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David V. Svintradze
Virginia Commonwealth University

Ramana M. Pidiparti
Virginia Commonwealth University

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Research Article

A Theoretical Model for Metal Corrosion Degradation

David V. Svintradze[1, 2] **and Ramana M. Pidaparti**[1]

[1] *Department of Mechanical Engineering, Virginia Commonwealth University, 401 W Main St., P.O. Box 843015, Richmond, VA 23284-3015, USA*
[2] *OCMB Philips Institute, Virginia Commonwealth University, Richmond, VA 23284, USA*

Correspondence should be addressed to Ramana M. Pidaparti, rmpidaparti@vcu.edu

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Many aluminum and stainless steel alloys contain thin oxide layers on the metal surface which greatly reduce the corrosion rate. Pitting corrosion, a result of localized breakdown of such films, results in accelerated dissolution of the underlying metal through pits. Many researchers have studied pitting corrosion for several decades and the exact governing equation for corrosion pit degradation has not been obtained. In this study, the governing equation for corrosion degradation due to pitting corrosion behavior was derived from solid-state physics and some solutions and simulations are presented and discussed.

1. Introduction

Pitting corrosion is known to be one of the major damage mechanisms affecting the integrity of many materials and structures in civil, nuclear, and aerospace engineering. 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. Pitting corrosion, a result of localized breakdown of such films, results in accelerated dissolution of the underlying metal. The corrosion mechanisms depend on the material composition, electrolyte and other environmental conditions [1–3]. The most corrosion models in literature are focused on the electrochemical reaction during the corrosion process [4–6]. Mathematical models are utilized to get a better understanding of the pitting corrosion process [1–3]. Models are included in a set of governing equations. Numerical modeling is especially important with the pitting corrosion because most governing equations do not have close form solutions to describe the process.

Pitting corrosion is a very complex process and may involve many mechanisms. In general, the corrosion degradation modeling should involve not only physico-chemical and environmental factors. The pitting corrosion mechanisms may initiate at multiple levels starting from nano to micro and macrolevels. Zavadil et al. [7] investigated the contribution of voids and their shapes at nanoscale at the Al/oxide interface to pit initiation and propagation in passive metals. Interestingly, Renner et al. [8] observed the initial corrosion at the atomic scale in single crystal alloy in sulphuric acid solution. Martin et al. [9] conducted in situ AFM detection of pit onset location on stainless steel and concluded that pits were randomly distributed at the nanoscale and revealed that 70% of the pits initiated at strain hardened areas resulting from mechanical polishing. At microscale, the pit initiation and propagation mechanism may depend on the metal microstructure along with chemical (electrochemical reactions), physical (film composition, surface texture) and mechanical (surface stresses). Experimental and theoretical studies have largely clarified the mechanism for the initiation of these microscopic pits as being caused by localized electro dissolution of metal at surface defects and inclusions [10–15]. There are no studies dealing with exact solution of time profile of pit growth and evolution of corroded degradation. In the paper, the general equations of pitting corrosion degradation mechanisms based on solid state physics are derived. These derived equations are exact solutions of time profile of corroded volume, which might be very useful for estimating the deterministic characteristics of metal corrosion.

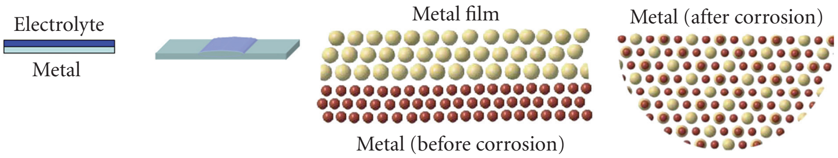


Figure 1: Schematic drawing of corrosion metal degradation under an electrolyte solution. Atoms in metal films are shown in yellow and metal atoms in red. If we assume that $\varepsilon_0^f = \varepsilon_0^M$, then the energy to move atom in metal film is to be same as energy needing to move atom in metal. The lateral force to move atom for Cu was measured $F = 17 \pm 3\, pN$ [17] and $x = 300$ pm, then approximate energy per atom was measured $E = F \cdot x = 5.1 \cdot 10^{-22}$ J; recalculating it per mol of atom we will have $\varepsilon_0^f = \varepsilon_0^M \approx 3 \cdot 10^2\,\mathrm{J} \cdot (\mathrm{mol})^{-1}$. $\varepsilon_0^f = \varepsilon_0^M \approx 5.1 \cdot 10^{-22}$ J (a) per atom; and $\varepsilon_0^f = \varepsilon_0^M \approx 3 \cdot 10^2\,\mathrm{J} \cdot (\mathrm{mol})^{-1}$ (b) per mol number of atoms. We use (1) as an estimation as we are calculating everything on number of atoms or on per atom.

2. Theoretical Model

Let us discuss isolated metal system and consider that the metal surface having two phases. On the metal surface, the metal film (oxide layer) is in equilibrium with the metal. The essential condition/parameter, is defined from the equilibrium condition as

$$\mu_M(T,P) = \mu_f(T,P), \tag{1}$$

where $\mu_M(T,P)$ and $\mu_f(T,P)$ are the chemical potentials of the components present in metal and film, respectively, at a given T, temperature, and P, pressure. Based on the statistical physics, and Debye interpolation formula, Helmholtz free energy of the isolated body [16] (metal) can be written as

$$F = N\varepsilon_0 + N\nu\left(3\ln\left(1 - e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right), \tag{2}$$

where $D(x) = (3/x^3)\int_0^x (z^3/(e^z - 1))dz$ is Debye function,$\nu = V\omega_M^3/6\pi^2\overline{u}^3 N$, $\theta = \hbar\omega_M$ is Debye characteristic temperature of the body, ω_M is vibration frequencies of atoms, N is number of atoms, and $\overline{u}$ is average velocity of sound in the metal. Since, we have two phases that are in equilibrium on metal surfaces, we can determine the chemical potentials as

$$\begin{aligned} \mu_M(P,T) &= \left(\frac{\partial F_M}{\partial N}\right)_{V,T}, \\ \mu_f(P,T) &= \left(\frac{\partial F_f}{\partial N}\right)_{V,T}. \end{aligned} \tag{3}$$

Using (1) and (3), and starting with the equilibrium conditions, we can determine the connection between free energies per atom at the border of metal-film surface, as

$$\varepsilon_0^f = \varepsilon_0^M, \tag{4}$$

where $\varepsilon_0^{f,M}$ are free energy per atom in film and metal, respectively. It should be mentioned that $\varepsilon_0^{f,M}$ is fixed energy, and for metal it can be calculated according to recently done atomic force microscopy data [13] (Figure 1).

Now, let us consider that the body (the metal) is in contact with the electrolyte solution (Figure 1) and the system, metal with the electrolyte solution, is isolated, then the film of the body starts to dissolute in solution [8, 10]. The task is to find and to predict time evolution of the corrosion degradation, in other words to derive the equation describing pit radii growth in time. As result of dissolution due to chemical reactions, we have changes in free energy. Since the process goes by itself, and we are discussing isolated system, the variation of the free energy of the system must be zero. Therefore, we have,

$$\delta F_M + \delta F_f + \delta F_S = 0. \tag{5}$$

The Equation (5) can be rewritten as

$$\frac{\partial F_M}{\partial n_M}\delta n_M + \frac{\partial F_f}{\partial n_f}\delta n_f + \frac{\partial F_S}{\partial n_S}\delta n_S = 0, \tag{6}$$

where $F_{M,f,S}$ indicates free energies of metal, film, and solution, respectively (throughout the manuscript we are using designation with multiple indexes M, f, S which simply indicate meaning of the parameter for the different system, for example, $F_{M,f,S} = F_M, F_f, F_S$ indicates free energies of metal, film, and solution, resp.). It is clear that variations in particles in the metal, the film, and the solution cause variations of the corroded volume. Therefore, the T, V, and P parameters in (2) are no longer constants. By taking into account that

$$\frac{\partial F_{M,f,S}}{\partial n_{M,f,S}} = \mu_{M,f,S}(T,P), \tag{7}$$

and chemical potential of the solution [16] is

$$\mu_S = \mu_0(P,T) + \sum_i \frac{n_i T}{N}\ln\left(\frac{n_i}{eN}\right) + \sum_i n_i\psi_i(P,T), \tag{8}$$

and using (2), (6)–(8), we get,

$$\begin{aligned} &\left[\varepsilon_0^M + \nu_M\left(3\ln\left(1 - e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right) + P_M\frac{dV_M}{dn_M}\right]\delta n_M \\ &\quad + \left[\varepsilon_0^f + \nu_f\left(3\ln\left(1 - e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right) + P_f\frac{dV_f}{dn_f}\right]\delta n_f \\ &\quad + \left(\mu_0(P,T) + \sum_i \frac{n_i T}{N}\ln\left(\frac{n_i}{eN}\right) + \sum_i n_i\psi_i(P,T)\right)\delta n_S = 0. \end{aligned} \tag{9}$$

Also, the conservation of number of particles requires that

$$\delta n_M + \delta n_f + \delta n_S = 0. \tag{10}$$

This is given as

$$\begin{aligned}&\left[\varepsilon_0^M + \nu_M\left(3\ln\left(1-e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right) + P_M\frac{dV_M}{dn_M}\right]\delta n_M\\ &\quad+\left[\varepsilon_0^f + \nu_f\left(3\ln\left(1-e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right) + P_f\frac{dV_f}{dn_f}\right]\delta n_f\\ &\quad=\left(\mu_0(P,T)+\sum_i\frac{n_iT}{N}\ln\left(\frac{n_i}{eN}\right)+\sum_i n_i\psi_i(P,T)\right)\\ &\qquad\times\left[\delta n_f+\delta n_M\right].\end{aligned} \tag{11}$$

It was mentioned earlier that the degradation process is always accompanied by chemical reactions that change the volume of corroded metal. Let us consider that chemical reactions go in a manner that $A + B \Leftrightarrow [AB] \rightarrow$ product then number of the elements A, B can be calculated as

$$\frac{dN_A}{dt} = \frac{dN_B}{dt} = -kN_AN_B, \tag{12}$$

where k is given by Collins-Kimball expression [18, 19] as

$$k = \frac{k_rk_D}{k_r+k_D}; \tag{13}$$

$k_D = 4\pi rD$ is rate constant; k_r is kinetic rate of the reaction; r is distance of the A and B closest approach equal to the sum of their radii; D is their relative diffusion coefficient. The diffusion coefficient can be determined according to Einstein equation

$$D = \frac{RT\sigma}{Z^2F^2C}, \tag{14}$$

(see [20]) where C is concentration of the reacting atoms (in our case, it will be metal atoms and some dissolved ions), σ is electrical conductivity, Z is the valence of the ion, F the Faraday constant, R the gas constant, and T the temperature. From (13) and (14), it follows that

$$k = \frac{k_rk_D}{k_r+k_D} = \frac{4\pi rRT\sigma k_r}{Z^2F^2Ck_r+4\pi rRT\sigma}. \tag{15}$$

Taking into account the theory of kinetic rate calculations, [18] we can calculate the volume of corroded metal. After some algebraic manipulations, we will have

$$\frac{dV_{M,f}}{dn_{M,f}} = \frac{dV_{M,f}}{dt}\frac{dN_{M,f}}{dt} = -k_{M,f}N_{M,f}N_{i,f,M}\frac{dV_{M,f}}{dt}, \tag{16}$$

where

$$D = \frac{RT\sigma_{f,M}}{Z_{i,f,M}^2F^2C_{i,f,M}}, \tag{17}$$

and $C_{i,f,M}$ concentrations are concentrations of ions reacting with film molecules and metal atoms, respectively, $V_{M,f} \equiv V_M, V_f$ is volume of the metal and the film, respectively. Taking all of these into account in (11), we will have

$$\begin{aligned}&\left[{\varepsilon_0}^M + {\varepsilon_0}^f + \left(\nu_M+\nu_f\right)\left(3\ln\left(1-e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right)\right]\\ &\quad-\left(P_Mk_MN_MN_{i,M}\frac{dV_M}{dt}\frac{\delta n_M}{\delta n_M+\delta n_f}\right.\\ &\qquad\left.+P_fk_fN_fN_{i,f}\frac{dV_f}{dt}\frac{\delta n_f}{\delta n_M+\delta n_f}\right)\\ &\quad=\mu_0(P,T)+\sum_i\frac{n_iT}{N}\ln\left(\frac{n_i}{eN}\right)+\sum_i n_i\psi_i(P,T).\end{aligned} \tag{18}$$

Now, let us discuss corrosion degradation step by step. Step 1 is breakdown of the film, meaning $|\delta n_f| \gg |\delta n_M|$ and $|\delta n_f + \delta n_M| \gg |\delta n_M|$ leads to the following simplification:

$$\begin{aligned}&P_fk_fN_fN_{i,f}\frac{dV_f}{dt}\\ &\quad=\left[\varepsilon_0^M + \varepsilon_0^f + \left(\nu_M+\nu_f\right)\left(3\ln\left(1-e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right)\right]\\ &\qquad-\left[\mu_0(P,T)+\sum_i\frac{n_iT}{N}\ln\left(\frac{n_i}{eN}\right)+\sum_i n_i\psi_i(P,T)\right].\end{aligned} \tag{19}$$

By similarity, Step 2 leads to $|\delta n_M + \delta n_f| \gg |\delta n_f|$ and $|\delta n_M| \gg |\delta n_f|$

Using (18), we have,

$$\begin{aligned}&P_Mk_MN_MN_{i,M}\frac{dV_M}{dt}\\ &\quad=\left[{\varepsilon_0}^M + {\varepsilon_0}^f + \left(\nu_M+\nu_f\right)\left(3\ln\left(1-e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right)\right]\\ &\qquad-\left[\mu_0(P,T)+\sum_i\frac{n_iT}{N}\ln\left(\frac{n_i}{eN}\right)+\sum_i n_i\psi_i(P,T)\right].\end{aligned} \tag{20}$$

Equations (19) and (20) completely predicts the behavior of the corroded metal volume in time and can be applied to any case, in general. However, it should be mentioned that the solution to (19) and (20) is not possible because functions

$$\begin{aligned}P_f &= P_M \equiv P(t),\\ T_f &= T_M \equiv T(t),\\ N_{M,f} &\equiv N_{M,f}(t)\end{aligned} \tag{21}$$

are unknown, in general.

In order to find the solution, let us consider some specific models and functions that take for parameters described in (19), (20), and (21). Before the discussion of models, we can further simplify general equations if we determine

$N_{M,f} \equiv N_{M,f}(t)$ functions. As discussed above (12), we can determine

$$N_{f,M} = N_{f,M,0}e^{-kN_{i,f,M}t}. \tag{22}$$

Therefore, finally from (19)–(22) we must have:

$$\begin{aligned} P_f k_f N_{f,0} e^{-kN_{i,f}t} N_{i,f} \frac{dV_f}{dt} &= \left[\varepsilon_0^M + \varepsilon_0^f + \left(\nu_M + \nu_f\right)\left(3\ln\left(1 - e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right)\right] \\ &\quad - \left[\mu_0(P,T) + \sum_i \frac{n_i T}{N}\ln\left(\frac{n_i}{eN}\right) + \sum_i n_i\psi_i(P,T)\right] \end{aligned} \tag{23}$$

$$\begin{aligned} P_M k_M N_{M,0} e^{-kN_{i,M}t} N_{i,M} \frac{dV_f}{dt} &= \left[\varepsilon_0^M + \varepsilon_0^f + \left(\nu_M + \nu_f\right)\left(3\ln\left(1 - e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right)\right] \\ &\quad - \left[\mu_0(P,T) + \sum_i \frac{n_i T}{N}\ln\left(\frac{n_i}{eN}\right) + \sum_i n_i\psi_i(P,T)\right]. \end{aligned} \tag{24}$$

It should be mentioned that in the first step on the left side of the (23), we have chemical potential of pure solvent while in (24), we have impurity rich solution with different chemical potential. The last two equations can be simplified if make some notations as,

$$\begin{aligned} f(t) &\equiv \frac{\left[\varepsilon_0^M + \varepsilon_0^M + \left(\nu_M + \nu_f\right)\left(3\ln\left(1 - e^{-\theta/T}\right) - D(\theta/T)\right)\right]}{P_f k_f N_{f,0} N_{i,f}} \\ &\quad - \frac{\left[\mu_0(P,T) + \sum_i (n_i T/N)\ln(n_i/eN) + \sum_i n_i\psi_i(P,T)\right]}{P_f k_f N_{f,0} N_{i,f}}, \\ M(t) &\equiv \frac{\left[\varepsilon_0^M + \varepsilon_0^M + \left(\nu_M + \nu_f\right)\left(3\ln\left(1 - e^{-\theta/T}\right) - D(\theta/T)\right)\right]}{P_M k_M N_{M,0} N_{i,M}} \\ &\quad - \frac{\left[\mu_0(P,T) + \sum_i (n_i T/N)\ln(n_i/eN) + \sum_i n_i\psi_i(P,T)\right]}{P_M k_M N_{M,0} N_{i,M}}. \end{aligned} \tag{25}$$

Then we will have:

$$dV_f = f(t)e^{k_f N_{i,f}t}dt, \tag{26}$$

$$dV_M = M(t)e^{k_M N_{i,M}t}dt. \tag{27}$$

Equations (27) and (28) will completely describe the corroded volume if we will be able to determine $f(t)$ and $M(t)$ functions.

After n times partial integrations of (26) and (27), we can find

$$\begin{aligned} \iiint_V dV_f &= \int_0^t f(t)e^{k_f N_{i,f}t}dt \\ &= \sum_{i=0}^{n} (-1)^i \left(\frac{1}{k_f N_{i,f}}\right)^{i+1} f^{(i)}(t)e^{k_f N_{i,f}t}, \end{aligned} \tag{28}$$

$$\begin{aligned} \iiint_V dV_M &= \int_0^t M(t)e^{kN_{i,M}t}dt \\ &= \sum_{i=0}^{n} (-1)^i \left(\frac{1}{k_M N_{i,M}}\right)^{i+1} M^{(i)}(t)e^{k_M N_{i,M}t}. \end{aligned} \tag{29}$$

Taking into account that

$$k_{M,f} = \frac{4\pi r_{M,f} RT\sigma_{M,f} k_{r,M,f}}{Z_{i,M,f}^2 F^2 C_{i,M,f} k_{r,M,f} + 4\pi r_{M,f} RT\sigma_{M,f}}, \tag{30}$$

($r_{M,f}$ is radius of metal atom and oxide layer molecule resp.) depends on diffusion coefficient, it is clear that the process can be further accelerated by variables from (30). Equations (28)–(30) are the exact solutions of time profile of corroded volume which might be very useful for estimating the deterministic characteristics of metal corrosion. The model system always has finite volume; so corrosion process is ending after a finite time.

We mention that if corrosion process has at least quasi-equilibrium manner, then $\delta n_f = \delta n_M$ so in (18) we will have that $\varepsilon_0^M = \varepsilon_0^f$, $T =$ const and is not changing during the process and $P_M = P_f = P(t)$, then (18) can be simplified as

$$\begin{aligned} \iiint_V dV_M &= 2\int_0^t M(t)e^{k_M N_{i,M}t}dt \\ &= 2\sum_{i=0}^{n} (-1)^i \left(\frac{1}{k_M N_{i,M}}\right)^{i+1} M^{(i)}(t)e^{k_M N_{i,M}t}, \end{aligned} \tag{31}$$

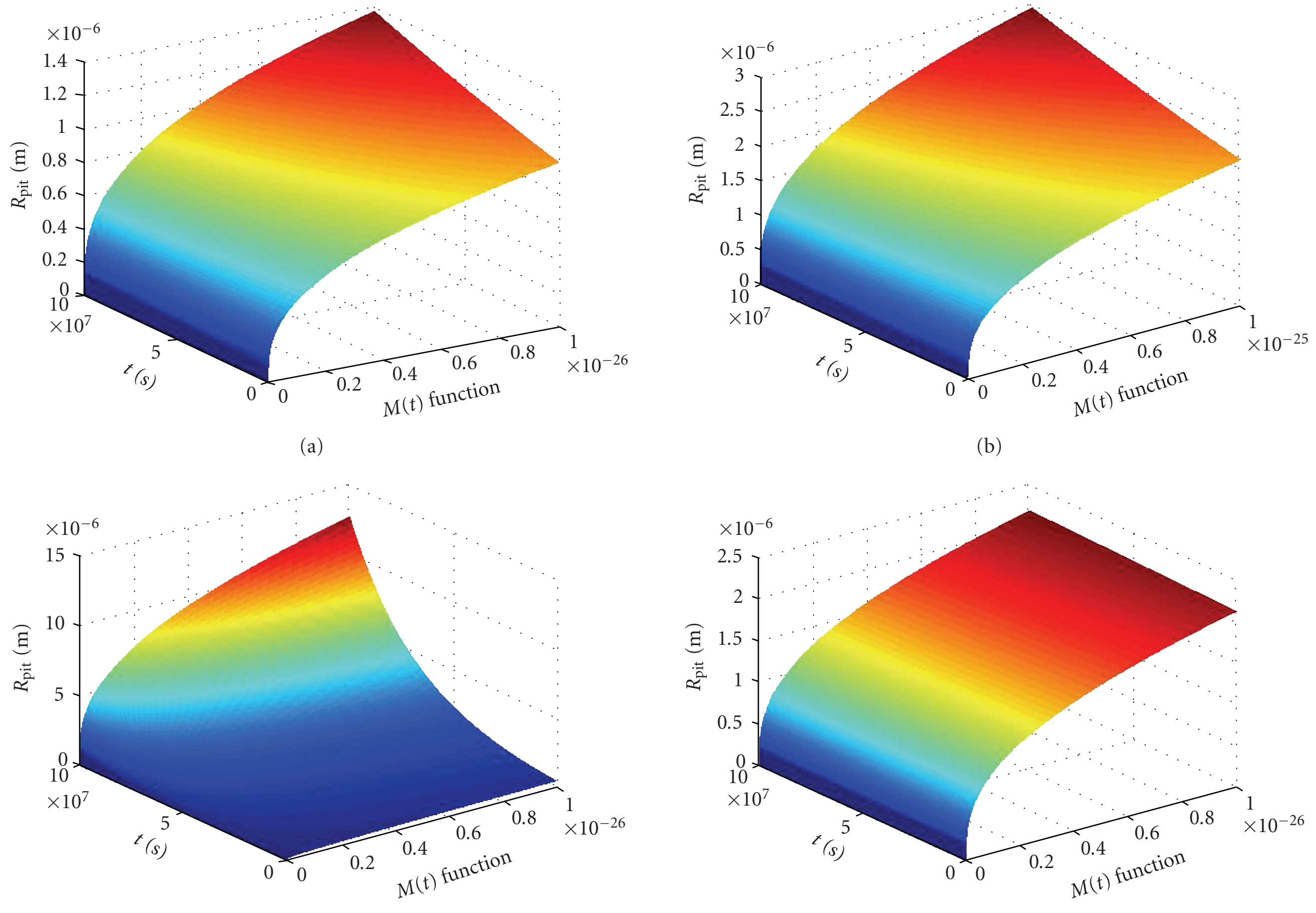
where $M(t)$ function is determined according to (25).

3. Results and Discussion

In order to see the trends in corrosion degradation process, specifically how the pit profile (radii) changes with time, computer simulations based on (31) using Matlab software were carried out with preposition that the pit has semispherical shape with radii R_{pit}.

The following assumptions were used in the analytical simulation. First, we propose that corrosion process takes place at least in a quasi-equilibrium manner. This assumption allows to further simplify (28)–(30) to (31), where $\varepsilon_0^M = \varepsilon_0^f$, $T =$ const and are not changing during the corrosion process, and $P_M = P_f = P(t)$. However, (31) still has parameters $k_M N_{iM}$ which are directly connected to chemical reactions.

Second, the assumptions are related to the estimations for $M(t)$ function variation and the $k_M N_{iM}$ parameters. Function $M(t)$ is related to the specific metal characteristics



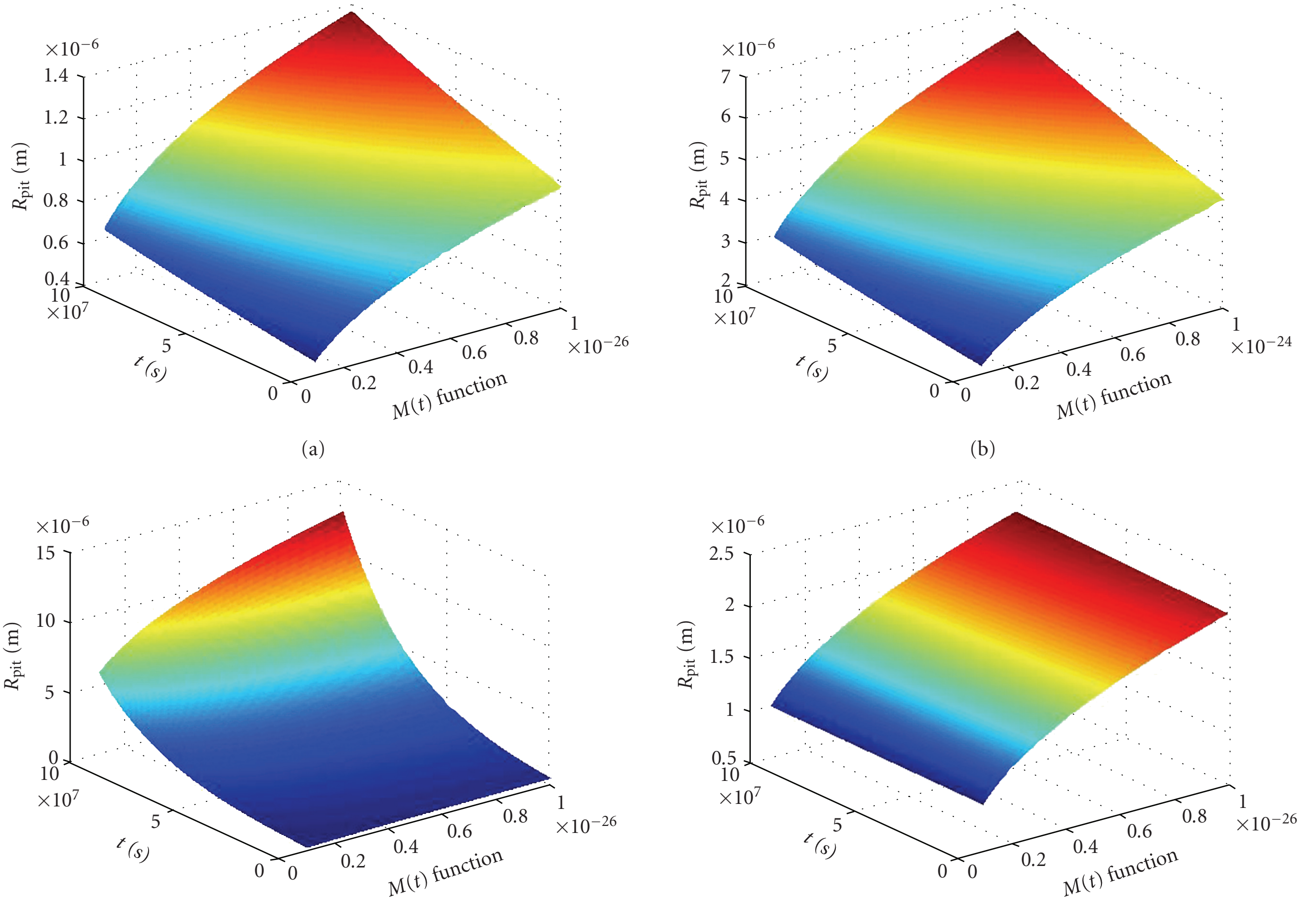
(a) (b)

(c) (d)

FIGURE 2: Simulations of time profile of pit radii for various parameters/functions. The range of $M(t)$ various function: (a) $M(t) \in (0, 10^{-25})$, $k_M N_{im} \sim 10^{-8}$, (b) $M(t) \in (0, 10^{-24})$, $k_M N_{im} \sim 10^{-8}$, (c) $M(t) \in (0, 10^{-25})$, $k_M N_{im} \sim 10^{-7}$, (d) $M(t) \in (0, 10^{-25})$, $k_M N_{im} \sim 10^{-9}$. Preposition of view $M(t) > 0$ because chemical potential of the components present in metal are always more than the chemical potential of any solution the line to near of $M(t) \sim 0$ are nonrealistic plots so these dictate us to estimate borders of $M(t)$ function more carefully.

(T = temperature, ω_M= vibration frequencies of metal atoms, and $\overline{u}$ = average velocity of sound) which is related to the chemical potential of the electrolyte. All the above parameters are directly or indirectly responsible for the degradation properties of the metal. We estimate that the $M(t)$ function using (25) and experimental data [17]. Specifically, we have used the experimental data [17] of diffusion coefficients to estimate the range of ion concentrations for in the term $1/k_M N_{M,O} N_{i,M,O}$ and AFM data [17] to estimate $\varepsilon_0^f = \varepsilon_0^M \approx 5.1 \cdot 10^{-22}$ J value (Figure 1) depending on the variation of different chemical ions and $k_M N_{M,O} N_{i,M,O}$ values (which are number of oxidized metal atoms and ions reacting with metal atoms and with oxygen). We have taken several different ranges for $M(t)$ function and $k_M N_{iM}$ parameters, which are given as: (a) $M(t) \in (0, 10^{-25})$ and $k_M N_{im} \sim 10^{-8}$; (b) $M(t) \in (0, 10^{-24})$, $k_M N_{im} \sim 10^{-8}$; (c) $M(t) \in (0, 10^{-25})$, $k_M N_{im} \sim 10^{-7}$; and (d) $M(t) \in (0, 10^{-25})$, $k_M N_{im} \sim 10^{-9}$ (see Figure 2). Also, for some fixed ranges of $M(t)$, parameters $k_M N_{iM}$ takes values $\sim 10^{-7}$, $\sim 10^{-8}$, $\sim 10^{-9}$ (Figure 3). The reason for taking many ranges for the parameters is to demonstrate that even such rough estimation for the rate of chemical reactions during the corrosion degradation, the $M(t)$ function, can be considered as a characteristic of the metal, giving reasonable results for pitting corrosion degradation.

The range of $M(t)$ function was determined based on (25) and experimental data [17] for a value of $\varepsilon_0^f = \varepsilon_0^M$, chemical potentials for solutions as given by standard tables, and parameter k_M was determined according to (30). The time profile of pit radii is shown in Figures 2 and 3 for various parameters and functions. The present predictions are compared qualitatively to the experimental data [21] by estimating $M(t)$ and $k_M N_{iM}$ parameters through a range but not strictly quantitatively. A good agreement is found between the present predictions and the experimental data for the trends in corrosion degradation. However, the quantitative predictions and comparison to the experimental data need more knowledge about the exact value of forces that are necessary to move atom from metal surface (that definitely depends on the kind of metal), exact knowledge of ion content of environment where the metal is placed and must be taken into account time variable nature of $k_M N_{iM}$ parameter. Simulations of time profile of pit radii for various parameters/functions showed that if $M(t) \approx 0$ (Figure 2) then the metal is very stable against the corrosion



(a)

(b)

(c)

(d)

FIGURE 3: The range of $M(t)$ function was estimated based on the designation of (25) and experimental data [17] and using $\varepsilon_0^f = \varepsilon_0^M \approx 5.1 \cdot 10^{-22}$ J value. Simulations were run for different range of $M(t)$ function and for different values of $k_M N_{im}$ parameter. Figures (a) & (b) indicate pit radii time profile for range of $M(t) \in [10^{-27}, 10^{-26}]$ and $M(t) \in [10^{-25}, 10^{-22}]$, respectively. Estimation intervals of $M(t)$ functions were taken by calculations based on given by standard tables of chemical potentials for solutions and for free energy per atoms, $k_M N_{iM} \sim 10^{-8}$ which was estimated based on (30). Figures (c) & (d) indicate pit radii time profile for fixed range of $M(t)$ functions $M(t) \in [10^{-27}, 10^{-26}]$ but for different $k_M N_{iM}$ parameter, $k_M N_{iM} \sim 10^{-7}$ and $k_M N_{iM} \sim 10^{-9}$, respectively.

degradation and pit radii is almost 0 with very slow changes if any, but we should mention that $M(t) > 0$ always (chemical potential of the components present in metal are always more than the chemical potential of any solution) so plots near to zero are nonrealistic plots. Estimations of the $M(t)$ functions based on the designation of (25) and experimental data [17], using $\varepsilon_0^f = \varepsilon_0^M \approx 5.1 \cdot 10^{-22}$ J value, give us following range $M(t) \in [10^{-27}, 10^{-26}]$ and $M(t) \in [10^{-25}, 10^{-22}]$ for different values of $k_M N_{im}$ parameter (Figure 3). Though even this rough estimations give us reasonable results. All the above parameters complicate finding an analytical solution of (31). More exact quantitative descriptions by the proposed theory of corrosion pit radii for specific metals under specific environments need further studies. This aspect of the research is being pursued as future work.

As we discussed above, to estimate range of variation for $M(t)$ function, the value for $\varepsilon_0^f = \varepsilon_0^M$ which is free energy per atom in metal needs to be estimated. This free energy per atom is estimated based on the AFM experimental data where the minimal force necessary to move the atom on the surface of the metal was measured. The lateral force to move atom for Cu was measured to be $F = 17 \pm 3$ pN [17] and $x = 300$ pm then approximate energy per atom $E = F \cdot x = 5.1 \cdot 10^{-22}$ J. After recalculating this value per mol of atom, this will be $\varepsilon_0^f = \varepsilon_0^M \approx 3 \cdot 10^2\ \mathrm{J} \cdot (\mathrm{mol})^{-1}$. $\varepsilon_0^f = \varepsilon_0^M \approx 5.1 \cdot 10^{-22}$ J (1) per atom.

In addition, the range of $k_M N_{im}$ parameter also needs to be estimated in which the value of k_M is related to rate of chemical reaction in the metal during the corrosion degradation and the parameter $N_{i,M}$ is related to the concentration of the ions reacting with metal atoms. Taking into account that

$$k_{M,f} = \frac{4\pi r_{M,f} RT \sigma_{M,f} k_{r,M,f}}{Z_{i,M,f}^2 F^2 C_{i,M,f} k_{r,M,f} + 4\pi r_{M,f} RT \sigma_{M,f}} \quad (32)$$

($r_{M,f}$ is radius of metal atom and oxide layer molecule, resp.) depends on diffusion coefficient, which is given by formula

$$D = \frac{RT\sigma_{f,M}}{Z_{i,f,M}^2 F^2 C_{i,f,M}} \quad (33)$$

($C_{i,f,M}$ are concentrations of ions reacting with film molecules and metal atoms, resp.). This value is estimated from the concentrations or number of reacting ions in the diffusion coefficient. The range for $k_M N_{im}$ parameter is estimated based on diffusion using the experimental data [20]. These estimations are not very strict, so we have used the range for the parameters, instead of one fixed value in the simulations.

4. Conclusions

In this study, the governing equation for corrosion degradation due to pitting corrosion behavior was derived. After several assumptions, some solutions and simulations are presented and discussed. The simulation results obtained indicate that the results are reasonable and further validation of the theory requires more experimental work. The theoretical model developed in this study has the following limitations. First, (28)–(30) completely describe corrosion degradation in time which cover many unknown parameters that are strictly mathematical, and determination of these parameters may be difficult. Second, we formulated the corrosion degradation problem as an isolated system rather than open system. Third, in our simulations, we considered an ideal situation, related to pitting degradation which has at least quasi-equilibrium manner (which is good estimation as the corrosion process is very slow). It should be mentioned that the developed corrosion degradation model is very general and without making any assumptions it will be very difficult task in order to get a solution for pitting corrosion degradation.

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