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Modified Fourier solution for diffusion governing law applied to blister formation and development

Yunan Prawoto *, Irwan H. Onn

Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia

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A B S T R A C T

This paper discusses about the equation derivation using *paper* and *pencil* approach. Further, using commercial softwares of *Mathematica*™ and *Abaqus*™, analytical and numerical approaches are developed to simulate the ionic transport needed to induce pressure that eventually causes the blister to propagate. The principle is useful not only for organic coating problem, but also for other materials involving delamination phenomena including other sophisticated surface engineering methods.

1. Introduction

According to Fick's law [1], diffusion can be expressed as:

$$\frac{\partial \phi(r,t)}{\partial t} = \nabla[D(\phi,r,t)\nabla\phi(r,t)] \tag{1}$$

or, as expressed in Cartesian coordinate:

$$\frac{\partial \phi(r,t)}{\partial t} = \sum_{i=1}^{3}\sum_{i=1}^{3}\frac{\partial}{\partial x_i}\left[D_{ij}(\phi,r,t)\frac{\partial \phi(r,t)}{\partial x_j}\right] \tag{2}$$

or, in Cylindrical coordinate:

$$\frac{\partial \phi(r,t)}{\partial t} = D(\phi,r,t)\cdot\left[\frac{\partial^2\phi(r,t)}{\partial r^2}+\frac{1}{r}\frac{\partial\phi(r,t)}{\partial r}+\frac{1}{r^2}\frac{\partial\phi(r,t)}{\partial\theta}\right] \tag{3}$$

For general usage, the approach assumes that the diffusion coefficient, D, is constant. In engineering problems, this is generally acceptable and often further simplification neglects the third term of Eq. (3), $\frac{1}{r^2}\frac{\partial\phi(r,t)}{\partial\theta}$, which therefore becomes:

$$\frac{\partial \phi(r,t)}{\partial t} = D\cdot\left[\frac{\partial^2\phi(r,t)}{\partial t^2}+\frac{1}{r}\frac{\partial\phi(r,t)}{\partial t}\right] \tag{4}$$

Eq. (4) is capable of describing basic engineering diffusion, and widely accepted and used. However, this equation is clearly not capable to describe the phenomenon of diffusion used in the development of coating degradation as seen in Fig. 1 [2,3].

Many researchers in the blister development modify Eq. (4) to include some other factors [4–7]. By adding a second term, the general form of diffusion equation becomes:

$$\frac{\partial \phi(r,t)}{\partial t} = \nabla[D\nabla\phi(r,t)] + C \tag{5}$$

where physical observations are included in the second term. Therefore, the equation takes the form of:

$$\frac{\partial \phi(r,t)}{\partial t} = \nabla[D\nabla\phi(r,t)] + \mu E\frac{\partial \phi(r,t)}{\partial t} \tag{6}$$

where t is the exposure time, D is the effective ion diffusion coefficient, μ is the average mobility of ions and E is the strength of the imposed unscreened electrical field. This type of model predicts the concentration profiles and cation flowing into a blister as a function of time, blister size, distance between the blister and defect, ion diffusivity and potential gradient.

Pommersheims was among the first to modify the diffusion equation and made experimental verification. His final equation for the coating blistering became [8,9]:

$$\frac{\phi(x,t)}{\phi(x,0)} = exp\left(-D(x,t)\frac{2\pi a\delta\eta}{Vh}(t-\Theta)\right) \tag{7}$$

with $\delta\eta$ being constants determined by experiments, V is the internal volume, t and Θ being the time factors, and h is the coating thickness. Subsequently, the solution is:

$$\frac{\phi_A}{\phi_0} = \frac{1}{\alpha}\left[1-e^{-\alpha\beta(t-\theta_i)}\right] \tag{8}$$

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* Corresponding author. Tel.: +60 167 279048; fax: +60 755 66159.
E-mail address: yunan.prawoto@gmail.com (Y. Prawoto).

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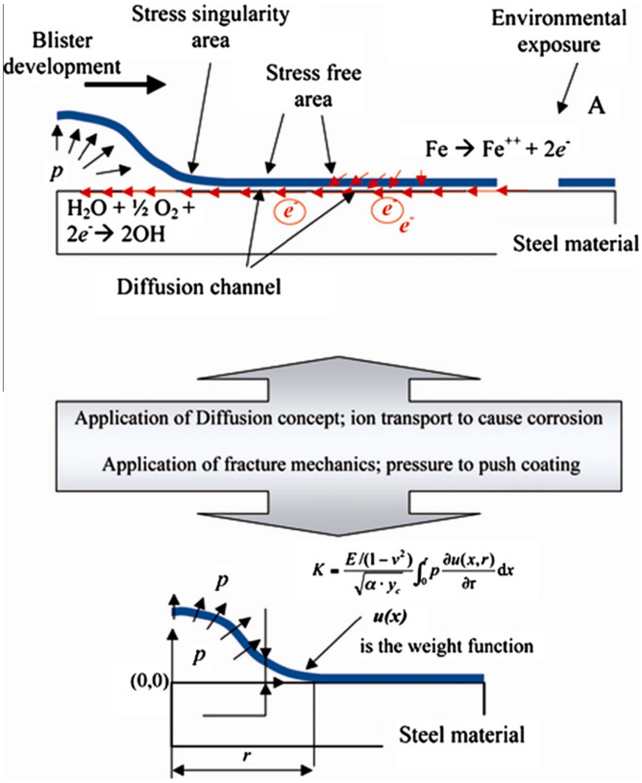

Fig. 1. Basic usage of fracture mechanics and diffusion concepts in blister development [2,3].

where, $\alpha = 1 - \left(\frac{p}{p^*}\right)$, and $\beta = 2\pi\delta D/(V \ln \frac{1}{k})$ is channel (gap between coating and base metal) height, with p as potential gradient, $p^* = \frac{1-k}{k \ln\left(\frac{1}{k}\right)}$, k is geometric aspect ratio (a/R), a is the radius of the blister, R is the distance from blister center to the scribe, t is the time, θ_i is the time needed to initiate blister formation, and V is the volume of the solution inside the blister. Materials engineers, and scientists alike, will be able to use Eq. (8) to make decision whether a coating blister development occurs or otherwise by varying the parameters in the equation. In this research, the author approaches the same problem by combining the concept of classical fracture mechanics with diffusion concept by using modified Fourier solutions.

2. Model description

Fig. 1 shows a case study on a blistering problem that is divided into two parts, namely diffusion and mechanics problems. The solutions to the mechanics part of the problem and its application are published separately as in references [2,3]. Therefore, further discussion on it is omitted. However, for convenience, the equation is once again presented. Using the mixed mode SIF (stress intensity factor) conditions, SED (strain energy density) factor for the blister growth is formulated as:

$$K_I = \int_0^r p_y \cdot \left(\frac{E/(1-\nu^2)}{\sqrt{\alpha \cdot y_c}}\right) \frac{\partial u(x,r)}{\partial r} dx = \frac{\alpha \cdot p_y E \sqrt{y_c}}{(1-\nu^2)} \tag{9}$$

and

$$K_{II} = \int_0^r p_x \cdot \left(\frac{E/(1-\nu^2)}{\sqrt{\alpha \cdot y_c}}\right) \frac{\partial u(x,r)}{\partial r} dx = \frac{\alpha \cdot p_x E \sqrt{y_c}}{(1-\nu^2)} \tag{10}$$

where p is pressure, y_c is the height of the blister, E is Young's modulus and other symbols used are coefficients currently verified by experimental approaches. Eventually, the mixed mode conditions are then combined using the SIF relation with SED factor into:

$$S = a_{11} \cdot K_I^2 + 2a_{12} \cdot K_I K_{II} + a_{22} \cdot K_{II}^2 \tag{11}$$

As in the present case where

$$\alpha = \int_0^r \frac{\partial u(x,r)}{\partial r} dx \tag{12}$$

SED factor is

$$S = \frac{\alpha^2 \cdot E^2 y_c}{(1-\nu^2)^2} \left(a_{11} \cdot p_y^2 + 2a_{12} \cdot p_x p_y + a_{22} \cdot p_x^2\right) \tag{13}$$

- Case 1, Crack retreat, S is less than S_{crit}.
- Case 2, Equilibrium, S is equal to S_{crit}, and
- Case 3, Crack propagate, S is more than S_{crit}.

The critical S_{crit} is similar to that of metal, and can be used to characterize either new sample or corroded sample with its adhesion decreased. S strain energy density coefficient postulated and proven experimentally first by Sih [10–13].

Similar with Eq. (8), the author proposes the modification by introducing the diffusion concept. Recall that Eq. (5) is widely accepted among the researcher in coating blistering. The current research further expanded the equation to:

$$\frac{\partial \phi(r,t)}{\partial t} = \nabla[D \nabla \phi(r,t)] + C_1 \frac{\partial \phi(r,t)}{\partial t} + C_2 \tag{14}$$

This equation also accommodates the osmosis effect from the coating into the metal part as well as from other substance inherited by the coating materials or materials being coated. Further manipulation to the equation leads to:

$$\frac{\partial \phi(x,t)}{\partial t} - D\frac{\partial^2 \phi(x,t)}{\partial x^2} = C_1 \delta(x)\delta(t) + C_2 \tag{15}$$

where new terms C_1, C_2 and $\delta(x)\delta(t)$ are introduced in addition to $\phi(x, t)$, and $D(\phi, t)$, which are commonly used in the traditional diffusion equation for density and diffusion coefficient. These new terms can then be adjusted according to the parameters introduced that are verifiable through experiment. Using the Fourier function and Dirac Delta functions, where the common forms are expressible as:

$$\phi(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} d\omega e^{ipx - i\omega t} \tilde{\phi}(p,\omega) \tag{16}$$

and

$$\delta(x - x_0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ip(x-x_0)} dp \tag{17}$$

Many assumptions can be set together with analytical solution. Depending on the assumption of the boundary conditions, some solutions can be as simple as:

$$\tilde{\phi}(r,t) = \delta(Dr^2 - it)\tilde{\phi}(r) + \frac{C_1}{2\pi} \frac{1}{Dr^2 - it} + C_2 t \tag{18}$$

where C_1 and C_2 are introduced as constants to accommodate the combination of the electrolytic anode–cathode system to synergies with osmotically driven diffusion. Therefore, the first part of the numerical verification of this research is to implement this equation. The main result is the ionic density ϕ which generates the corrosion with the reaction of:

$$H_2O + \frac{1}{2}O_2 + 2^{e-} \rightarrow 2OH^- \tag{19}$$

underneath the coating, where the oxygen is reduced, and

$$Fe \rightarrow Fe^{++} + 2^{e-} \tag{20}$$

at the scribes, or any location, where the steel has direct contact with corrosive environment and the iron forms an anode. The