한국부식학회지
J. Corros Sci. Soc. of Korea
Vol. 22, No. 2, June, 1993
〈총 설〉

핏팅 모델링을 위한 통계적 접근 방법에 대한 개요

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A Review of Stochastic Approach to Pitting Corrosion Modeling

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1. Introduction

In recent years, increasing costs and social consequencies of structual failures in systems ranging from regular consumer products to sophisticated nuclear power reactors have resulted in increased public awareness and, consequently, the demand for assuring structural reliability. An inescapable element in the reliability of structures is that apart from the presence of initial manufacturing and/or fabrication defects, flaws appear during the service life of the structure as a result of the material's exposure to time-dependent degradation processes such as pitting corrosion, corrosion fatigue, and stress-corrosion cracking(SCC), etc.

Corrosion is a material degradation process essentially consisting of the reaction of a metal exposed to a reactive environment that can, in general, be divided into two main classes, general and local.[1] Concerning on the latter, pitting corrosion is a form of localized corrosion that is exceedingly destructive since a perforation resulting from a single pit can cause complete failure. Furthermore, pits can produce premature service failure since they usually provide sites for crack initiation.

Evans[2] had stated that a study of corrosion probability might often possess greater practical importance particularly for localized corrosion. Further he emphasized that a knowledge of the exact velocity is less important than the assessment of the statistical risk of its starting. Passivity breakdown is a typical phenomenon showing a statistical and probabilistic nature, triggering the initiation of pitting corrosion, which might be potential sites leading to crevice corrosion or stress corrosion cracking. A lot of data on localized corrosion showing a wide scatter have been accumulated in laboratories and fields, but could not be analyzed quantitatively unless statistical and probabilistic approaches are introduced.

The objectives of the statistical and probabilistic approach for analyzing the scattered data of localized corrosion are roughly divided into two categories. The first is simply to get the representative values or degree of variation of the distribution of scattered data for evaluating the corrosion behaviour more quantitatively. The second is to manifest a basic mechanism of localized corrosion which exhibits intrinsically a randomness or probabilistic properties.[3,4]

The present paper reviewed firstly some examples of statistical distributions observed for SCC, crevice corrosion and pitting corrosion and secondly the stochastic model describing the pit birth, pit death, and pit growth processes.

2. Failure Time Distribution of Localized Corrosion

Recent studies[5] have shown that the distribution of failure time of SCC obeys a Weibull or exponential distribution. The Weibull distribution is one of the extreme value distributions, which is expressed as

$$F(t)=1-\exp\left[-\frac{(t-t_0)^a}{b}\right] \tag{1}$$

, where F(t) is the cumulative distribution of failure time, t, and t_0, a and b are a location, shape and scale parameters, respectively. If the shape parameter is unity, then the Weibull distribution reduced to the exponential distribution.

The distribution of pits on the surface had been found to obey a Poisson distribution by Mears and Brown.[6] The two dimensional distribution of pits is given by

$$P(n)=M^n\exp(-M)/n\,! \tag{2}$$

, where P(n) is the probability for finding n pits in unit area and M is a mean or expected value of n. Complete random occurrence of pit formation results in a Poisson distribution, but mutual interaction of pit formation causes a distortion in the shape of the distribution as discussed by Mears and Brown.[6]

When a mean rate of pit generation is $\lambda(s^{-1})$, the expected value for finding n after time t is equal to λt. Consequently, Eq. (2) becomes

$$P(n)=(\lambda t)^n\exp(-\lambda t)/n\,! \tag{3}$$

The probability to exceed the time, t_1, for detecting a first pit in unit area is then reduced to the following equation :

$$P(t_1>t)=P(n=0)=\exp(-\lambda t) \tag{4}$$

Then a cumulative survival probability of the pit formation with time is

$$P(t)=\exp(-\lambda t) \tag{5}$$

and the probability density function of Eq. (5) is given by

$$dP(t)/dt=-\lambda P(t) \tag{6}$$

Thus, the exponential distribution is deduced simply from a Poisson stochastic process. This type of the distribution has been often observed in laboratory experiments as well as in the field exposure as discussed before. The exponential distribution deduced from a simple Poisson process is commonly observed for the first failure time of SCC, crevice formation, and pitting corrosion.

3. Parameters Controlling Pit Initiation

Several different mechanisms for the initiation of pitting corrosion have been proposed.[7,8] It is agreed that corrosion pits propagate as a result of the development and maintenance of a high local acidity or high concentration of aggressive anions. As far as the nucleation of pits is concerned, authors have emphasized, among other phenomena, inhomogeneity in the metal, cracking and slow healing of the passive film, development of critical acidity levels in microscopic flaws, defect transport in passive films, and aggressive ion (chloride) adsorption or incorporation into localized areas of the passive film, including adsorption of halide ions into a transitional complex or local thinning of the oxide layer under chloride islands.

4. Markoff Process

A randomly selected system is put into operation at time $t=0$. We consider the time of its failure as experimental outcome. The space is the positive t axis. We define a random variable X such that $X(t)=t$. Thus, X is the time of failure of the system. Denoting by $F(x)$ the distribution X, we conclude that F(t) is the probability that the system will fail prior to time t and

$$1-F(t)=P\{X>t\} \tag{7}$$

is the probability that the system will not fail prior to time t.

The pit generation process is a stochastic process having Markoff property whose past has no influnce on the future if its present is specified.[9] This means the following : If $t_{n-1}<t_n$, then

$$P\{X(t_n)\le x_n|X(t),\ t\le t_{n-1}\}=P\{X(t_n)\le x_n|X(t_{n-1})\} \tag{8}$$

From this it follows that if $t_1<t_2<\cdots<t_n$, then

$$P\{X(t_n)\le x|X(t_{n-1}),\cdots,X(t_1)\}=P\{X(t_n)\le x_n|X(t_{n-1})\} \tag{9}$$

The above definition holds for discrete-time process if $X(t_n)$ is replaced by X_n. From Eq. (9) it follows that

$$f(x_n|x_{n-1},\cdots,x_1)=f(x_n|x_{n-1}) \tag{10}$$

The chain rule can be expressed as follows :

$$f(x_1,\cdots,x_n)=f(x_n|x_{n-1},\cdots,x_1)\cdots f(x_2|x_1)f(x_1) \tag{11}$$

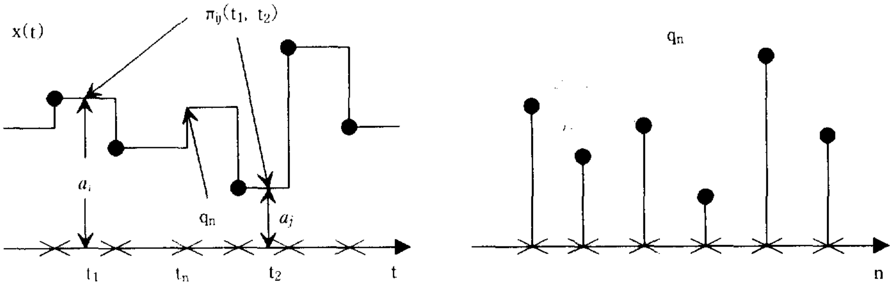
Applying the chain rule Eq. (11) to Eq. (10), we obtain

$$f(x_1,\cdots,x_n)=f(x_n|x_{n-1})f(x_{n-1}|x_{n-2})\cdots f(x_2|x_1)\ f(x_1) \tag{12}$$

Conversely , if Eq. (12) is true for all n, the process X_n is Markoff, because, in this case,

$$f(x_n|x_{n-1},\cdots,x_1)=\frac{f(x_1,\cdots,x_{n-1},x_n)}{f(x_1,\cdots,x_{n-1})}=f(x_n|x_{n-1}) \tag{13}$$

If the present is specified, then the past is independent of the future in the following sense : If $k<m<n$, then



(a) (b)

Fig. 1. A continuous-time Markoff chain.

$$f(x_n, x_k|x_m)=f(x_n|x_m)f(x_k|x_m) \quad (14)$$

A continuous-time Markoff chain is a Markoff process X(t) consisting of a family of staircase functions(discrete states) with discontinuities at the random points t_n(Fig. 1a). The values

$$q_n=X(t_n^{+}) \quad (15)$$

of X(t) at these points (Fig. 1b) form a discrete-state Markoff sequence called the Markoff chain imbedded in the process X(t). A Markoff chain X(t) is specified in terms of the underlying point process t_n and the imbedded Markoff chain q_n. We denote by

$$p_i(t)=P\{X(t)=a_i\} \quad (16)$$

the *state probabilities* of X(t) and by

$$\pi_{ij}(t_1, t_2)=P\{X(t_2)=a_j|X(t_1)=a_i\} \quad (17)$$

its *transition probabilities*. These functions are such that

$$\sum_j \pi_{ij}(t_1, t_2)=1 \quad \sum_i p_i(t_1)\pi_{ij}(t_1, t_2)=p_j(t_2) \quad (18)$$

A Markoff process X(t) is homogeneous if its transition probabilities depend upon the difference $\tau=t_2-t_1$

$$\pi_{ij}(\tau)=P\{X(t+\tau)=a_j|X(t)=a_j\} \quad \tau\geq 0 \quad (19)$$

From the above it follows with $\alpha=t_3-t_2$ that

$$\pi_{ij}(\tau+\alpha)=\sum_r \pi_{ir}(\tau)\pi_{rj}(\alpha) \quad (20)$$

This is the Chapman-Kolmogoroff equation for continuous-time Markoff chains and it can be written in a vector form

$$\Pi(\tau+\alpha)=\Pi(\tau)\Pi(\alpha) \quad \tau,\alpha\geq 0 \quad (21)$$

where $\Pi(\tau)$ is a matrix with elements $\pi_{ij}(\tau)$. Transition matrix $\Pi(\tau)$ of a continuous-time chain X(t) can be determined in terms of the matrix.

$$\Pi'(0^{+})=\Lambda\equiv\begin{bmatrix}\beta_{11}, & \cdots, & \beta_{1n}\\ \cdots & \cdots & \cdots\\ \beta_{n1}, & \cdots, & \beta_{nn}\end{bmatrix} \quad (22)$$

whose elements $\beta_{ij}=\pi'_{ij}(0^{+})$ are the derivatives with respect to time from the right of the elements $\pi_{ij}(\tau)$ of $\Pi(\tau)$. These derivatives will be called the *transition probability rates* of X(t). Clearly, $\sum_j \beta_{ij}=0$ because $\sum_j \pi_{ij}(\tau)=1$ and since

$$\pi_{ij}(\tau)=\delta[i-j]=\begin{cases}1 & i=j\\ 0 & i\neq j\end{cases} \quad (23)$$

we conclude with $\lambda_i=-\beta_{ii}$ that

$$\lambda_i=\sum_j \beta_{ij}\geq 0 \quad \beta_{ij}\geq 0 \quad i\neq j \quad (24)$$

In the above, we have assumed that $\pi_{ij}(\tau)$ is differentiable at $\tau=0^{+}$. This is so only if the probability that there is one discontinuity point in the interval(t, $t+\Delta t$) is of the order of Δt

$$P\{X(t+\Delta t)=a_j|X(t)=a_i\}=\begin{cases}1-\lambda_i\Delta t & i=j\\ \beta_{ij}\Delta t & i\neq j\end{cases} \quad (25)$$

Differentiating Eq. (21) with respect to α and setting $\alpha=0$, we obtain

$$\Pi'(\tau)=\Pi(\tau)\Lambda, \ \Pi(0)=I \quad (26)$$

This is a system of linear differential equations with constant coefficients and its initial condition $\Pi(0)$ is the identity matrix. Solving Eq. (26), we obtain

$$\Pi(\tau)=\exp^{\Lambda t} \quad (27)$$

We have thus expressed $\Pi(\tau)$ in terms of the transition rate matrix Λ.

The state probabilities $p_i(t)$ satisfies a similar system : Denoting by P(t) a vector with elements $p_i(t)$, we conclude from Eq. (18) that

$$P(t+\tau)=P(t)\Pi(\tau) \quad (28)$$

Differentiating Eq. (28) with respect to τ and setting $\tau=0$, we obtain

$$P'(t)=P(t)\Lambda \quad (29)$$

This is a system of N equations of the form

$$p'_i(t)=-\lambda_i p_i(t)+\sum_j \beta_{ji} p_j(t) \quad \beta_{ji}\geq 0 \quad i\neq j \quad (30)$$

Its formal solution is

$$P(t)=P(0)\exp^{\Lambda t} \quad (31)$$

We have, thus, expressed P(t) in terms of the Λ and the initial state probabilities $p_i(0)$. If X(t) is stationary, then $p_i(t)=p_i=$constant. Hence

$$\lambda_i p_i=\sum_j \beta_{ji} p_j, \quad \sum_i p_i=1 \quad (32)$$

This is a system expressing the state probabilities of a stationary process in terms of the transition rates β_{ij}.

We detail the stochastic models describing the pit birth, pit death, and pit growth processes as follows.

Pit birth stochastic process—A birth process is a Markoff chain X(t) consisting of a family of increasing staircase functions(Fig. 2). The process X(t) takes values 1,2,3,$\cdots$ and it increases by 1 at the discontinuity points t_i(birth times). From the definition it follows that the transition rates β_{ij} are different from zero only if $i=j$ or $i=(j-1)$. Thus,

$-\beta_{ii}=\lambda_i$ and $\beta_{i(i+1)}=\lambda_i$; if otherwise, $\beta_{ij}=0$

Hence, the process is specified in terms of the parameter λ_i

$$\begin{aligned} &P\{X(t+\Delta t)=n \mid X(t)=n\}=1-\lambda_n \Delta t \quad n\geq 1 \\ &P\{X(t+\Delta t)=n \mid X(t)=n-1\}=\lambda_{n-1}\Delta t \quad n>1 \end{aligned} \quad (33)$$

Hence

$$\begin{aligned} &p_1(t+\Delta t)=p_1(t)(1-\lambda_1 \Delta t) && n=1 \\ &p_n(t+\Delta t)=p_n(t)(1-\lambda_n \Delta t)+p_{n-1}(t)\lambda_{n-1}\Delta t && n>1 \end{aligned}$$

This yields

$$\begin{aligned} &p'_1(t)=-\lambda_1 p_1(t) && n=1 \\ &p'_n(t)=-\lambda_n p_n(t)+\lambda_{n-1} p_{n-1}(t) && n>1 \end{aligned} \quad (34)$$

Note that the difference $X(t_2)-X(t_1)$ equals the number of discontinuity points t_i in the interval(t_1, t_2). This shows that a birth process is completely specified in terms of the point process t_i. Assuming that the rate of increase of X(t) is independent of its present state, $\lambda_n=\lambda=$constant. Setting $\lambda_n=\lambda$ in Eq. (34), we obtain

$$\begin{aligned} &p'_1(t)+\lambda p_1(t)=0 && p_1(0)=1 \quad n=1 \\ &p'_n(t)+\lambda p_n(t)=\lambda p_{n-1}(t) && p_n(0)=0 \quad n>1 \end{aligned} \quad (35)$$

This yields

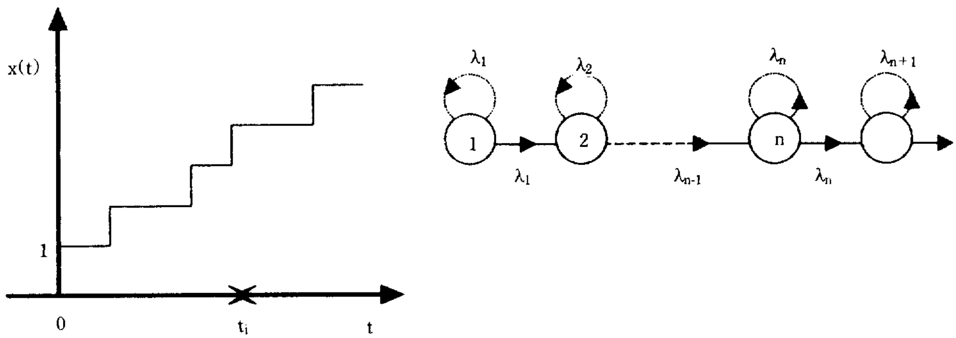


Fig. 2. Birth process.

$$p_{n+1}(t)=\frac{\exp^{-\lambda t}(\lambda t)^n}{n\,!} \tag{36}$$

The above is the probability that $X(t)=n+1$ and it equals the probability that the number of points $X(t)-X(0)$ in the interval$(0, t)$ equals n.

Pitting process is a series of events which are randomly distributed in time and space over the metal surface. Every event follows the same rules. Detailed analysis of the scatterd data of induction time for pit generation on stainless steel[3,4,10] and high nickel alloy[11,12] have been reported. Any distribution observed in the experiment could not fit the simple exponential distribution, but a distorted one, some of them showing convex curves and others concave ones. For example, it had been found in the analysis of the pit formation process of Type 304 stainless steel in 3.5wt% NaCl, that the curves of log(survival probability) vs. time show clear three slopes as shown in Fig. 3.[3] This feature of the curve was explained by assuming series and parallel combination of the simple birth stochastic process.

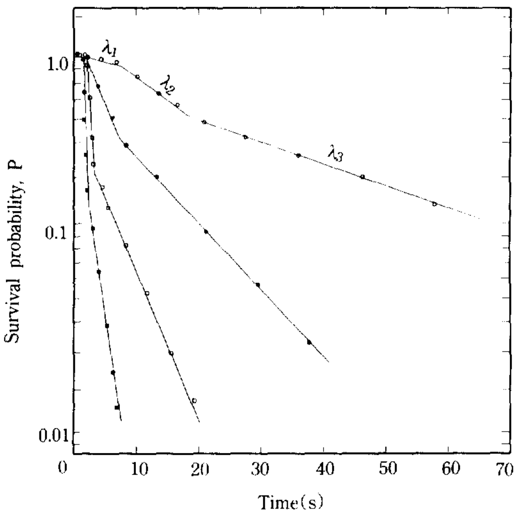


Fig. 3. Survival probability plotted as a function of induction time for pit generation of Type 304 steel(from Reference[3]).

Other features of the curves observed in the experiment are shown schematically in Fig. 4, in which the alternate models to provide the corresponding feature are indicated on the curves. As illustrated in Fig. 4, proposed models are deduced by assuming a parallel or series combinations of the elemental Poisson process which shows the exponential distribution.

Illustrated models could be divided into two main categories of A and B(Figs. 5 and 6). The model A assumes only a birth operating and for the model B, both of the birth and death stochastic process are considered in pit formation process. Both models further include sub models which assume parallel or series combination of the elemental Poisson process :

Pit birth and death stochastic process—Experimental data on the survival probability curve for pit generation reported by Baroux[10] had demonstrated that a more general feature of the curve is not straight, but exhibits a long tail towards extended time just illustrated as B1 in Fig. 4. He

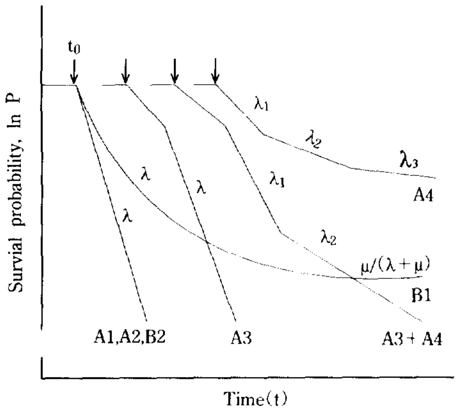


Fig. 4. Schematic illustration of ln P vs. time curves expected for various stochastic models (from Reference[3]).

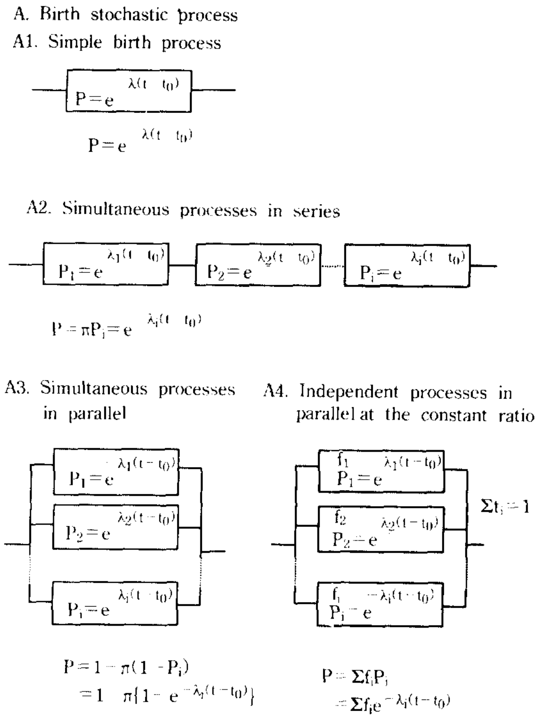


Fig. 5. Series or parallel combination of the elemental Poisson process leading to various models (from Reference[3]).

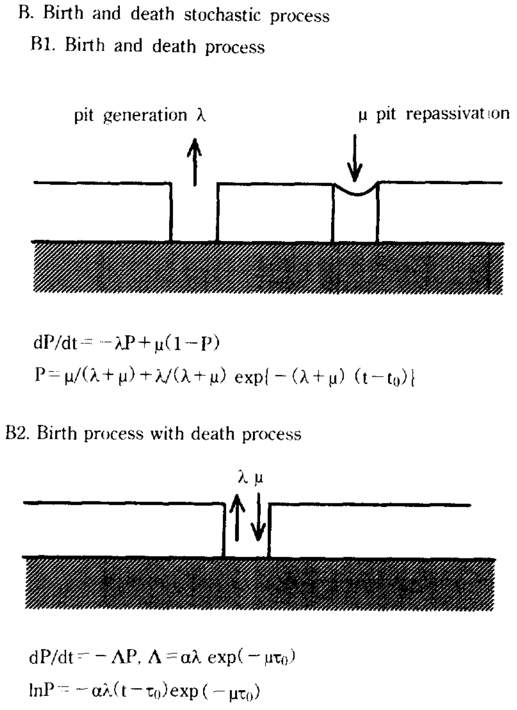


Fig. 6. Schematic illustration of the birth and death stochastic process(from Reference[3]).

observed similar long tail curves, but only discussed an initial pit generation rate which changes with time due to ageing. Williams *et al.*[13] proposed a birth stochastic model with a death process to simulate the electrochemical noise data before and after macroscopic size pit formation. The curves deduced from the model proposed by Williams *et al.*[13] is catagorized as a series combined birth and death stochastic model and called B2 as shown in Fig. 4.

In our laboratory, pit embryo generation rate $\lambda(t)$ was determined as a function of exposure time in 0.1M Na_2SO_4 + 0.02M HCl solution at various applied potentials for Al-1wt.% Si-0.5wt.% Cu alloy thin film. The result is demonstrated in Fig. 7.[14] The generation rate $\lambda(t)$ initially decreased

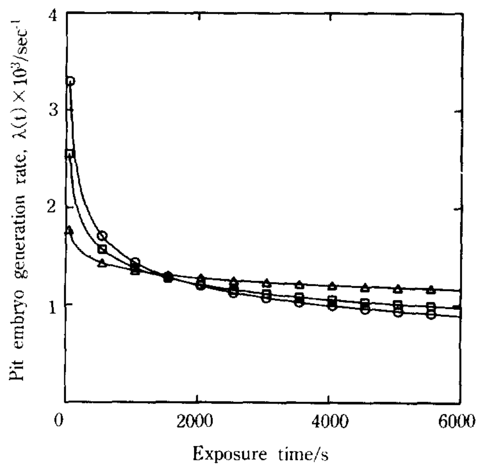


Fig. 7. Plots of pit embryo generation rate versus exposure time for Al-1wt.% Si-0.5wt.% Cu alloy thin film at applied potentials of : ○, $-350mV_{SCE}$; □, $-400mV_{SCE}$; △, $-450mV_{SCE}$.

rapidly and then remained nearly constant with exposure time at a given applied potential. It is noted that the generation rate $\lambda(t)$ is raised with applied potential prior to a certain exposure time, while it is lowered with applied potential after the exposure time. The plots of $\lambda(t)$ against exposure time suggest that the survival probability for pit embryo generation is determined by the birth and death process illustrated as B1 in Fig. 4.

The birth and death stochastic model is derived as follows. Suppose now that a Markoff chain takes the values 0,1,2, $\cdots$ and its discontinuity equal $+1$ or -1(Fig. 8). We then say that X(t) is a birth-death process. In this case, λ_{ij} is different from zero only if $i=j$ or $(j-1)$ or $(j+1)$. Hence, X(t) is specified in terms of the two parameters

$$\lambda_i=\beta_{i(i+1)},\ \mu_i=\beta_{i(i-1)} \tag{37}$$

Thus, $-\beta_{ii}=\lambda_i+\mu_i$ and

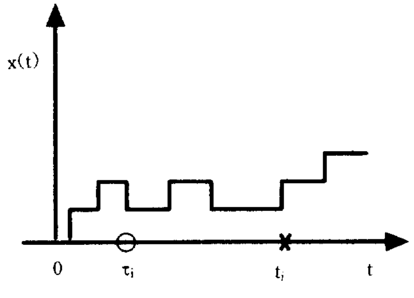
$$\begin{aligned} &P\{X(t+\Delta t)=n|X(t)=n-1\}=\lambda_{n-1}\Delta t\\ &P\{X(t+\Delta t)=n|X(t)=n\}=[1-(\lambda_n+\mu_n)\Delta t]\\ &P\{X(t+\Delta t)=n|X(t)=n+1\}=\mu_{n+1}\Delta t \end{aligned} \tag{38}$$

From the above, it follows that

$$\begin{aligned} &p'_0(t)+\lambda_0 p_0(t)=\mu_1 p_1(t) \qquad n=0\\ &p'_n(t)+(\lambda_n+\mu_n)p_n(t)=\\ &\qquad \lambda_{n-1}p_{n-1}(t)+\mu_{n+1}p_{n+1}(t) \quad n>0 \end{aligned} \tag{39}$$

Statistics of pit growth – Previous models on the statistics of pit growth advanced by Fleischmann's group[13,15~17] used the statistics of current time transient resulting from random nucleation process followed by a deterministic evolution of the current to the resulting growth centers previously developed in some detail for electrocrystallization.[18,19] They assume that all pits evolve according to a deterministic law $i=cu$, where i is the current density, and c is a deterministic evolution coefficient, and u is the age of the pit. Unfortunately, throughout that work no attempt has been made to introduce a stochastic description of the pit growth process.

According to the model by Mola *et al.*,[20] the stochastic approach to pit growth is described as follows. Pit growth proceeds when at a certain time $\tau_1>\tau_0$, a second element of volume ΔV, adjacent to the first one, is corroded. This process is repeated so that at times τ_k, $k=1,2,\cdots$, the pit volume changes from $k\Delta V$ to $(k+1)\ \Delta V$ in a similar way as that employed above for pit birth, except that in the present case, the growth probability of one pit is directly proportional to γ_k, the pit surface area at that particular time i. e., the rate of the process is determined by the pit surface value γ_k. It can be also noticed that the same model might be applied to the pit growth



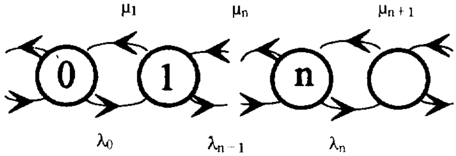


Fig. 8. Birth and death process.

stages under diffusion control, provided that the dependence of γ_k on the growth geometry is modified. We suppose that the pit volume at times t becomes $V(t)=k(t)\Delta V$. Likewise it is further assumed that :

1. No pit volume decrease is possible.

$$P\{k(t+\Delta t)<k(t)|k(t)=j\}=0 \quad (40)$$

2. The probability for pit growth in a small time interval Δt is proportional to Δt and the pit surface area γ_k.

$$P\{k(t+\Delta t)-k(t)=1|k(t)=j\}=\gamma_k\Delta t \quad (41)$$

3. Pit growth takes place as a stepwise process, each step involving a simple element of volume.

$$P\{k(t+\Delta t)-k(t)=0|k(t)=j\}=1-\gamma_k\Delta t \quad (42)$$

4. At $t=0$ the pit volume is zero.

$$P\{k(t)=0\}=1 \quad (43)$$

By calling

$$P_j(t)=P\{k(t)=j\} \quad (44)$$

According to the description on parameters controlling pit initiation, it results

$$P_0(t)=P\{k(t)=0\}=P(\tau_0\geq t)=\exp(-\gamma_0 t) \quad (45)$$

For the pit volume to reach $j\Delta V$ remains unchanged between t and $t+\Delta t$, or that the pit volume changes from$(j-1)\Delta V$ to $j\Delta V$ in going from t to $t+\Delta t$. That is

$$P_j(t+\Delta t)=P_j(1-\gamma_k\Delta t)+P_{j-1}(t)\gamma_{j-1}\Delta t \quad (46)$$

Then

$$dP_j/dt=-\gamma_jP_j(t)+\gamma_{j-1}P_{j-1}(t) \quad (47)$$

The solution of this equation is

$$P_j(t)=\gamma_{j-1}\int_0^t P_{j-1}(t')\exp[-\gamma_j(t-t')]dt' \quad j=1,2,\cdots \quad (48)$$

On the basis of the pit growth process given by Eqs. (45) and (48) and the knowledge of the surface pit value γ_j, a τ_j value can be randomly generated. The surface of every pit is then subdivided into γ_j area elements, each one of them being randomly chosen by assuming an equal ***a priori*** probability. The volume element of material is to be subsequently corroded at the time τ_j. Therefore, the greater the number of faces that an element of volume has in common with the surface pit area, the larger the probability of being corroded in the following time interval.

The model described pit growth as a discrete process involving a series of successive events, each one of them implying a loss of material at the corroding phase associated with a volume ΔV. Thus, if V_{max} denotes the largest pit volume attained after a certain time in a corrosion experiment, one can write

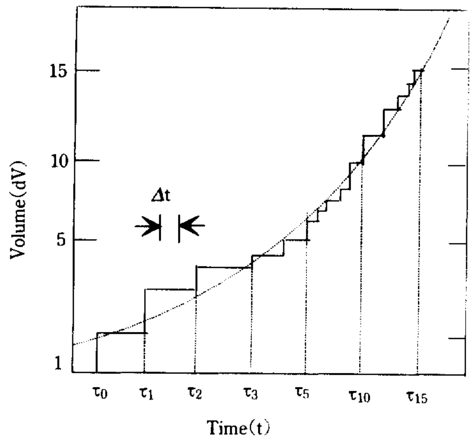


Fig. 9. (——) Stochastic simulation of a typical growth process for a single pit.(----) The deterministic$(t-\tau_0)^2$ law in dimensionless units of time (Δt) and volume(δV)(from Reference[20]).

$$V_{max} = N_{max}\Delta V \tag{49}$$

, where N_{max} can be referred to as the resolution degree for the pit volume. A typical growth process for a single pit is shown in Fig. 9 where the solid line represents the stepwise process as predicted from the model and the dashed line the approximate deterministic law.

According to the electrochemical reaction related to thee corrosion process, there is a direct relationship between δm, the amount of material loss and δQ the corresponding electrical charge. Therefore, the current intensity, i_k, related to pit growth should be directly proportional to the number of events per unit time(rate). Let ΔN_k be the number of events occuring during the interval Δt_k, then

$$i_k = \Delta N_k / \Delta t_k \tag{50}$$

, where i_k and Δt_k are given in dimensionless units. A typical experiment for the initial stages of pit growth is depicted in Fig. 10. In this case the values of $\tau_{0i}(i=1, 2, \cdots)$, the birth time of the i-th pit, are indicated, and the pit current is obtained from Eq. (50), on the assumption that the contribution of N_k results from different growing pits.

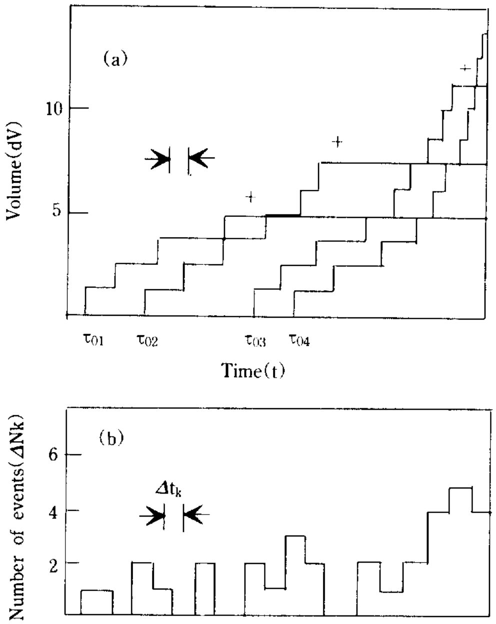


Fig. 10. (a) A typical stochastic experiment describing the initial stages of pit growth. Pit birth times(τ_{0i}) are indicated in dimensionless units of time(Δt) and volume(δV). Crosses indicate pit deaths. (b) Number of events(ΔN_k) per unit time (Δt_k) corresponding to the stochastic experiment shown in Fig. 9a. Pit current i_k can be obtained from $i_k = (\Delta N_k)/(\Delta t_k)$(from Reference[20]).

5. Discussion

The susceptibility of various metals to localized corrosion has been tested in several media to validate the stochastic analysis approach.[3,4,10~12] However, very few thorough comparisons are available because so far there have not been a sufficient number of investigations of this type, and various experimental conditions are not totally equivalent. More attention should be paid to the procedure used for creating the pitting conditions: Introduction of the halides ions before or after the potential shift toward high anodic polarization is of great significance in influencing the history of the protective layer.

The interpretation of the survival probability curve in terms of birth and death processes seems problematic if only the stable pits are taken into account. The general equation as a birth and death stochastic process presented in the present review paper is given in Eq. (39), which gives for $n=0$ (as it is supposed that $P(t, -1)=0$). For relatively low pitting activity, it can be supposed that at most one pit can exist on the surface, have $P(t, 1) = 1 - P(t, 0)$. Thus, Eq. (39) becomes

$$p'_0(t)+\lambda_0 p_0(t)=\mu_1[1-p_0(t)] \quad (51)$$

The above yields the equation used by Shibata *et al.*,[4] which is given by

$$P=\mu/(\lambda+\mu)+[\mu/(\lambda+\mu)]\exp[-(\lambda+\mu)(t-t_0)] \quad (52)$$

, where t_0 is incubation time, before which no pit generation probability is expected. However, this simplified model leads to a survival probability that tends toward a limit $\mu/(\lambda+\mu)$. Instead, the full sequence of the general Eq. (39) predicts a survival probability that tends toward zero for long times. That is, after an elapse of long period, the stationary state is attained. In this case, $p'_n(t)=0$ with $\alpha_n=\lambda$ and $\beta_n=\mu$ and Eq. (39) yields

$$\lambda p_0=\mu p_1,\ (\lambda+\mu)p_n=\lambda p_{n-1}+\mu p_{n-1} \quad (53)$$

From this it follows readily that

$$p_0=1-\frac{\lambda}{\mu},\ p_n=p_0\left(\frac{\lambda}{\mu}\right)^n$$

$$=\left(1-\frac{\lambda}{\mu}\right)\left(\frac{\lambda}{\mu}\right)^n \quad \mu>\lambda \quad (54)$$

When the value of n is large at a given t, p_n approaches zero. This conclusion is more realistic. The death rate can not be obtained by only taking into account the counting of the stable pits without analyzing the prepitting stage. The investigation of this stage is particularly attractive because its investigation could lead to a nondestructive technique for evaluting the resistance of metals to localized attack in a given medium.

6. Conclusions

From this review, it can be concluded that the stochastic approach is very powerful in investigating the localized corrosion, even if not the only one, since pitting is largely dominated by random parameters. The use of the stochastic approach has led to the possibility of testing microscopic models much more rigorously than has been possible hitherto.

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