Mechanochemical Corrosion: Modeling and Analytical Benchmarks for Initial Boundary Value Problems with Unknown Boundaries

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Abstract In this paper various corrosion models are considered. Difficulties of the modeling of stress corrosion of constructional elements and the need for developing closed-form solutions are highlighted. A new analytical solution is presented for the plane problem of the mechanochemical corrosion of an elastic plate with an elliptical hole under uniform remote tension. The rate of corrosion is supposed to be linear with the maximum principal stress at a corresponding point on the hole surface. The solution obtained can serve for the study of the mechanochemical effect on the corrosion damage propagation. It is proved that the stress concentration factor at a noncircular hole can either increase or decrease, or stay invariant during the corrosion process, depending on the relationship between the corrosion kinetics constants and applied stress.

Keywords Mechanochemical corrosion · General corrosion · Corrosion kinetics · Pitting · Lifetime · Analytical solution

1 Mechanochemical Corrosion Models

“The problems of corrosion are universal, but the control measures are not,” N. Sethurathinam, Executive Director, (Refineries Division), Indian Oil Corporation, said [14]. For example in India, the annual loss due to corrosion has been estimated at about 4 per cent of the country’s Gross Domestic Product [14]. Corrosion is a natural phenomenon defined as the deterioration of a material or its properties due to an interaction with its environment. Corrosion can cause not only expensive but also extremely dangerous damage of constructions from underground pipelines to aircraft fuselages.

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V.K. Singh et al. (eds.), *Modern Mathematical Methods and High Performance Computing in Science and Technology*, Springer Proceedings
in Mathematics & Statistics 171, DOI 10.1007/978-981-10-1454-3_25

Most structures are exploited being subjected to both mechanical loads and operating environments. The combined action of mechanical loads and chemically active media has been the subject of study for more than 100 years. It was observed that such conditions may activate the process of so-called stress corrosion, which is more severe than the simple superposition of damages induced by stresses and electrochemical corrosion acting separately [17, 23, 27]. With regard to general corrosion facilitated by stress, the term "mechanochemical corrosion" was introduced [8, 9]. According to E.M. Gutman, corrosion may often be considered as uniform in the case of elastic deformation. In plastic region, significant electrochemical heterogeneity of the surface may be developed; therefore, the term "mechanochemical corrosion" is not always applicable. General wear can occur both under the formation of a closed protective coating, and in the absence of oxide or biofilms. The formation of a passive film, shift in solution pH, and the change in concentration of reactants can show inhibiting effects, when the corrosion rate can be supposed to follow an exponential decay with time [18, 26].

There exists a number of different approaches to the problems of stress corrosion, based on physical and chemical mechanics of materials, thermodynamics, continuum mechanics, and fracture mechanics. E.M. Gutman proposed an exponential dependence of the rate of the anodic dissolution of deformed metal on the stress value. On the basis of his theory several elegant mathematical models of the corrosion of pipe elements were developed [1, 9, 10]. The theory of the mechanochemical effect of dissolution in terms of the chemical affinity was formulated by A.I. Rusanov. According to his work [23], dissolution rate is a quadratic function of strain-components. The case of dissolution/evaporation of a bent plate was examined in details theoretically and experimentally; the effect of the strain sign observed in the experiments was explained by the existence of surface tension [23]. Interesting discussion of the mentioned results is available in literature. Based on the concept of chemical affinity tensor, the authors of [5–7] studied the kinetics of the stress-assisted chemical reaction sustained by the diffusion of gas through an elastic solid. Some spherically symmetric problems were solved there. The effect of the sign and value of the reaction front curvature were also examined.

Note that due to the highly complex structure of metals and alloys [26], development of a thermodynamic model that takes into account all the details of their structure and competing processes, seems to be very difficult to realize. Thus, we have to rely on experimental results. A lot of experimental data demonstrated a linear dependence of the metal corrosion rate on the effective stress [18]. Beginning with the pioneering work by V.M. Dolinskii [3], this dependence is often used for engineering calculations [10, 11, 16, 19].

When corrosion rates depend on stresses, and stresses, in turn, depend on changing (due to corrosion) geometry of an element, one has to solve an initial boundary value problem with unknown boundaries. Such problems are mostly studied by numerical methods. However, several analytical solutions have been found for the uniform mechanochemical dissolution of structural elements, e.g., by the authors of [1, 3, 4, 9, 11, 16, 25].

For example, consider the system of equations for the problem of the double-sided mechanochemical corrosion of an elastic thick-walled spherical vessel under internal p_r and external p_R pressure [25]. The inner r and outer R radii of the sphere change with time t because of corrosion. The corrosion velocities on the inside and outside, denoted by υ_r and υ_R, respectively, can be approximated by the expressions [18]:

$$\upsilon_r = \frac{dr}{dt} = \upsilon_r^0 \exp\left(-bt\right) \quad \text{at} \quad |\sigma_1(r)| \le \left|\sigma_r^{th}\right|, \tag{1}$$

$$\upsilon_R = -\frac{dR}{dt} = \upsilon_R^0 \exp\left(-bt\right) \quad \text{at} \quad |\sigma_1(R)| \le \left|\sigma_R^{th}\right|, \tag{2}$$

and

$$\upsilon_r = \frac{dr}{dt} = \left[a_r + m_r\sigma_1(r)\right] \exp\left(-bt\right) \quad \text{at} \quad |\sigma_1(r)| \ge \left|\sigma_r^{th}\right|, \tag{3}$$

$$\upsilon_R = -\frac{dR}{dt} = \left[a_R + m_R\sigma_1(R)\right] \exp\left(-bt\right) \quad \text{at} \quad |\sigma_1(R)| \ge \left|\sigma_R^{th}\right|. \tag{4}$$

Here, $b,\ \upsilon_r^0,\ \upsilon_R^0,\ m_r,\ m_R,\ \sigma_r^{th}$, and σ_R^{th} are experimentally determined constants; $a_r = \upsilon_r^0 - m_r\sigma_r^{th};\ a_R = \upsilon_R^0 - m_R\sigma_R^{th}$; σ_r^{th} and σ_R^{th} are threshold stresses; σ_1 is the maximum principal stress on the relevant surface:

$$\sigma_1(r) = \frac{p_r r^3 - p_R R^3}{R^3 - r^3} + \frac{(p_r - p_R)R^3}{2\left(R^3 - r^3\right)}, \tag{5}$$

$$\sigma_1(R) = \frac{p_r r^3 - p_R R^3}{R^3 - r^3} + \frac{(p_r - p_R)r^3}{2\left(R^3 - r^3\right)}. \tag{6}$$

As one can see, these stress components increase (in absolute value) with time due to the change in the radii r and R and accelerate corrosion process more and more. Thus, we have to solve simultaneous equations (1)–(6). Analytical solution to this problem is presented in [25].

Numerical investigation of the problems with unknown changing boundaries requires high qualification. Unfortunately, using finite element software even for static problems not always leads to appropriate results. In such situations, analytical solutions can serve as benchmarks for numerical analysis and can help to identify the role of mechanochemical effect in damage propagation observed in specimens under study.

In practice, structural elements are often designed to have supplementary thickness as a corrosion allowance that can increase to a considerable amount of additional metal. However, these calculations are not wholly adequate and can lead to a substantial cost increase [2]. Using the models with reduced thickness for the strength calculation of solids with nonuniform damages can also lead to significant errors [24].

2 Problem of the Mechanochemical Corrosion of a Plate with an Elliptical Hole

Previously obtained solutions (e.g., [20–22]) for the mechanochemical corrosion of elastic or elastic–plastic thick-walled cylinders and spheres can be applied to the problems of corrosion of a large enough solid with a small cylindrical or spherical cavity under uniform tension or compression. However, those solutions do not allow to observe the change in the shape of the cavity. In the framework of the theory involved, the hole remains circular during the corrosion process. Nevertheless, the results presented below demonstrate that even a nearly circular hole can grow nonuniformly under uniform remote tension.

2.1 Problem Formulation

Consider the first fundamental problem for a linearly elastic, isotropic infinite plane S bounded by an elliptic contour L with the semi-axes A and B ($A \geq B$). The plane is supposed to be subjected to remote uniform tension p. The cavity surface is stress free and exposed to mechanochemical corrosion defined as material dissolution. In this case the hole, associated with the contour L, grows with time t. Let A_0 and B_0 be the semi-axes of the ellipse L at the initial moment $t = 0$. According to [18], the rate of corrosion, v, is linear with the maximum principal stress at corresponding points on the surface:

$$v(s) = \frac{d\delta(s)}{dt} = a + m\,\sigma(s), \quad s \in L(t), \tag{7}$$

where a and m are empirically determined constants of corrosion kinetics; $d\delta$ is an increment (due to material dissolution) of the hole size in the direction of the normal to its contour L.

It is required to track the change of the hole geometry with time.

2.2 Problem Solution

Stress distribution on the elliptic contour L in the plane S under remote tension have been found in [15] by the use of the transformation of the region S on to the infinite plane with a circular hole, $|\zeta| > 1$. The relevant transformation is

$$z = R\left(\zeta + \frac{M}{\zeta}\right), \quad R > 0, \quad 0 \leq M < 1, \tag{8}$$

where $z = x + iy$ and $\zeta = \rho e^{i\theta}$. The ellipse L (with the center at the origin of the coordinate system $0xy$) is then mapped on to the circle $|\zeta| = 1$, so that $A = R(1 + M)$ and $B = R(1 - M)$. Corresponding stress components on the contour $|\zeta| = \rho = 1$ are

$$\sigma_{\theta\theta}(\theta) = 2p\,\frac{1 - M^2}{1 - 2M\cos 2\theta + M^2}, \quad \sigma_{\rho\theta}(\theta) = \sigma_{\rho\rho}(\theta) = 0. \tag{9}$$

According to some experimental data, we can assume that the hole remains elliptical during the corrosion process. Then, Eqs. (8) and (9) should hold true at any t for A and B (and consequently, R and M) growing with time.

Therefore, we have to solve simultaneous equations (7)–(9) at $\theta = 0$ and $\theta = \pi/2$, where the values of $\sigma(0)$, $\sigma(\pi/2)$, A, and B change synergetically. Solution of this problem can be expressed in an implicit form through a new variable $\eta = A/B$:

$$t = -\frac{B_0}{a - 2pm}\left(\frac{(\eta_0 - 1)^{a+2pm}}{\eta_0^{2pm}}\right)^{1/(a-2pm)} \int\limits_{\eta_0}^{\eta} \left(\frac{\eta^{2pm}}{(\eta - 1)^{2a}}\right)^{1/(a-2pm)} d\eta, \tag{10}$$

where $\eta_0 = A_0/B_0$.

Equation (10) gives a point-to-point correspondence between t and η. For every η we can then find

$$B = B_0\left(\frac{\eta^{2pm} \quad (\eta_0 - 1)^{a+2pm}}{\eta_0^{2pm} \quad (\eta - 1)^{a+2pm}}\right)^{1/(a-2pm)} \tag{11}$$

and

$$A = \eta B. \tag{12}$$

Thus, we obtain a one-to-one relationship between t, A, and B.

If $A_0 = B_0 = R_0$, then the shape of the hole remains circular for the corrosion process and its radius R grows with the constant rate

$$\frac{dR}{dt} = a + 2pm \tag{13}$$

for any values R_0, a, m, and p. Therefore,

$$R = R_0 + (a + 2pm)\,t. \tag{14}$$

2.3 Calculation Results

The evolution of the hole under corrosion condition can be quite different depending on the relationship between the corrosion kinetics constants a and m, the traction value p, and the initial axes ratio A_0/B_0.

When the mechanochemical effect is weak enough as compared to the constant rate component a, the hole grows almost uniformly. Limiting case of the constant rate corrosion—when $m = 0$ and $a = 0.2(l_c/t_c)$—is demonstrated in Fig. 1 for the holes with the initial semi-axes $A_0 = 1.25(l_c)$, $B_0 = 1(l_c)$ (dashed lines) and $A_0 = 3(l_c)$, $B_0 = 1(l_c)$ (solid lines). Gradually increasing contours of both the holes correspond to the times $t = 0;\ 0.56;\ 1.25;\ 2.14;\ 3.33;$ and $5(t_c)$, respectively.

Here and below, l_c, t_c, and p_c are appropriate units of length, time, and stress, respectively.

Another limiting case of the pure mechanochemical corrosion—when $m = 0.008(l_c/[t_c p_c])$ and $a = 0$—is shown in Fig. 2 for the holes with the same as above initial semi-axes $A_0 = 1.25(l_c)$, $B_0 = 1(l_c)$ (dashed lines) and $A_0 = 3(l_c)$, $B_0 = 1(l_c)$ (solid lines). Gradually increasing contours of the first hole (dashed lines) correspond to the times $t = 0;\ 3.29;\ 6.27;\ 8.99;\ 11.49;$ and $13.81(t_c)$. Growing contours of the second hole (solid lines) correspond to $t = 0;\ 0.99;\ 1.88;\ 2.70;\ 3.45;$ and $4.14(t_c)$. The graph is built for $p = 10(p_c)$.

It was proved that when the mechanochemical effect is weak ($a > 2mp$), the ratio $\eta = A/B$ decreases with time, tending to unity. For example, for the cases demonstrated in Fig. 1, the ratio η is equal to 1.25; 1.225; 1.2; 1.175; 1.15; and 1.125 (for the gradually increasing dashed contours) and 3; 2.8; 2.6; 2.4; 2.2; and 2 (for the gradually increasing solid contours), respectively. Therefore, the stress concentration factor near the hole decreases as well and approaches 2. In this case the durability of the plate is not reduced.

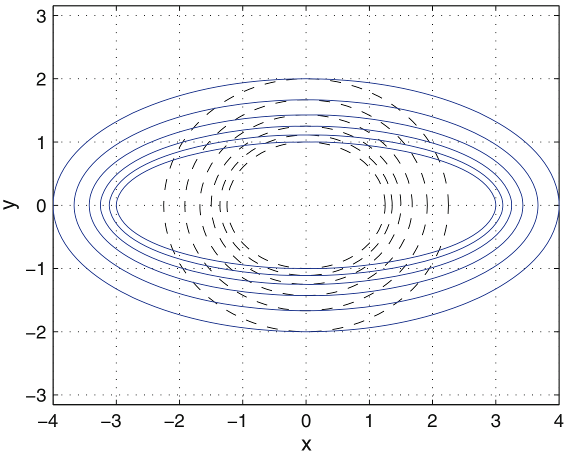

Fig. 1 Gradually growing contours of the holes with $A_0 = 1.25$, $B_0 = 1$ (*dashed lines*) and $A_0 = 3$, $B_0 = 1$ (*solid lines*) corresponding to the times $t = 0;\ 0.56;\ 1.25;\ 2.14;\ 3.33;$ and 5. The case of constant rate corrosion

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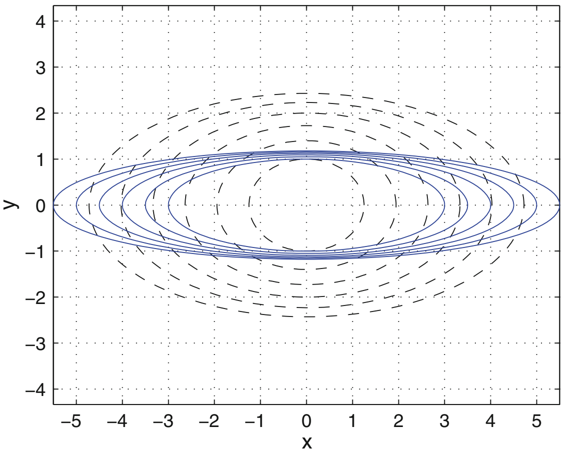

Fig. 2 Gradually increasing contours of the hole with $A_0 = 1.25$, $B_0 = 1$ (*dashed lines*) corresponding to the times $t =$ 0; 3.29; 6.27; 8.99; 11.49; and 13.81 and of the hole with $A_0 = 3$, $B_0 = 1$ (*solid lines*) corresponding to the times $t =$ 0; 0.99; 1.88; 2.70; 3.45; and 4.14. The case of pure mechanochemical corrosion

When the mechanochemical effect takes place at $a < 2mp$, the ratio η grows. This fact must be borne in mind when using Eq. (10) to plot the dependencies $t(\eta)$. For the cases demonstrated in Fig. 2, the ratio η is equal to 1.25; 1.39; 1.53; 1.67; 1.81; and 1.94 (for the gradually increasing dashed contours) and 3; 3.(3); 3.(6); 4; 4.(3); and 4.(6) (for the gradually increasing solid contours), respectively. It is seen that the greater the initial aspect ratio η_0 is, the faster η grows. Moreover, the corrosion in the direction of A-axis is accelerated with time. Therefore, the stress concentration factor increases and the durability of the plane decreases. In this case the lifetime of the plane can be determined by formula (10) with a certain critical value $\eta*$ (corresponding to a strength limit) for η.

If $A_0 = B_0 = R_0$, then the stress concentration factor is equal to 2 at any t and for any values R_0, a, m, and p and there is no need to use Eqs. (10)–(12) for lifetime assessment. Despite the mechanochemical effect, the rate of corrosion remains constant for the corrosion process (see Eqs. (13)–(14)).

3 Conclusion

All the discussed analytical solutions can serve as benchmarks for numerical analysis implemented by the use of an appropriate corrosion rate model. Moreover, they can help to identify the role of mechanochemical effect in damage propagation observed in experiments.

The analytical results proposed here show that the stress concentration factor at a noncircular hole can either increase or decrease, or stay invariant during the corrosion process, depending on the relationship between the corrosion kinetics constants and applied stress.

I would like to note that in addition to the developing numerical methods and computational techniques it is reasonable to create a single integrated data bank of closed-form solutions for various initial/boundary value problems. That would be a powerful aid for solving applied problems worldwide.

Acknowledgments I am very grateful to the organizing committee of the International conference on "Modern Mathematical Methods and High Performance Computing in Science & Technology (M3HPCST-2015)" for the invitation and support for my participation in this conference.
I would like to thank S.M. Khryashchev (specialist in differential calculus [12, 13]) for his helpful advises. This work is partially supported by the Russian Foundation for Basic Research (project No. 16-08-00890).

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