potentiostatic electrochemical corrosion process. The developed MATLAB model is a cellular automaton (CA), which is defined by a parabolic partial differential equation (PDE) commonly used in diffusion models. The PDE for this model is modified through experimentation on metal specimens. Using the initial surface topography and experimental electrochemical parameters, the developed model may predict the metal surface condition during the corrosion process. This corroded surface topography can be further analyzed to predict material failure.

I. Introduction

The mechanisms underlying surface corrosion and pitting corrosion can be complex and can vary depending on the specific material and environmental conditions involved. Surface corrosion can be caused by a range of electrochemical and chemical reactions, including oxidation, reduction, and dissolution. Pitting corrosion, on the other hand, is a form of localized corrosion that occurs when a small area of the material is exposed to a more corrosive environment than the surrounding area, leading to the localized breakdown of the protective layer and the formation of pits or cavities.

In both cases, the formation of corrosion products on the surface of the material can have significant effects on the material's performance, including changes in its appearance, texture, and mechanical properties [1, 2]. Effective mitigation strategies for surface and pitting corrosion typically involve a combination of design, material selection, and surface treatment techniques, aimed at minimizing the exposure of the material to corrosive environments and promoting the formation of a protective layer on the surface.

A. Corrosion Research

Corrosion is a complex process that can be influenced by a range of factors, including environmental conditions, material properties, design factors, electrochemical properties, and microbial factors. Effective corrosion mitigation strategies typically involve a combination of approaches, aimed at minimizing the impact of these factors and promoting the formation of a protective layer on the material surface.

Researchers have attempted to develop deterministic models to predict the rate and type of corrosion that a material may experience [3, 4]. However, this has proven difficult because there are many factors that influence corrosion, and these factors are often subject to statistical distributions [5]. For example, the environmental conditions that a material is exposed to may vary over time and space, leading to variations in the rate and type of corrosion that occurs. Similarly, the properties of the material itself, such as its microstructure, may also vary over time and space, leading to variations in its susceptibility to corrosion.

Because of these statistical distributions, deterministic models may not accurately capture the complex interactions between the many factors that influence corrosion. Instead, there is a growing need for more probabilistic

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models in corrosion research. Probabilistic models can consider the variability of the many factors that influence corrosion and provide a more accurate prediction of the likelihood and severity of corrosion [6].

Probabilistic models can be developed using a range of techniques, including Monte Carlo simulations, which use random sampling to simulate the variability of the input parameters. These simulations can be used to generate a distribution of possible outcomes, which can be used to estimate the probability of different corrosion outcomes. Overall, the development of probabilistic models is an important area of research in corrosion science. These models can provide a more accurate and reliable prediction of the likelihood and severity of corrosion and can help to inform the development of more effective corrosion mitigation strategies.

B. Motivation

Corrosion is a major concern in the aerospace industry, as it can impact the safety, performance, and longevity of aircraft and other aerospace structures. Corrosion can cause material degradation and loss of strength, leading to structural failure, and it can also impair the function of critical components such as engines, sensors, and avionics. Corrosion is particularly problematic in the aerospace industry because of the harsh operating conditions that aircraft are exposed to [7]. Aircraft are often exposed to high humidity, extreme temperatures, and corrosive substances such as saltwater and deicing fluids. Additionally, the use of dissimilar metals in aircraft structures can lead to galvanic corrosion, which can further accelerate the corrosion process.

Effective corrosion research is essential in the aerospace sector, as it can help to ensure the safety and longevity of aircraft designs. Research can help to identify the most effective corrosion mitigation strategies, such as the use of corrosion-resistant coatings, cathodic protection, and regular inspection and maintenance programs [8]. One of the challenges in studying corrosion in the aerospace industry is that it often occurs at a macroscopic scale, where expensive tools or special devices are not required to track corrosion propagation. This means that researchers can focus on the macroscopic material properties of the material and the effects of corrosion on these properties [9]. This allows researchers to develop models to predict the long-term behavior of the material and to design corrosion-resistant materials that can withstand the harsh operating conditions of the aerospace environment.

II. Background

Pitting corrosion and surface corrosion are two types of corrosion that occur when a metal is exposed to a corrosive environment. These types of corrosion involve the redox reaction mechanism, which is a chemical reaction that involves the transfer of electrons from one species to another. During pitting corrosion, a small pit or cavity is formed on the surface of the metal [10]. This occurs when the metal is exposed to a corrosive environment, such as an aqueous solution containing chloride ions. The chloride ions can react with the metal to form metal chloride, which then undergoes a redox reaction [11].

Surface corrosion is a more general term that refers to the loss of material from the surface of a metal due to chemical or electrochemical reactions. The mechanism of surface corrosion is similar to that of pitting corrosion, involving redox reactions between the metal and the corrosive species in the environment. However, surface corrosion typically occurs more uniformly across the surface of the metal, rather than in localized pits.

Standard accelerated corrosion tests are widely used in the corrosion research and engineering industry to evaluate the corrosion resistance of materials, coatings, and products. These tests are designed to simulate the corrosive conditions that a material may be exposed to in real-world environments, and they provide a way to compare the corrosion resistance of different materials. Two commonly used test methods for accelerated corrosion are cyclic salt spray chambers and electrochemical methods using a potentiostat. The cyclic salt spray chamber is relatively simple and inexpensive to operate, but it has limited ability to simulate real-world conditions and can produce inconsistent results. On the other hand, the potentiostat is more complex and expensive, but it can provide more detailed information about the electrochemical behavior of the material [12, 13]. In a potentiostatic test, a constant potential is applied to the metal surface, and the current flowing between the working electrode and the counter electrode is measured. This test is useful for measuring the rate of corrosion and the effectiveness of corrosion inhibitors or coatings in protecting the metal surface [14], and it is the test of choice for this project.

III. Approach

The first step in the corrosion modeling timeline is to determine a suitable type of model to build. This depends on computational power, model complexity, and the current state of similar research. The type of framework which has been selected is the cellular automaton model, for its computational efficiency, ability to model complex interactions [15, 16], and common utilization in the field of corrosion research [17, 18]. After completing the model

construction, the second step is to correct it or train it, based on experimental data. Experimental data such as weight loss and topography can be compared to the model to determine its efficacy.
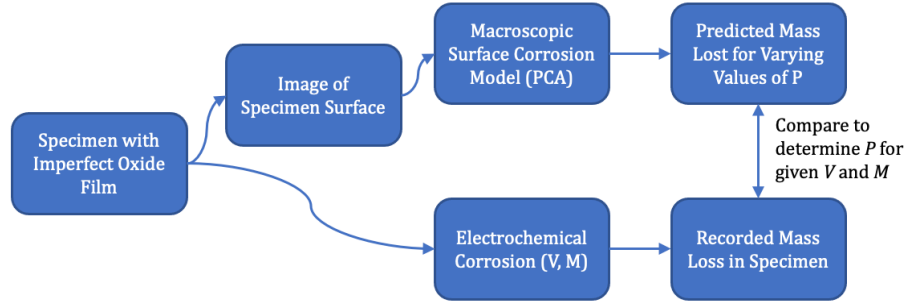

Fig. 1 Plan for correcting the PCA through electrochemical experiments.

Finally, the model should be validated through some metric other than those used to correct it or train it. For example, weight loss and topography should not be used for validation if they were used in the correction of the model in the first place. Rather, this project aims to eventually use a mechanical approach to analyze the accuracy of the model. This may be done through stress concentration analysis or other mechanical testing methods.
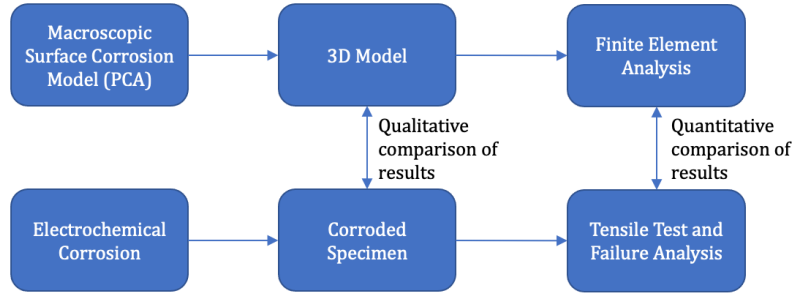

Fig. 2 Plan for validating the PCA through mechanical testing.

Cellular automata (CA) are mathematical models that simulate complex dynamic systems with simple and localized rules. They consist of a grid of cells, where each cell has a state and evolves over time according to a set of rules. The rules are typically defined based on the state of the cell's neighbors, and they can be deterministic or probabilistic. By incorporating probabilistic rules and local interactions, these models can capture the inherent randomness and non-linearity of the corrosion process, which is critical for accurate predictions and modeling of real-world phenomena. This type of model is known as a probabilistic cellular automaton (PCA), which is the more specific type of model used in this research.
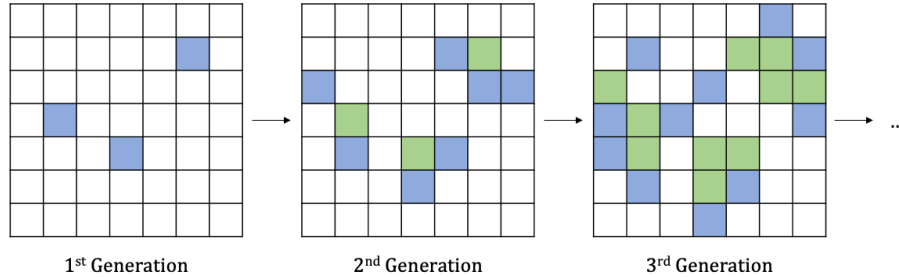

Fig. 3 Simple PCA; blue represents a new cell, and green represents ones from the previous generation.

IV. Model Development

This modeling approach follows closely with some models for partial differential equations (PDEs). In computational engineering methods, it is often times preferrable to discretize PDEs and solve them numerically [19].

When a two-dimensional parabolic PDE is discretized, known functions govern the diffusion of one cell to its neighboring cells. These functions are often derived from statistical distributions, such as Maxwell-Boltzmann distributions used in chemical kinetics. In this PCA, the governing rules are simply based on probabilities and statistical distributions. The model simulates corrosion progression at the mesoscale by defining a matrix of cells that represent the material surface. With every iteration, each cell is assigned a set of probabilities for corrosion propagation. The probabilities are based on environmental conditions such as temperature, humidity, and exposure to corrosive agents, as well as material properties such as composition, microstructure, and defects. The progression of corrosion is determined by iteratively applying the probabilities to each cell and its neighboring cells. PCA models are based on a statistical approach that considers the inherent variability processes [20], such as corrosion propagation in this case. The probabilities used in the model can be calibrated using experimental data.

Parabolic PDEs appear frequently in nature [21]. All parabolic PDEs take on the form

$$u_t = Ku_{xx}$$

where K is a constant. For example, in the heat equation, the first time derivative is related to the double spatial derivative by a constant:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

where α is the thermal diffusivity of the material. Similarly, the PCA is governed by a single constant which is related to statistical distributions. For this project, this constant is referred to as the corrosion propagation constant and is represented by P. For this model, P is directly related to the rate of corrosion propagation across the metal surface and operates on the domain $0 \leq P \leq 1$. In other words, a value of P closer to unity will lead to a relatively faster rate of corrosion propagation and a value of P closer to zero will lead to a relatively slower rate of propagation. A value of P equal to unity will describe perfect diffusion in a Moore neighborhood, and a value of P equal to zero will describe no diffusion whatsoever.

P is applied in the model as an additional logical statement to each of the basic cellular automaton rules. Since the basic rules are dictated by the status of the cell's neighbors, the value of P will affect the likelihood of which a cell will gain a "corroded" status given that its neighbors already have this status. When there is no limit to the spread of corrosion, or an absence of an additional rule involving P, the propagation is not accurate of what is expected.
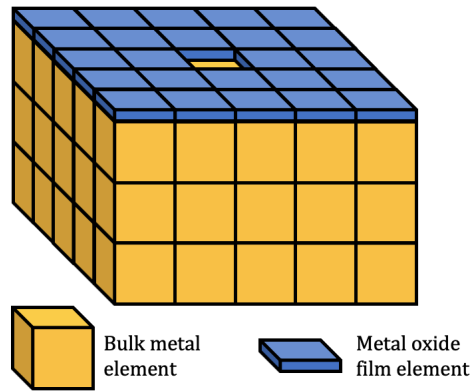

Fig. 4 Simplified model captured by the PCA; the breach in the metal oxide serves as a "seed" point.

In the development of this model, several key assumptions have been made:
  i.   Surface is planar and not subject to any stresses
  ii. All corrosion "seed" points are known
  iii. Oxide film layer is negligibly thin compared to bulk material thickness
  iv. Corroded material fully dissolves in solution, and essentially disappears from the main surface.
  v.   Spreading of corroded material to a cell is dependent on an affirmative corroded status of neighboring cells
  vi. Penetration of corroded material is dependent on an affirmative corroded status of a majority of neighboring cells
  vii. Spreading and penetration of corroded material are dependent on a probabilistic distribution which is related to physical parameters
  viii. Corrosion of specimen is limited to only the visible surface
  ix. Microscopic corrosion phenomena (~1nm) are negligible

Fig. 5 Example of an input image of the initial surface, with induced pits.

The model inputs include: an image of the initial surface, the number of iterations to be calculated, and the width of the image in millimeters. Firstly, the model discretizes the surface by dividing the image of the initial surface according to the given width. Each cell in the discrete surface measures 0.1 millimeters by 0.1 millimeters. Not only does this achieve the goal of tracking mesoscopic and macroscopic behavior, but it also makes this model compatible with most modern cameras. After discretizing the surface, the model isolates all visible surface imperfections and edges, which are seed cells for the corrosion. This is done through several image-processing operations, which MATLAB executes efficiently.
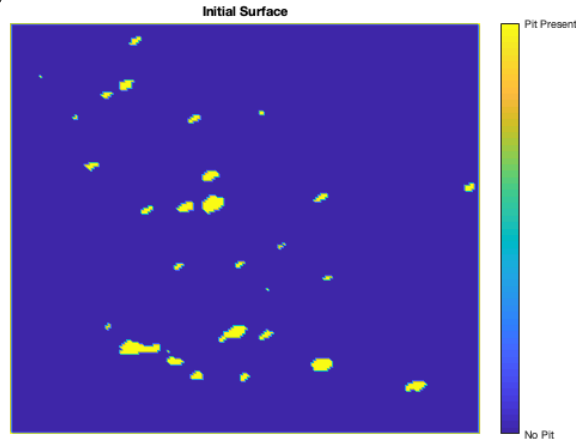

Fig. 6 Isolated pits, or "seed" points.

There are two transformations that cells may undergo: transition from a non-corroded status to a corroded status ("spreading") or gain a more severe corroded status ("penetration"). Cell transformation rules are dictated in part by the status of its neighbors. The neighbors are defined according to the Moore neighborhood model, as opposed to the Von Neumann neighborhood or radial neighborhood models. All three models are commonly used in cellular automata, but the Moore neighborhood has been selected because it is more accurate than the Von Neumann neighborhood at the expense of slightly more expensive computations. The radial neighborhood may be slightly more accurate, but it would come at the expense of more complicated update rules since the planar domain is square-shaped.
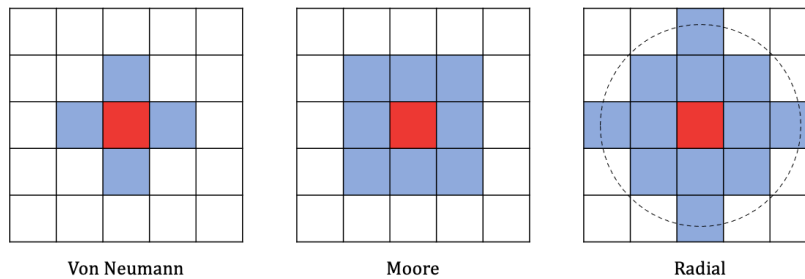

Fig. 7 Standard neighborhoods used in CA models.

The rules are repetitively applied to the entire surface for the defined number of iterations, which may be linearly linked to time. In the case of this model, one iteration corresponds to one minute in an active corrosion cell.

The model outputs for each complete run include: a two-dimensional "heatmap" of the final surface topography, a three-dimensional mesh of the final surface, the maximum penetration depth, projected area of effect, and material losses based on corroded material.
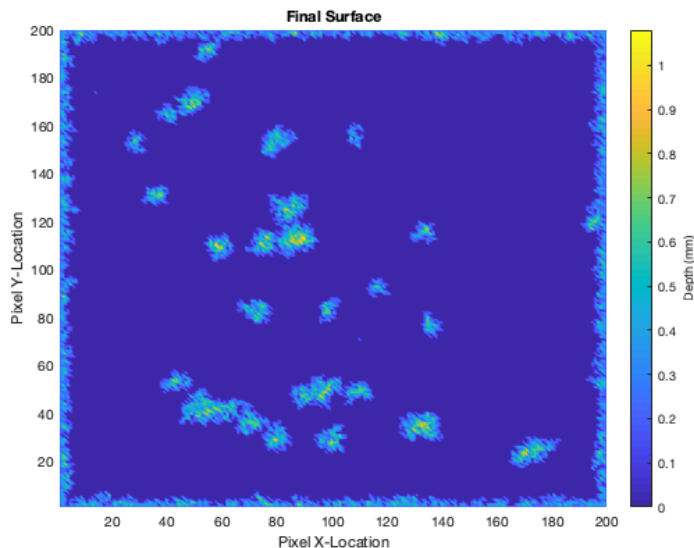

Fig. 8 2D heatmap of surface result from PCA with P = 0.005.

The corroded material is represented initially as a negative volume but may simply be converted to lost mass via the known density of the material. Some model outputs may be used to correct or train the model, such as mass loss or affected area, by comparing to experimental results. Other model outputs, such as the 3D surface mesh, may be used in simulations to observe stress concentrations or other mechanical phenomena.
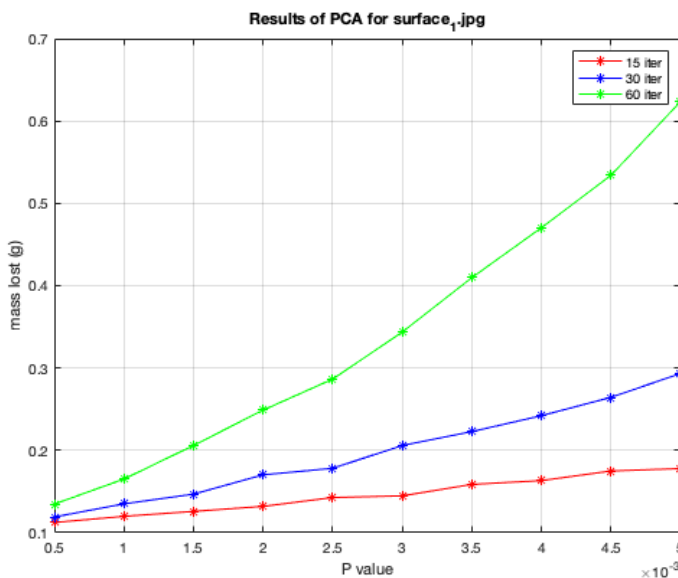

Fig. 9 Mass loss results from the PCA with varying values for time and for P.

V. Experimental Procedure

Since the model is primarily composed of matrix operations performed in MATLAB, it can be run multiple times with different values for P with little impact on computation time. In other words, the PCA can be repetitively run for each potentiostatic experiment to observe preferrable results. By comparing the results of the experiment to the PCA— qualitatively, the topography, and quantitatively, the mass loss—an accurate value for P may be determined.

For the experimental procedure, a three-electrode corrosion cell is constructed, using a Gamry general-use potentiostat. The potentiostat is computer-controlled and is used to precisely control and monitor the voltage and current of the cell. In the potentiostatic system, voltage is held constant.

A three-electrode electrochemical corrosion cell is a common experimental setup for studying corrosion behavior of metallic materials. The cell consists of three electrodes, a working electrode (WE), a counter electrode (CE), and a reference electrode (RE), which are immersed in an electrolytic solution. The WE is the metallic material being studied, in this case, a steel specimen. The CE is a graphite rod, which is used to complete the circuit and to provide the necessary electrons for the electrochemical reaction. The RE is an Ag-AgCl wire, which provides a stable reference potential for the measurement of the electrochemical potential of the working electrode.
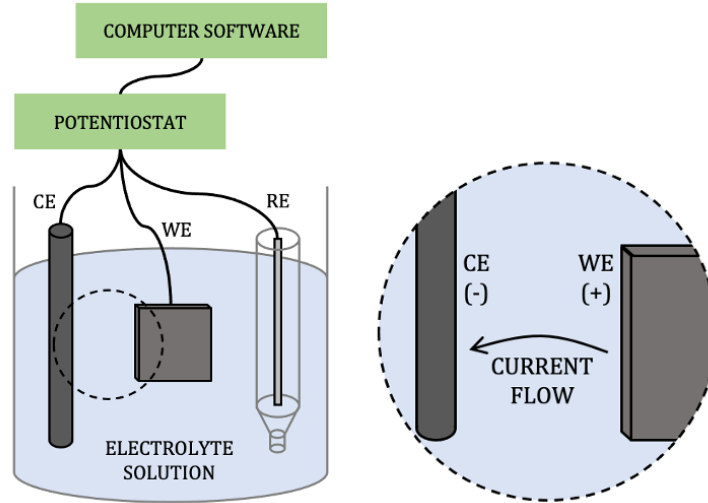

Fig. 10 Three-electrode corrosion cell configuration.

In the case of the electrolytic solution used in this setup, it is a solution of NaCl and water. When the cell is set up and a positive electrical potential is applied, electrochemical reactions take place at the surface of the steel specimen. The corrosion products formed during the reaction are dissolved in the electrolytic solution, and the resulting current is measured between the WE and CE.

In the potentiostatic system, the voltage is held constant for the duration of the experiment. For the purposes of this project, the parameters which are variable across the experiments are the applied voltage (V) and the solution concentration (M). Both are known to be directly related to the rate of corrosion, but this study intends to find a relationship that relates to the corrosion propagation constant, P. In other words, it is desirable to determine a relationship where P is a function of V and M, through linear regression.

For each of the defined experiments listed in the table, a new steel specimen was used as the WE. Each of these specimens contained artificially induced pits, which served as the "seed" points for corrosion propagation in the PCA. The alloy used, ASTM A36 steel, has a relatively thick protective oxide film and these pits were meant to penetrate it.

Table 1 Results of preliminary electrochemical experiments.

Time Elapsed (seconds)	Applied Voltage (volts)	Electrolyte Solution Concentration (mol/L)	Initial Mass of Specimen (grams)	Final Mass of Specimen (grams)	Mass Lost (grams)	Corresponding Value of P ($* 10^{-3}$)
3,600	1.2	3.422	20.554	20.324	0.230	1.7
3,600	1.0	4.278	21.067	20.505	0.562	4.6
1,800	1.2	2.995	20.881	20.674	0.207	3.1
1,800	1.0	3.422	20.656	20.468	0.188	2.7
43,200	0.4	1.711	20.724	20.477	0.247	-

C. Results

Multivariable linear regression is performed, where time (t), applied voltage (V), and solution concentration (M) are the independent variables and P is the dependent variable. The results of the linear regression are shown below, with added data points correlating to scenarios where P is equal to zero. The resulting formula becomes:

$$P = (-0.000720881) + t(5.28877 * 10^{-7}) + V(-0.000236845) + M(0.000500709)$$

Table 2 Multivariable linear regression statistics.

Regression Statistics	
Multiple R	0.776332314
R Square	0.602691862
Adjusted R Square	0.523230234
Standard Error	0.000938374
Observations	19

Table 3 Coefficient information from regression.

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	-0.000720881	0.00081704	-0.8823051	0.39153211
X Variable 1: *t*	5.28877E-07	1.7684E-07	2.99064946	0.00914518
X Variable 2: *V*	-0.000236845	0.00103823	-0.2281235	0.82263081
X Variable 3: *M*	0.000500709	0.00014153	3.53777587	0.00298311

VI. Conclusions

Further testing should be performed to evaluate the accuracy of the relationship found above. This relationship does align with the expectations that a more concentrated solution should result in a faster rate of corrosion. In other words, the corrosion rate (P) is directly related to the solution concentration (M). However, similar relationship with voltage (V) is expected but not observed.

Current results only study one alloy—ASTM A36 steel—which is a low-carbon steel. This steel is known to have a relatively thick oxide film, which may skew results. Future studies intend to incorporate other alloys, such as ASTM A684 steel, which is a high-carbon steel with a relatively thin oxide film layer. Furthermore, it may be preferrable to study differences in the manufacturing methods of the specimens. Currently, specimens are cut from sheet stock material using a CNC water jet cutter. Future studies may study the effect of additive manufacturing methods, using devices like the DMP Flex 350, which can 3D print low-carbon steel alloys. By adding more experimental data, the model accuracy should not be limited to one material and manufacturing method.

One major shortcoming of the PCA is that it does not consider pit propagation, or penetration, in any direction other than normal to the surface. In practice, pits can form radially, with overhanging material at the surface. Due to the configuration of this model, this corrosion characteristic is not considered. However, this model is attempting to describe macroscopic effects, so this should have little impact on the results.

D. Future Considerations

While the PCA shows great potential in modeling corrosion, there is still a need to validate the model against real-world phenomena. Model validation should not consider mass lost or affected area, since both of these metrics are used in its correction, which was the calculation of the rate factor, P. One promising alternative avenue for validation is through stress concentration analysis, which can provide a more quantitative measure of corrosion damage and its effects on bulk mechanical properties.
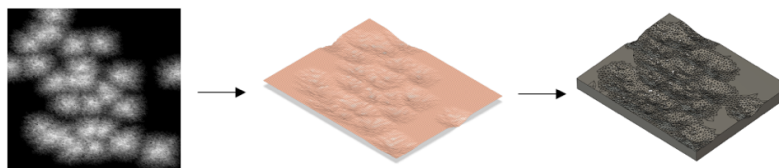

Fig. 11 Method for preparing a 3D model for finite element analysis.

One possible approach for validation is to use finite element analysis (FEA) to simulate the mechanical behavior of the corroded surface based on the output from the PCA. The corroded surface topography can be reconstructed in a 3D model, to be used in a physics simulation software like Ansys. The FEA results can then be compared to experimental results from tensile testing or other relevant mechanical tests. Overall, the use of stress concentration analysis for validation of the PCA holds great promise for advancing the understanding of corrosion and its effects on materials. As such, this future research aims to further develop and refine this approach, with the ultimate goal of improving the accuracy and reliability of the corrosion model.

Acknowledgments

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