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The stochastic model of pitting corrosion of metals

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Abstract. Considering that pitting corrosion is a stochastic process, the purpose of this paper is to use stochastic theory to investigate the growth process of pitting corrosion of metals. Based on the mechanism of pit growth and nonequilibrium statistical theory, the time evolution equations of pit depth and corrosion rate are obtained, and the probability density function can be derived by solving Fock-Plank Equation. Subsequently, the failure probability or reliability of metals is calculated based on the weakest link model of pitting corrosion. Finally, the stochastic model is used on the aircraft aluminum alloy LD2. Furthermore, this methodology can be applied to analyze the reliability and predict the pitting life of metals.

1. Introduction

Pitting corrosion is one of the common and highly destructive localized corrosion types, which is likely to cause catastrophic damage without any obvious signs in metals and alloys. Accordingly, it is more dangerous than uniform corrosion [1, 2]. Due to the inhomogeneity of the component, heat-treatment temperature, the surface state of metal [3-5] and temperature, pH, etc., of the corrosive environment [6, 7], the pitting corrosion of metal can be dealt with the stochastic theory. Shekari E *et al* [8] used the non-homogenous Markov process to investigate the model of maximum pit depth, and calculated the burst pressure of a defected pipe. Caleyo *et al* [9-11] established the stochastic model of pitting corrosion by Monte Carlo simulation method and obtained the probability distribution of pitting corrosion depth and rate in underground steel pipeline. In this work, considering that pitting corrosion of metal can be regarded as an uniform environment superimposed by inhomogeneous fluctuation, Xing's nonequilibrium statistical theory [12,13] is used to investigate the pitting corrosion.

2. The stochastic equation of pitting corrosion

According to the nonequilibrium statistical theory, the corrosion rate should obey the following generalized Langevin equation [14]

$$v = \frac{\mathrm{d}a}{\mathrm{d}t} = K(a,t) + F(a,t) = K(a,t) + \beta(a)\,f(t) \tag{1}$$

where a is the pit depth; $K(a,t)$ is the transportation rate, the deterministic part of the corrosion rate; $F(a,t) = \beta(a)\,f(t)$ is the fluctuation rate, the stochastic part of the corrosion rate; $\beta(a)$ is the fluctuation amplification function; $f(t)$ is the fluctuation function, which satisfies Gaussian distribution. The stochastic nature of pitting corrosion allows one to regard the pitting corrosion as a Markov process [15].

The Fock-Plank equation [14], which is equivalent to (1), can be derived as follows

$$\frac{\partial P(a_0,a;t)}{\partial t}=-\frac{\partial}{\partial a}\left\{\left[K(a,t)+\frac{Q\beta(a)}{2}\frac{\partial\beta(a)}{\partial a}\right]P(a_0,a;t)\right\}+\frac{Q}{2}\frac{\partial^2}{\partial a^2}\left[\beta^2(a)P(a_0,a;t)\right] \tag{2}$$

This is a stochastic partial differential equation, which describes the growth process of pitting corrosion, where Q is the fluctuation growth coefficient, $P(a_0,a;t)\mathrm{d}a$ is the probability that the initial pit depth a_0 grows into the depth between a and $(a+\mathrm{d}a)$ at time *t*, it is obvious that $P(a_0,a;t)\mathrm{d}a$ satisfies normalization condition.

3. Pit depth and probability density function

3.1. Pit depth and corrosion rate

Normally, pitting corrosion can be regarded as two physical processes: the metastable pitting (the pit generation process) and the stable pitting (the pit growth process) [16,17].

Metastable pitting consists of the metastable pit nucleation, growth and the process of the metastable pit growth to stable pit [18]. Frankel *et al* [19] considered the corrosion current density of metastable pit to be a constant, the period of pitting corrosion from occurring to nucleation can be defined as the pit initiation time t_{d}, for the corrosion current density, there is

$$I_{\mathrm{corr}}=i_{\mathrm{a}} \qquad 0<t<t_{\mathrm{d}} \tag{3}$$

where i_{a} is a constant, which is independent of the corrosion time *t*.

Stable pitting follows the growth of metastable pit. The passive film of the metal surface is destroyed at some point, aggressive anionic species (such as Cl^-, Br^- or $ClO4^-$ and so on) flow into the pit and promote the transition from metal atoms to ions. On the one hand, the ions form corrosion current by diffusion. On the other hand, corrosion products and environment hinder the diffusion of ions. This process can be equivalent to the charging process of RC circuit, and the corrosion current density of stable pitting (after the pit initiation time) can be proposed as

$$I_{\mathrm{corr}}=i_{\mathrm{a}}\exp\left[-\lambda(t-t_{\mathrm{d}})\right] \qquad t\ge t_{\mathrm{d}} \tag{4}$$

where λ is the attenuation parameter of corrosion current density. Equation (4) is similar to the current density formula in the anodic dissolution model which is proposed by Ford [20,21]. Substituting equations (3) and (4) into Faraday formula [22], the transportation rate $K(a,t)$ of the equation (1) can be derived as follows

$$K(a,t)=\begin{cases}\dfrac{Mi_{\mathrm{a}}}{ZF\rho} & 0<t<t_{\mathrm{d}}\\[2ex] \dfrac{Mi_{\mathrm{a}}}{ZF\rho}\exp\left[-\lambda(t-t_{\mathrm{d}})\right] & t\ge t_{\mathrm{d}}\end{cases} \tag{5}$$

where *M* is the atomic weight of metal cation, *Z* is the valence of metal cation, ρ is the metal density, and *F* is the Faraday constant. Integrated equation (5), the time evolution of pit depth can be expressed as

$$a=\frac{Mi_{\mathrm{a}}t_{\mathrm{d}}}{ZF\rho}+\frac{Mi_{\mathrm{a}}}{ZF\rho\lambda}\left\{1-\exp\left[-\lambda(t-t_{\mathrm{d}})\right]\right\} \qquad t\ge t_{\mathrm{d}} \tag{6}$$

If $t\to\infty$, equation (6) becomes

$$a_{\mathrm{m}}\approx\frac{Mi_{\mathrm{a}}t_{\mathrm{d}}}{ZF\rho}+\frac{Mi_{\mathrm{a}}}{ZF\rho\lambda} \tag{7}$$

where a_m is regarded as the maximum pit depth.

3.2. Probability density function of pitting corrosion

According to equations (5) and (6), the transportation rate can be written as

$$K(a,t)=\frac{Mi_a t_d \lambda}{ZF\rho}+\frac{Mi_a}{ZF\rho}-a\lambda \qquad t\ge t_d \tag{8}$$

Let

$$A=\frac{Mi_a}{ZF\rho}, \qquad \beta(a)=1+t_d\lambda-\frac{a\lambda}{A} \tag{9}$$

The transportation rate $K(a,t)$ in equation (8) can be regarded as an average value $\bar{v}$. In fact, due to the inhomogeneous fluctuations of the material and corrosive environment, the atomic weight of metal cation, the corrosion current density, the valence of metal cation, and the metal density should be $M\pm\Delta M$, $i_a\pm\Delta i_a$, $Z\pm\Delta Z$, $\rho\pm\Delta\rho$. The corrosion rate of equation (1) should be written as

$$v=\frac{(M\pm\Delta M)(i_a\pm\Delta i_a)}{(Z\pm\Delta Z)(\rho\pm\Delta\rho)F}\beta\approx\frac{Mi_a}{ZF\rho}(1\pm\eta)\beta=\bar{v}\pm\eta\bar{v} \tag{10}$$

where η is the sum of relative deviations of the four physical quantities M, i_a, Z, ρ

$$\eta=\frac{\Delta M}{M}+\frac{\Delta i_a}{i_a}+\frac{\Delta Z}{Z}+\frac{\Delta\rho}{\rho} \tag{11}$$

The fluctuation growth coefficient has been obtained in the [14]

$$Q=\eta^2A^2\tau \tag{12}$$

where τ is the pitting life of the metal.

Substituting equations (8), (9), (12) into equation (2), the probability density function $P(a_0,a;t)$ of pitting corrosion can be expressed by the following equation

$$P(a_0,a;t)\mathrm{d}a=\frac{1}{\sqrt{2\pi Qt\beta(a)^2}}\exp\left\{-\frac{U(a)^2}{2Qt}\right\}\mathrm{d}a \tag{13}$$

where $U(a)$ is expressed as

$$U(a)=\frac{A}{\lambda}\ln\left(\frac{t_d\lambda A+A-a_0\lambda}{t_d\lambda A+A-a\lambda}\right)-At \tag{14}$$

It can be seen that $P(a_0,a;t)$ varying with the pit depth can be fitted to the logarithmic normal distribution function.

It is assumed that $P(t,a)\mathrm{d}t$ is the probability of finding the pit depth a in the range of time $(t,t+\mathrm{d}t)$ over the period of time $t\in(0,\infty)$

$$P(t,a)\mathrm{d}t=\frac{A\exp[-\lambda(t-t_d)]}{\sqrt{2\pi Qt\beta(a)^2}}\exp\left\{-\frac{U(a)^2}{2Qt}\right\}\mathrm{d}t \tag{15}$$

The initial and boundary conditions of $P(t,a)$ are given by

$$P(t = t_{\mathrm{d}}, a) = \delta(a - a_0), \qquad P(t \to \infty, a) = 0 \tag{16}$$

It indicates that pits of any depth cannot exist in an infinite time. That is to say, the pitting life of the metal is always limited.

4. Failure probability and reliability

Generally, there are a large number of pits in the metal. Let *S* denote the surface area of material and *N* denote the number of pits per unit area of material, so the total number of pits *G* is *SN*. The material will be perforated due to pitting corrosion when the pit depth reaches the material thickness, on the basis of the weakest link model of pitting corrosion, the failure probability of material $P_{\mathrm{f}}(t)$ during the time interval $0-t$ is

$$P_{\mathrm{f}}(t) = 1 - \left[1 - \int_0^t P(t, a_{\mathrm{m}})\mathrm{d}t\right]^{G-1} \approx 1 - \exp\left[-(G-1)\int_0^t P(t, a_{\mathrm{m}})\mathrm{d}t\right] \tag{17}$$

where a_{m} is the maximum pit depth, it can be assumed as the thickness of the material.

According to the [13], the integral $\int_0^t P(t, a_{\mathrm{m}})\mathrm{d}t$ in equation (17) can be approximately expressed as

$$\int_0^t P(t, a_{\mathrm{m}})\mathrm{d}t \approx \frac{1}{\sqrt{\pi}} \int_X^\infty \exp(-X^2)\mathrm{d}X \approx \frac{1}{\theta X^{10}} \tag{18}$$

where θ is a constant, and *X* is $U(a_{\mathrm{m}}) / \sqrt{2Qt}$.

Substituting equation (18) into equation (17), $P_{\mathrm{f}}(t)$ can be approximately expressed as

$$P_{\mathrm{f}}(t) \approx 1 - \exp\left\{-\frac{(G-1)}{\theta X^{10}}\right\} \tag{19}$$

Therefore, the reliability of metal $R(t)$ is the probability that the material can work safely without perforation within time interval $0-t$ in the corrosive environment, which can be deduced by the equation (19).

$$R(t) = 1 - P_{\mathrm{f}}(t) \approx \exp\left\{-\frac{(G-1)}{\theta X^{10}}\right\} \tag{20}$$

5. Application in the aircraft aluminum alloy LD2

5.1. Calculation of pit depth and corrosion rate

The theory is used on the pitting corrosion of aircraft aluminum alloy LD2, according to the accelerated corrosion test in [23, 24], the parameters are selected as follows: $\rho = 2.7 \times 10^3\ \mathrm{kg\,m^{-3}}$, $M = 27.18 \times 10^{-3}\ \mathrm{kg\,mol^{-1}}$, $F = 96500\ \mathrm{C\,mol^{-1}}$, $t_{\mathrm{d}} = 2 \times 3.1536 \times 10^7\ \mathrm{s} = 2\ \mathrm{yr}$, $i_{\mathrm{a}} = 0.009\ \mathrm{A\,m^{-2}}$, $Z = 3$, $\lambda = 5.71 \times 10^{-9}\ \mathrm{s^{-1}} = 0.18\ \mathrm{yr^{-1}}$. Then, the curves of pit depth and corrosion rate over corrosion time can be drawn by using the equations (6) and (10), as shown in figures 1 and 2 (η is 0.2).

It can be seen from figure 1, the pit depth *a* increases with corrosion time *t*, and the maximum pit depth a_{m} is around 74 μm. When the corrosion time takes $5/\lambda$, the pit depth *a* reaches $0.993a_{\mathrm{m}}$, so the approximation of pitting life τ of aluminum alloy is 20 years. Figure 2 shows that the corrosion rate *v* decreases with corrosion time *t*. In addition, the theoretical simulation results present the general trend of pit depth and corrosion rate versus corrosion time, which provides the basis for calculation of probability density function.

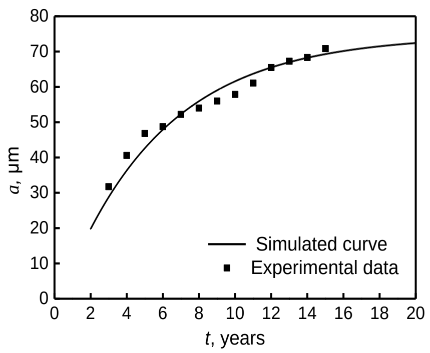


Figure 1. Comparison between the theoretical results and the experimental data of pit depth versus corrosion time.

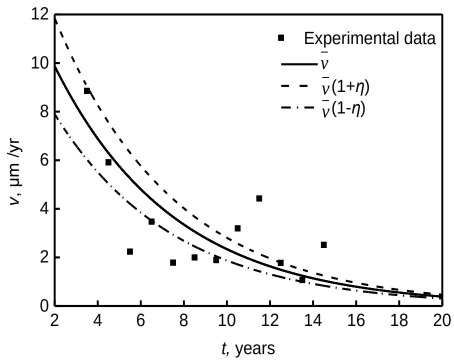


Figure 2. Comparison between the theoretical results and the experimental data of corrosion rate versus corrosion time.

5.2. Calculation of probability density function

According to equations (13) and (15), the curves of probability density function $P(a_0, a; t)$ and $P(t, a)$ are plotted respectively, as shown in figures 3 and 4.

Figure 3 shows that the distribution of the probability density function $P(a_0, a; t)$ tends to be high in the middle and lower at both ends, but it's not a Gaussian distribution. The maximum probability density $P(a_0, a; t)$ is corresponding to the most probable pit depth a_p, which can be used to predict the most probable pit depth a_p in different corrosion time ranges. For instance, when the corrosion time is 4 years, the pit depth a is the most likely to be 45-55 μm. As the corrosion time increases, the peak value of curve shifts to the right, and the shape of the curve becomes narrower. That is to say, pits grow up continuously, and most of the pit depths are concentrated around the most probable pit depth when the corrosion time t is larger.

Figure 4 shows that the maximum probability density function $P(t, a)$ is corresponding to the most probable corrosion time t_p, which can be used to predict the most probable corrosion time range of different pit depths. For instance, pit depth a of 50 μm is the most likely to occur at the time range 4-5 years.

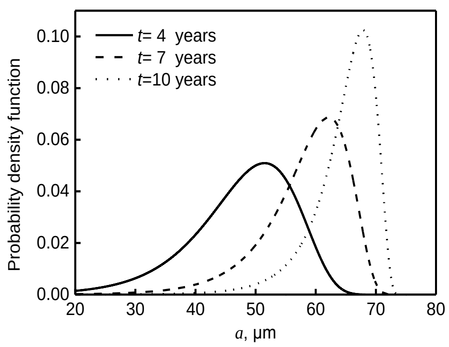


Figure 3. Probability density function $P(a_0, a; t)$ at different corrosion times.

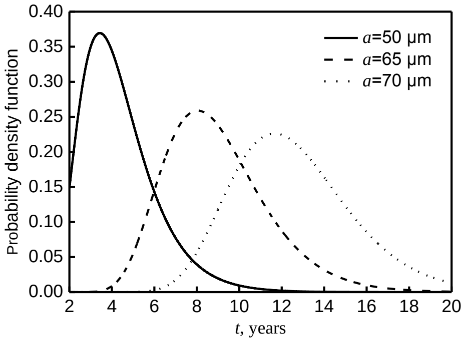
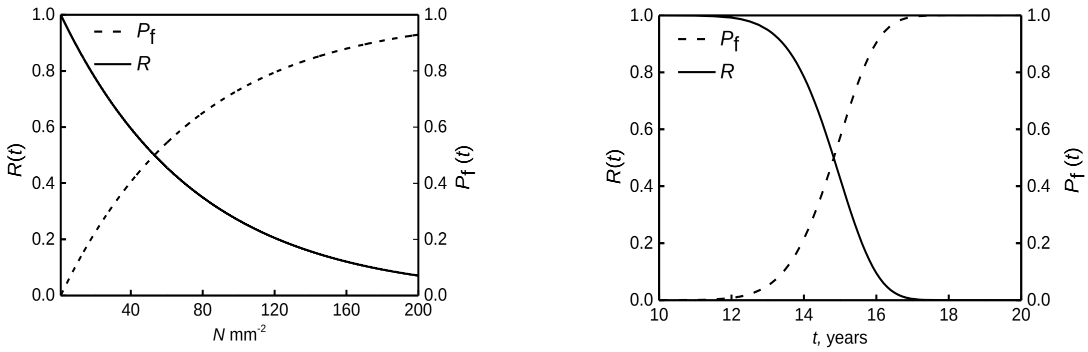


Figure 4. Probability density function $P(t, a)$ at different pit depths.

5.3. Calculation of failure probability and reliability

Substituting the surface area S=1 mm^2 and the pit density N of aluminum alloy into the equations (17) and (20), therefore, the failure probability P_f and the reliability R of aluminum alloy can be calculated, as shown in figure 5.

As can be seen from figure 5(a), at the same corrosion time, the greater the pit density, the lower the reliability, and the easier it is to perforate the aluminum alloy, so improving corrosion resistance and the reliability of the material can reduce pit density, and an example is the nanocrystalline material which has been studied by Pan C *et al* [25]. As shown in figure 5(b), when the corrosion time *t* is less than 12 years, the reliability is close to 1, denoting that aluminum alloy will not be perforated due to pitting corrosion. But when the corrosion time increases to the limit value (about 20 years), the failure probability P_f basically reaches 100%, while the reliability *R* is reduced to zero.



(a) (b)

Figure 5. Time curves of the failure probability and reliability. (a) versus pit density (t=15 year) and (b) versus corrosion time (N=67 mm^{-2}).

6. Conclusions

In conclusion, the pit depth, corrosion rate and the maximum pit depth of metal with corrosion time are calculated. Establishing and solving the Fock-Plank Equation of pitting corrosion, the probability density functions $P(a_0, a; t)$ and $P(t, a)$ are calculated, which can be used to predict the most probable pit depth in different time ranges and the most probable corrosion time range of different pit depths. Moreover, the failure probability and reliability of metal are estimated by using the weakest link model of pitting corrosion, which is dependent on the pit density *N*, corroded area *S*, corrosion time *t*, etc., the safety period of pitting corrosion of metal can be deduced.

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