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Degradation Modeling of 2024 Aluminum Alloy During Corrosion Process

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Corrosion is one of the most damaging mechanisms in aluminum alloys used in aerospace engineering structures. In this article, the degradation behavior of AA 2024-T3 as a function of time under corrosive conditions is studied through experiments and modeling. Corrosion experiments were conducted on AA 2024-T3 specimens under controlled electrochemical conditions. The chemical element alloy map was investigated through EDS technique for evaluation purposes. Based on the experimental data, an analytical model is developed relating the material loss to the degradation during the corrosion process. The analytical model uses genetic algorithms (GAs) to map the relationship through optimization. The results obtained from GAs were compared with a standard non-linear regression model. The results obtained indicate that a quadratic relationship exists in time between the material loss due to corrosion and the degradation behavior of the alloy. Based on the good results obtained, the present approach of degradation modeling can be extended to other metals.

Keywords AA 2024-T3, corrosion experiment, degradation model, EDS, genetic algorithms

1. Introduction

General corrosion and especially pitting corrosion is known to be one of the major damage mechanisms affecting the integrity of many aerospace structures made from high strength aluminum alloys (Ref 1). Corrosion pits generally initiate due to some chemical or physical heterogeneity at the surface, such as inclusions, second phase particles, flaws, mechanical damage, or dislocations. Aluminum alloys contain numerous constituent particles, which play an important role in corrosion pit formation (Ref 2). To better understand particle-induced pitting corrosion in 2024/T3 and 7075/T6 aluminum alloys, optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques have been used (Ref 3).

It is well known that corrosion has a strong effect on the fatigue life of aluminum alloys used in aerospace structures (Ref 4-7). Corrosion can lead to accelerated failure of structural components under fatigue loading conditions. Fatigue cracks usually initiate from the corrosion pit sites. Under the interaction of cyclic load and the corrosive environment, cyclic loading facilitates the pitting process, and corrosion pits, acting as geometrical discontinuities, lead to crack initiation and propagation and then final failure. Understanding and prediction of corrosion damage are very important for the structural integrity of materials and structures.

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Corrosion mechanisms depend on the material composition and microstructure, electrolyte and other environmental conditions (Ref 1-3). Most of the previous work on corrosion has been focused on chemical processes and electric currents and potentials, and limited growth and simulations models, see for example, Frantziskonis et al. (Ref 8), Malki and Baroux (Ref 9), and Pidaparti et al. (Ref 10). While much is understood regarding corrosion damage from electrochemical factors, and alloy microstructure, there are no studies dealing with the evolution of chemical elements behavior due to corrosion in aerospace metals.

Biologically inspired optimization techniques, such as genetic algorithms (GAs), tend to mimic the basic Darwinian concepts of natural selection, and has been used in many applications in material science and metallurgy. A review of GAs applications in materials design and processing was investigated by Chakraborti (Ref 11). Several other GA applications include, material characterization (Ref 12), design optimization of composites (Ref 13-15), and metal forming process optimization (Ref 16, 17). Zhang et al. (Ref 14) have developed an approach for selecting optimal material constituent compositions and microstructures according to the determined or optimized material properties using GAs. Franulovic et al. (Ref 15) have studied a material model describing elastic-plastic behavior of a material under cyclic load. Because of the complexity and nonlinearity of the material constitutive model for description of low-cycle fatigue behavior its parameter identification was carried out using GAs (Ref 15). Castro et al. (Ref 16) have proposed an approach to optimal design of shape and process parameters in metal forging using GA. They concluded that the developed GA presents advantages over sensitivity-based methods: the algorithm is not sensitivity-dependent, runs well even for discontinuous derivative fields, discrete design variables and does not introduce iteration-dependent numerical errors. Wei et al. (Ref 17) have integrated finite element (FE) analysis and GA to solve the optimal process parameters of sheet metal forming by transforming multi-objective problem into a single-objective problem.

They showed that their method could be used as a powerful tool for the parameters optimization of stamping process design. A brief introduction to GAs is presented below.

GAs first developed by John Holland (Ref 18), which is based on mechanisms derived from biology, as their name implies. These algorithms start with an initial pool of potential solutions called a *population*. Each potential solution is called a *chromosome*, and each unknown parameter in the *chromosome* is called a *gene*. *Genes* are represented in binary notation by *bits*. The process is initiated by first generating the *population* using a random number generation scheme. Biological operations are performed on this *population* to minimize a prescribed objective function to obtain the final solution. The operations consist of *selection* (the *selection* of *parents* from the *population* for *breeding*), *crossover* (the creation of *children*), and *mutation* (the random changing of a *chromosome*). The *selection* process is based on the *fitness* of each *chromosome*. *Fitness* is determined from the value of the objective function. Thus, in the *crossover* process, *chromosomes* (potential solutions) with high *fitness* values are used to create *children* or new solutions with potentially higher *fitness* values. The process is repeated over a number of *generations* or iterations until some specified criterion is met. *Mutation* is used to randomly create new solutions in the *population* pool to avoid convergence to a local minimum.

The robustness of GAs have resulted in their use in diverse fields such as optimization in engineering and computer science, structural optimization, automatic programming and machine learning, biotechnology, economics and social sciences, financial forecasting, art, music, and so on. The "Handbook of Genetic Algorithms" by Davis (Ref 19) covers a wide range of applications of GAs in the real world. Due to several demonstrated applications of GAs in the past, in this research, GAs was used as robust non-gradient-based optimization procedure to minimize the error between the linear/quadratic models and the experimental data of material loss due to corrosion.

For the past few years, the authors have been studying the structural integrity and durability issues related to aging aircraft aluminum and structures. The goal of our study is aimed at developing controlled experiments and computational models to comprehensively investigate the evolution of degradation in the corrosion process. The developed algorithms might be useful for manipulating various parameters for material design applications.

The objective of this study is to systematically investigate the degradation of AA 2024-T3 as a function of time and relate this information to material loss due to corrosion. Corrosion experiments were conducted on metal samples under controlled electrochemical conditions and their chemical element alloy map is investigated through EDS technique. An analytical model is developed relating the material loss to the degradation of the constitutive phases with major alloy elements during the corrosion process. The analytical model uses GAs to map the relationship through optimization. The results obtained from GAs were compared with a standard non-linear regression model.

2. Experiments

The material used was an aluminum alloy 2024-T3 which was received in sheet form (12″ × 12″ with a nominal thickness of 1.5 mm. The weight percentage chemical composition of the alloy is 93.0% Al; 4.5% Cu; 1.45% Mg; 0.25% Fe; 0.11% Si; 0.09% Zn; 0.02% Ti, and 0.01% Cr. In order to see how major alloy elements (Al and Cu) in AA 2024-T3 behavior during the corrosion process, experiments were conducted to analyze their contributions through controlled corrosion experiments and EDS techniques. All specimens were cut into 5 × 5 cm in size to test them in corroded cell over specified time intervals. Nail polish was used to coat most of the samples, except in small circles where corrosion was allowed to take place. Sodium chloride crystals and deionized water were mixed thoroughly with a stirrer to prepare a solution of sodium chloride (NaCl). Figure 1 illustrates the manner in which the electrochemical cell was setup for doing the corrosion degradation experiments along with the specimen details. The electrochemical cell consists of an electrolyte and three electrodes; working, reference, and auxiliary electrodes. The sample which had to corrode was used as working electrode. Reference electrode which is a platinum wire was used to measure the working electrode potential. A reference electrode should have a constant electrochemical potential as long as no current flows through it. The auxiliary electrode, graphite is a conductor that completes the cell circuitry. The electrolyte creates the environment for corrosion by providing ions. Ideally the electrode which is supposed to be corroded is kept as an anode, and potential voltage is supplied to cell to initiates the corrosion process.

All the experiments were conducted at room temperature. After all the electrodes were placed correctly on the various parts of the electrochemical cell, GAMRY-Electrostatic-Potential-PotentiostaticInstrumentsPC3/300 potentiostat/galvanostat/ZRA with Framework (version 3.11) and DC 105 program were

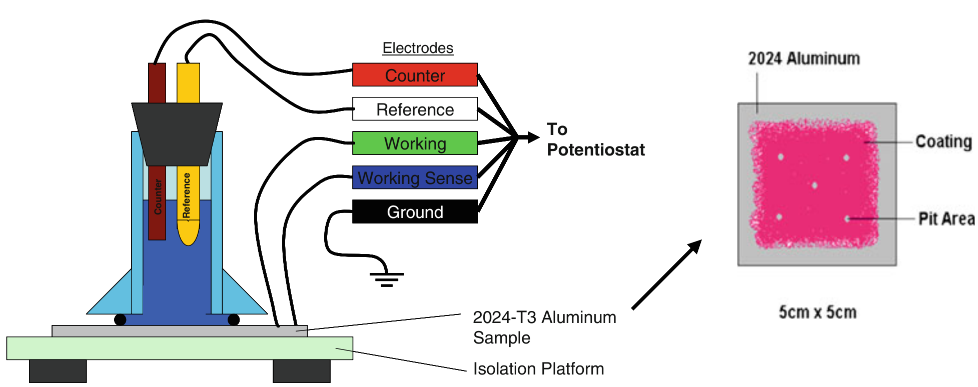

Fig. 1 Schematic of the experimental setup of the corrosion cell in electrochemical experiments

used to obtain electrochemical measurements. The GAMRY Electostatic-Potential-Potentiostatic program added a constant potential to the electrochemical cell, and recorded the potential and current at every minute. Samples were corroded for a varying time frames (0-48 h), electrode voltages (−430 to −630 V), and NaCl molarities (1-5 M).

The material loss due to corrosion at each time step was obtained using the current from the program. The rate of corrosion is proportional to the rate of electrons transferred between the electrode and the electrolyte. The current (I_{corr}) flowing through the electrochemical cell is measured and using the Faraday's law, and the corrosion rate (CR) can be calculated as,

$$CR = I_{corr} K \; EW/(\rho A) \quad \text{(Eq 1)}$$

where I_{corr} is current which is obtained from Gamry Electrochemical set-up, K is a constant, in this case 3272 mm/(amp × cm × year), EW is the equivalent weight of the metal (in grams), ρ is density in g/cm^2, and A is area in cm^2. Using the above equation, the corrosion rate as a function of time is obtained for AA2024 alloys.

The surface morphology along with the chemical elemental alloy map at each time of corrosion was also obtained. Point analysis of the corroded region was also conducted through Energy Dispersive x-ray Spectrometry (EDS) to determine the intensity and concentration of alloy's elements present after corrosion, and to estimate the degradation during the corrosion process. Experimental data of material loss and the chemical point analysis count (related to degradation of constituent phases) was then used in developing an analytical model.

3. Analytical Model

An analytical model to map the degradation of the constitutive phases in aluminum AA 2024-T3 alloy with various exposure times during the corrosion process was developed using GAs. The results obtained from the GAs are compared to a standard non-linear regression analysis. The details of the model development are given below.

Initially, a linear relationship in terms of time is assumed between the material loss and the degradation behavior of alloy composition elements (i.e., aluminum and copper), which is given as,

$$\text{Material loss} = (\alpha_1 t + \alpha_2) D_{Al} + (\alpha_3 t + \alpha_4) D_{Cu} + \alpha_5 \quad \text{(Eq 2)}$$

where D_{Al} and D_{Cu} are the loss counts from EDS for alloy's compositions such as aluminum and copper, respectively, and α_1, α_2, α_3, α_4, and α_5 are the linear model parameters.

Next, a quadratic model in terms of time has been considered, which is given as,

$$\begin{aligned}\text{Material loss} = {} & \left(\alpha_1 t^2 + \alpha_2 t + \alpha_3\right) D_{Al} \\ & + \left(\alpha_4 t^2 + \alpha_5 t + \alpha_6\right) D_{Cu} + \alpha_7 \end{aligned} \quad \text{(Eq 3)}$$

In order to determine the model parameters (alphas), two techniques were used. These include GAs and non-linear regression, which are briefly described.

3.1 Genetic Algorithms

In this article, bit string GA with parameters as shown in Table 1 was employed and the algorithm is performed using GA toolbox of Matlab. In Matlab, the GA Toolbox supports the offsetting and scaling method of Goldberg (Ref 20) and the linear-ranking algorithm of Baker (Ref 21). Rank fitness scaling removes the effect of the spread of the raw scores. It scales the raw scores based on the rank of each individual instead of its score. The rank of an individual is its position in the sorted scores: the rank of the fittest individual is 1, the next fittest is 2, and so on (Ref 22). The rank scaling function assigns scaled values so that:

Table 1 Various parameters used in the GA implementation

Parameter	Value
Number of generations	500
Population size	1500
Elite count	100
Fitness scaling function	Rank
Crossover method	Scattered
Mutation method	Gaussian
Selection	Stochastic uniform

1. The scaled value of an individual with rank n is proportional to $1/\sqrt{n}$.
2. The sum of the scaled values over the entire population equals the number of parents needed to create the next generation.

The selection function chooses parents for the next generation based on their scaled values from the fitness scaling function. An individual can be selected more than once as a parent, in which case it contributes its genes to more than one child. In Matlab, the stochastic uniform selection option lays out a line in which each parent corresponds to a section of the line of length proportional to its scaled value. The algorithm moves along the line in steps of equal size. At each step, the algorithm allocates a parent from the section it lands on (Ref 22).

Elite count is the number of individuals with the best fitness values in the current generation that are guaranteed to survive to the next generation. In other words, it specifies the number of elite children that will be considered in the next generation too. When elite count is at least 1, the best fitness value can only decrease from one generation to the next. Higher elite count causes the fittest individuals to dominate the population (Ref 22).

Crossover options specify how the GA combines two individuals to form a crossover child for the next generation. Scattered crossover function creates a random binary vector and selects the genes where the vector is a 1 from the first parent, and the genes where the vector is a 0 from the second parent, and combines the genes to form the child (Ref 22).

In Matlab, the GA toolbox applies mutations using the option that you specify on the Mutation function. The Gaussian option, adds a random number, or mutation, chosen from a Gaussian distribution, to each entry of the parent vector. Typically, the amount of mutation, which is proportional to the standard deviation of the distribution, decreases at each new generation (Ref 22). Figure 2 shows an overview of the GA implementation process. After 500 generations of evolution, the optimum coefficients have been obtained.

3.2 Non-Linear Regression Analysis

In order to compare the results from GA, we also performed the non-linear regression analysis as follows:

$$y = f(X, \beta) + \varepsilon \quad \text{(Eq 4)}$$

where y is the vector of observations from experiments (material loss), X is the matrix of input variables (degradation of chemical elements Al or Cu), β is the vector of unknown parameters to be estimated, and e is the vector of random disturbances.

In this study, polynomial function is considered as the nonlinear function and the regression was carried out using Statistics toolbox in Matlab software.

To evaluate the test results, Correlation coefficients τ_k are given below was used in this study:

$$\tau_k = \frac{\sum_{t=1}^{n} (x_t - \bar{x})(x_{t+k} - \bar{x})}{\sum_{t=1}^{N} (x_t - \bar{x})^2} \quad \text{(Eq 5)}$$

where x_t is a data value at time step t, k is the lag, and the overall mean is given by:

$$\bar{x} = \sum_{t=1}^{N} \frac{x_t}{N} \quad \text{(Eq 6)}$$

4. Results and Discussion

Figure 3 shows the typical degradation of constitutive phases having aluminum and copper compositions in AA 2024 alloy over a specimen corroded at 4, 8, 14, and 18 h obtained from chemical element map using Energy Dispersive x-ray Spectrometer (EDS). The composition of the Al over the corroded regions at various times shows that constitutive phases degraded by various amounts spatially over the corroded region. Similar observation is seen for the composition of Cu as well. The spatial variation, which is reflected as a change in texture is also seen. It has been observed that at 28 h of corrosion, there are black spots in the EDS picture reflecting that both the Al and Cu are degraded in those regions. In order to observe the overall degradation and the microstructure, the SEM of corroded specimens at 4 and 18 hrs are shown in Fig. 4.

The normalized degradation (through point count analysis from EDS) of constitutive phases having aluminum and copper compositions in AA 2024 alloy during the corrosion process is shown in Fig. 5. The normalized value corresponds to the respective values at time = 0. In general, the constitutive phases having various compositions in AA 2024 alloy degrade over a period of time. The constitutive phases having aluminum

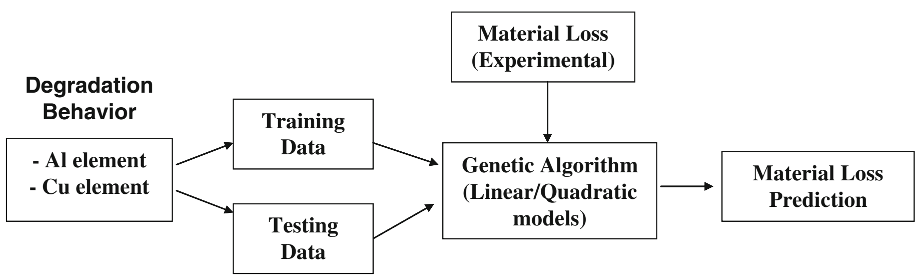

Fig. 2 An overview of the GA model prediction of material loss due to corrosion

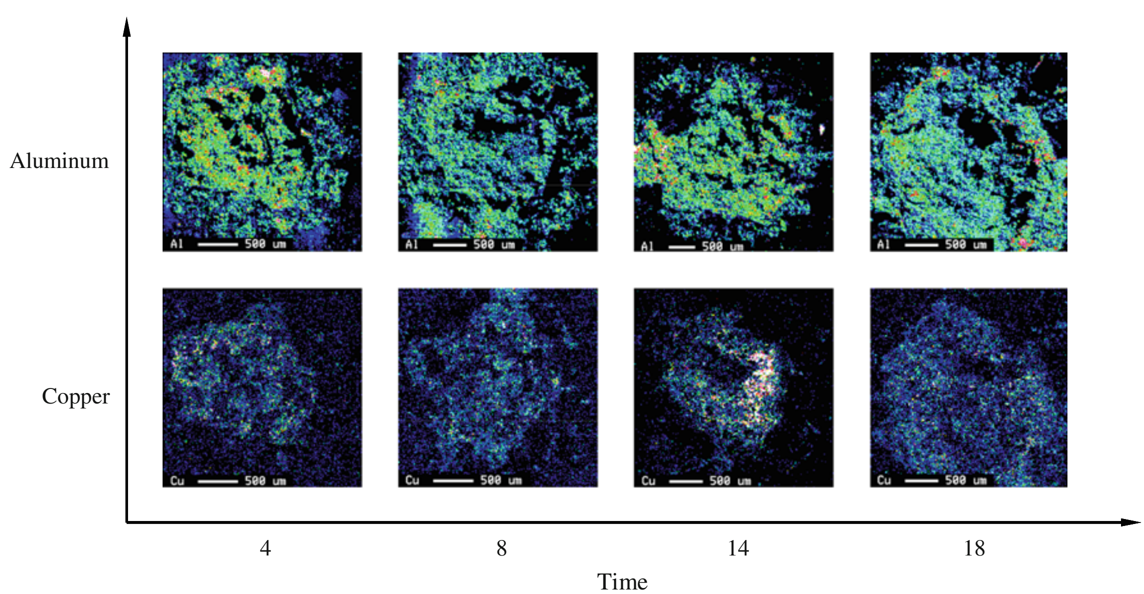

Fig. 3 Degradation behavior of aluminum and copper chemical elements in AA 2024 alloy over a specimen corroded at 4, 8, 14, and 18 h

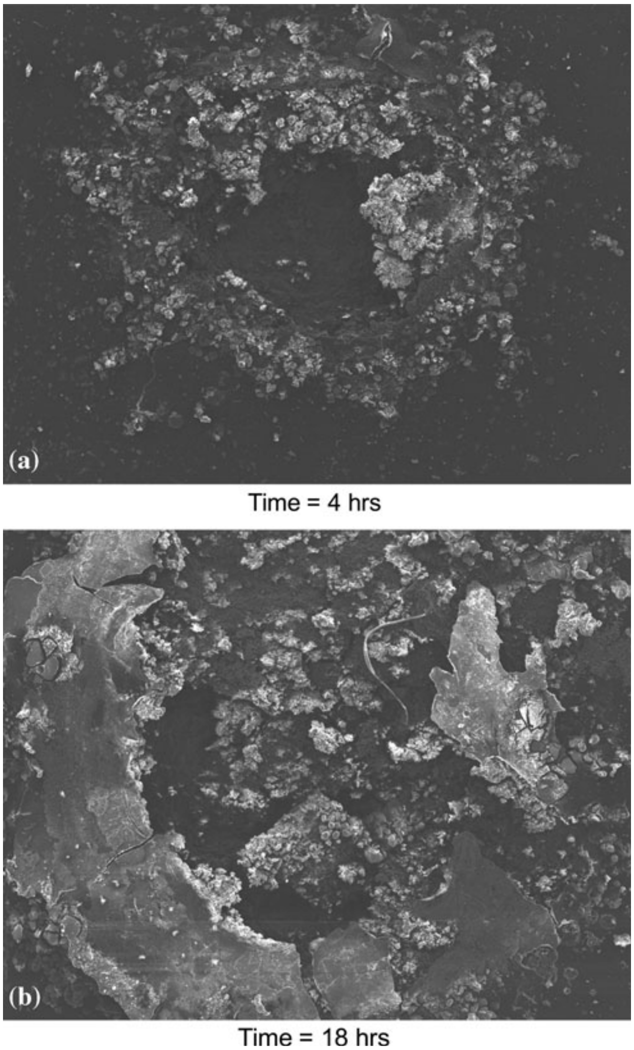

Fig. 4 SEM of degradation behavior of AA 2024 alloy over a specimen corroded at 4 (a) and 18 h (b)

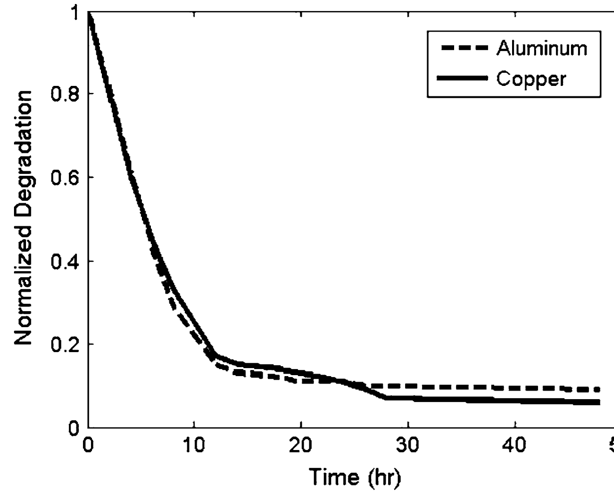

Fig. 5 Normalized degradation of constitutive phases having aluminum and copper compositions in AA 2024 alloy over a 48-h period of corrosion

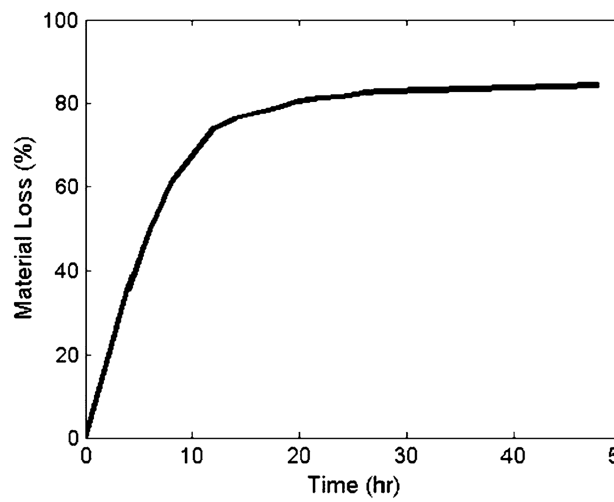

Fig. 6 Material loss as a function of corroded time

and copper compositions degraded about 91 and 94%, respectively, in about 48 h for the conditions considered in this study. The trends of degradation through experiments showed that constitutive phases having aluminum and copper compositions degraded most rapidly within 14 h. The results of normalized material loss of corroded specimens over a time period of 48 h are shown in Fig. 6.

The model performance of the GA was validated after training both the linear and the quadratic models. Figure 7 shows the comparison of results between GA predictions and the experimental data for both linear and quadratic models. Both the linear and the quadratic models predict the material loss reasonably well to the experimental data. However, quadratic model predictions are more accurate than the linear model predictions. It should be pointed that in the GA predictions not all the experimental data was used (70% experimental data was used for training and the remaining data was used for testing). In general, it can be seen from Fig. 7 that a good correlation is obtained between the GA predictions and the experimental data. The correlation coefficient (R) between the experimental data and the models obtained from GA and non-linear regression analyses are 1 and 0.99, respectively.

To further validate the generalization performance of the GA in capturing the degradation behavior, the GA predictions were compared to a standard non-linear analysis and presented in Fig. 8. The optimal coefficients are obtained using GA and non-linear regression analysis are presented in Table 2. A very good agreement was found between the GA predictions and the non-linear regression analysis and both are comparable to the experimental data. These validations are further testimony that the developed GA model was able to predict the degradation behavior reasonably well.

In order to observe the relative contribution of constitutive phases with aluminum and copper compositions in the material loss due to corrosion, the results are presented in Fig. 9 using the validated model. It is interesting to see the contribution trend is non-linear with time. Initially, degradation of the constitutive phases with aluminum and copper compositions contribution increases and after a specific time, the trend changes, i.e., Al composition contribution decreases, whereas Cu composition contribution increases with increasing time.

This is very interesting observation. Overall, the results presented in Fig. 6 to 9 illustrate that the model predictions are very reasonable for degradation behavior due to corrosion process.

5. Conclusions

Experimental measurements were conducted on AA 2024 alloy specimens to observe the degradation behavior of constitutive phases with aluminum and copper compositions (Al and Cu) in AA 2024 alloy during the corrosion process. The chemical composition maps were obtained through the EDS technique through point analysis. The constitutive phases with aluminum and copper compositions degraded about 91 and 94%, respectively, in about 48 h for the conditions considered in this study. A GA model is developed for the analysis and prediction of the mapping between degradation behavior to the material loss during the corrosion process. The results obtained from the study indicate that overall, the GA predictions compared reasonably well with the experimental data and the non-linear regression analysis. The preliminary results obtained demonstrate that through a comprehensive

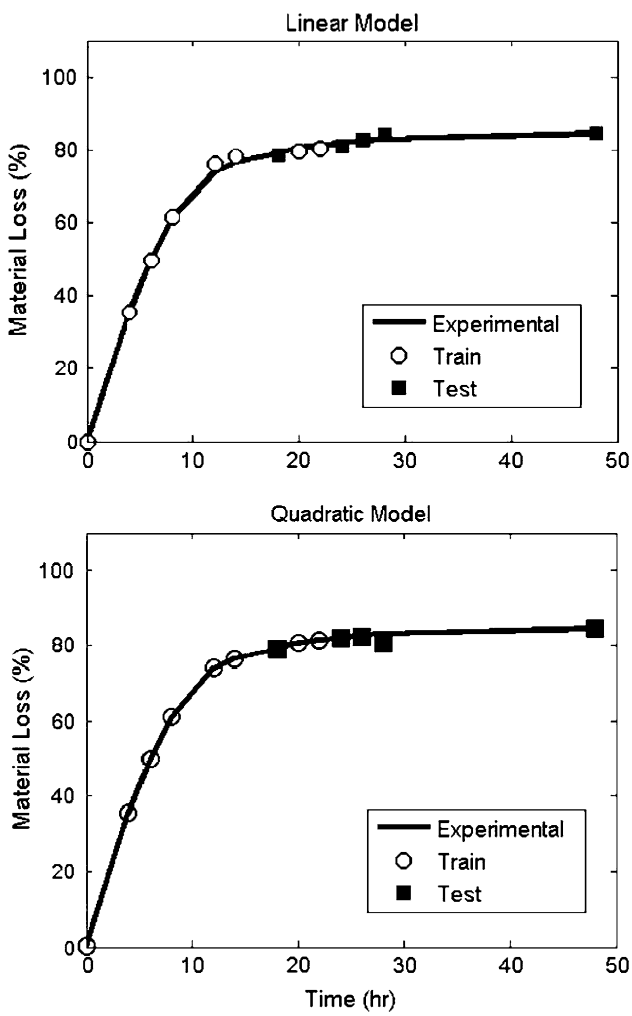

Fig. 7 Comparison of GA models (linear and quadratic) with the experimental data

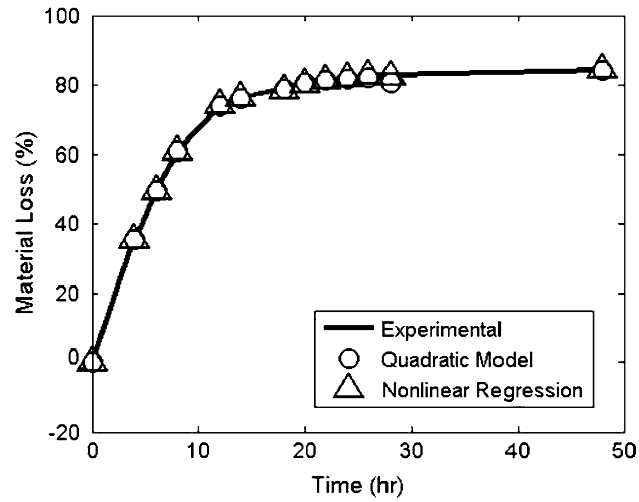

Fig. 8 Comparison of quadratic GA and non-linear regression models with the experimental data

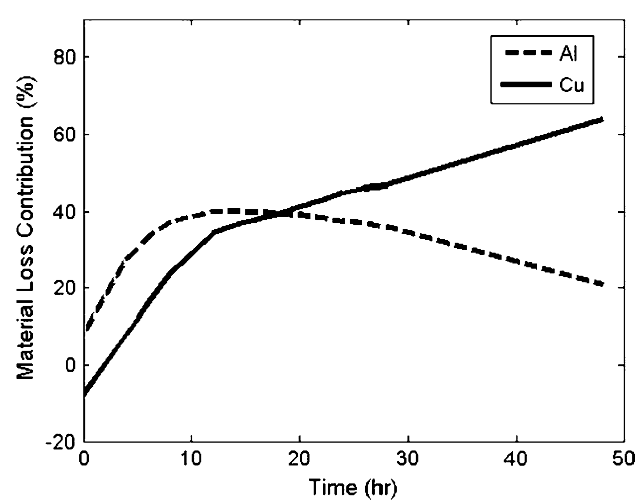

Fig. 9 Contribution of Al and Cu chemical elements in AA 2024-T3 alloy in the material loss due to corrosion obtained from the model

Table 2 Model parameters in the GA and the non-linear regression analysis

Model	α_1	α_2	α_3	α_4	α_5	α_6	α_7
GA (linear)	0.3545	16.4259	0.2529	76.3005	92.7262	N/A	N/A
GA (quadratic)	0.1069	0.0912	27.2810	0.1944	0.5565	57.1142	84.3954
Non-linear regression	0.1567	3.0480	35.3506	0.2304	2.8626	51.0897	86.4244

study with more experimental data, a better corrosion-resistant material can be designed by controlling the degradation behavior of the constitutive phases during the corrosion process using the developed GA model.

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