

Statistical model of stress corrosion cracking based on extended form of Dirichlet energy

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Abstract. The mechanism of stress corrosion cracking (SCC) has been discussed for decades. Here I propose a model of SCC reflecting the feature of fracture in brittle manner based on the variational principle under approximately supposed thermal equilibrium. In that model the functionals are expressed with extended forms of Dirichlet energy, and Dirichlet principle is applied to them to solve the variational problem that represents SCC and normal extension on pipe surface. Based on the model and the maximum entropy principle, the statistical nature of SCC colony is discussed and it is indicated that the crack has discrete energy and length under ideal isotropy of materials and thermal equilibrium.

Keywords. Stress corrosion cracking; variational principle; Dirichlet principle; maximum entropy principle.

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1. Introduction

Stress corrosion cracking, or SCC, is seen on various types of metal surfaces and it is a significant menace for the pipeline industry since it often causes structural failure on the pipe wall without any preceding signs and brings devastating consequence. The causes of SCC have been discussed for a long time. Phenomenally, it is known that the occurrence of SCC needs high tensile stress and temperature under corrosive circumstance [1], however regarding microscopic mechanism it is still disputable. Further, high-pH SCC and near-neutral pH SCC must be considered individually [2,3]. While it is widely recognized that the intergranular crack can be transformed into SCC [4], some experimental results suggest the predominant influence of hydrogen embrittlement on that transition process [5] and others show the existence of oxygen rupture [6]. To understand the mechanism of SCC from atomistic viewpoint, some theoretical models have been proposed [7,8].

Here, however, SCC is dealt with as the event on a continuous and quasielastic body approximately for the sake of easier treatment analytically.

SCC is thermodynamically not a stable phenomenon [9]. However, as the crack growth speed is relatively slow in the early stage of SCC, it may be treated approximately as the equilibrium state in sufficiently short period. Then the variational principle would be applicable to the state of SCC, that is, the crack should occupy the lowest energy state. The energy state of the crack actually means that of the material in which the crack resides, and the lowest energy state corresponds to that of minimized Dirichlet energy. In the following sections we consider first the models of individual SCC derived from extended form of Dirichlet energy, then the ensemble of SCC, or SCC colony, is discussed based on one of those models applying thermodynamics and statistical mechanics to elucidate its nature.

2. Variational principle and extended Dirichlet energy

It is known that the minimal surface area surrounded by fixed boundary is approximated by the solution of Laplace equation which is induced from the following variational principle:

$$E[\varphi] = \frac{1}{2} \int_W |\nabla\varphi(x, y)|^2 dx dy \rightarrow \text{minimum}, \quad (1)$$

where φ is the displacement of the pipe surface and $E[\varphi]$ is called the Dirichlet energy [10]. In the above formulation it has been supposed that the potential energy is proportional to the area of the pipe surface W , while generally SCC occurs in a brittle manner and brings discontinuous change on $\varphi(x, y)$. It suggests the necessity to expand the form of Dirichlet energy shown above in order to represent the displacement other than that proportional to the surface area. Hence, we consider first the following quasi-Dirichlet energy $E_S[\varphi]$:

$$\begin{aligned} E_S[\varphi] &= \int_W dx dy \int d|\nabla\varphi(x, y)| \arctan(|\nabla\varphi(x, y)|) \\ &= \int_W dx dy \left\{ \frac{|\nabla\varphi(x, y)|^2}{2} - \frac{|\nabla\varphi(x, y)|^4}{3 \cdot 4} + \frac{|\nabla\varphi(x, y)|^6}{5 \cdot 6} - \dots \right\}. \end{aligned} \quad (2)$$

As the hoop stress is predominant on pipe surface in general, we assume that the displacement to axial direction is negligible in sufficiently small area W and φ is the function of radial direction only as shown in figure 1, i.e.,

$$\varphi(x, y) = \varphi(x), \quad (3)$$

where x is the radial coordinate and y is the axial coordinate.

Then the above equation for quasi-Dirichlet energy $E_S[\varphi]$ is simplified as

$$\begin{aligned} E_S[\varphi] &= \int_0^D dx \int d\varphi_x(x) \arctan(\varphi_x(x)) \\ &= \int_0^D dx \left\{ \frac{\varphi_x(x)^2}{2} - \frac{\varphi_x(x)^4}{3 \cdot 4} + \frac{\varphi_x(x)^6}{5 \cdot 6} - \dots \right\}, \end{aligned} \quad (4)$$

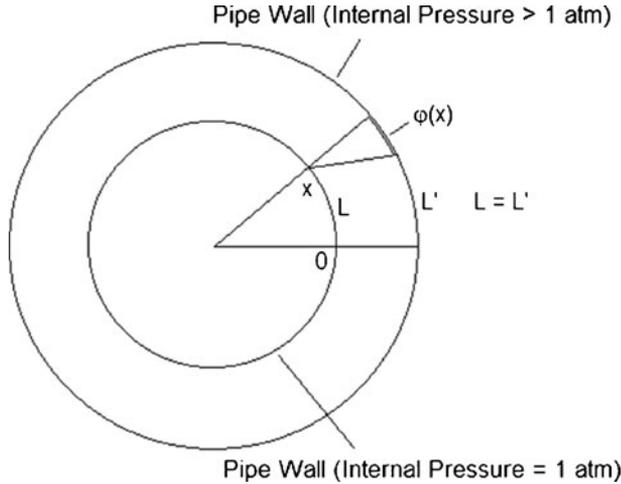


Figure 1. Radial coordinate and displacement.

where $\varphi_x(x) = d\varphi(x)/dx$. Applying the variational principle formally to that quasi-Dirichlet energy, we get

$$\begin{aligned}
 -\frac{d}{dx} \frac{d}{d\varphi_x} \int d\varphi_x(x) \arctan(\varphi_x(x)) &= -\frac{d\varphi_x}{dx} \frac{d}{d\varphi_x} \arctan(\varphi_x(x)) \\
 &= -\frac{\varphi_{xx}}{1 + \varphi_x^2} = 0,
 \end{aligned}
 \tag{5}$$

where $\varphi_{xx} = d^2\varphi/dx^2$. Thus, φ must satisfy the following equation at the stationary condition:

$$\varphi_{xx} = 0, \quad \text{i.e.} \quad \varphi = C_1x + C_2,
 \tag{6}$$

where C_1 and C_2 are constants or

$$\varphi_x \rightarrow \pm\infty.
 \tag{7}$$

Two examples of the solution expressed with (6) and (7) are illustrated in figure 2 where $\varphi(0) = 0$ and $\varphi(D) = a$ are the boundary conditions. Figure 2a is the ordinary solution corresponding to (6), while figure 2b is the combination of solutions (6) and (7) and shows a discontinuous change at x_M corresponding to (7). The total strain energy between 0 and D on the latter is null, while the former has a positive value. They are physically interpreted as the pipe surface before (figure 2a) and after (figure 2b) the fracture under a certain constant tensile stress.

The model shown here explains how fracture happens. However, actually, the occurrence of SCC does not always mean the immediate structural failure, but in some cases the energy released from SCC is used for deforming the material around the crack. In terms of quasi-Dirichlet energy, it should not be null in the latter case, but vary according to the size of the crack. It implies that this model describes the behaviour of structural failure

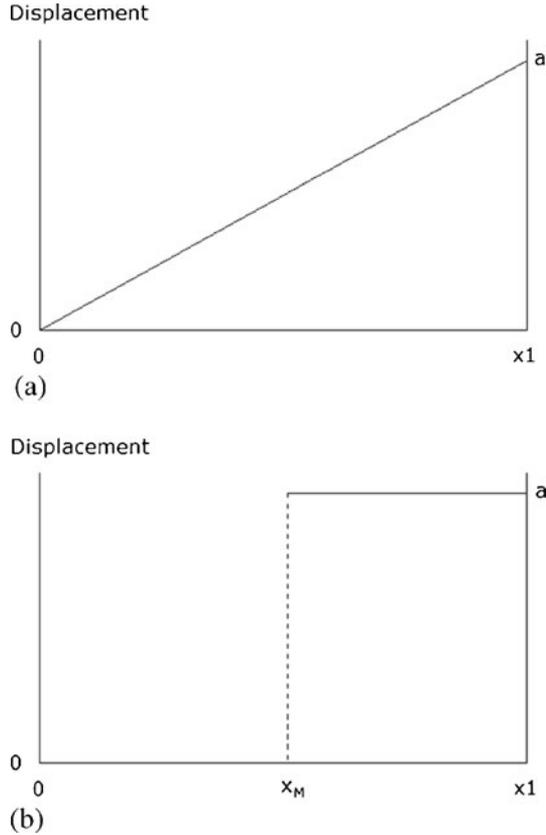


Figure 2. Continuous and discontinuous solutions under quasi-Dirichlet energy.

in completely brittle materials rather than that of SCC. Hence we consider secondly the following quasi-Dirichlet energy:

$$E_L[\varphi] = \frac{1}{2} \int_W dx dy \frac{|\nabla\varphi(x, y)|^2}{1 + \beta|\nabla\varphi(x, y)|^2}, \quad (8)$$

where β is a constant and > 0 , and where β is determined by the properties of the material of the pipe wall. As well as the former case, it is simplified using condition (3) to one-dimensional integral as

$$E_L[\varphi] = \frac{1}{2} \int_0^D dx \frac{\varphi_x(x)^2}{1 + \beta\varphi_x(x)^2}, \quad (9)$$

where x is the radial coordinate.

Applying the variational principle formally to the above quasi-Dirichlet energy, we get

$$-\frac{d}{dx} \frac{d}{d\varphi_x} \frac{1}{2} \frac{\varphi_x(x)^2}{1 + \beta\varphi_x(x)^2} = -\frac{\varphi_{xx}(1 - 3\beta\varphi_x^2)}{(1 + \beta\varphi_x^2)^3} = 0. \quad (10)$$

Therefore, φ must satisfy the following equations at the stationary condition:

$$\varphi_{xx} = 0 \quad \text{or} \quad \varphi_x = \pm \frac{1}{\sqrt{3\beta}} \quad \text{or} \quad \varphi_x \rightarrow \pm\infty. \quad (11)$$

Two examples of the solution are illustrated in figure 3. Figure 3a is the solution $\varphi = C_0x$ and figure 3b is the combination of solutions: $\varphi_1 = C_1x$, $\varphi_2 = (x/\sqrt{3\beta}) + C_2$ and $\varphi_3 = C_3x + C_4$ (C_0, \dots, C_4 : constants) corresponding to three ranges having the length A , S and B respectively. Since φ_2 has the constant derivative $1/\sqrt{3\beta}$ which is not null, quasi-Dirichlet energy shown in figure 3b is not null and the longer interval φ_2 has, the greater the energy it stores. Thus, we could regard the displacement expressed with φ_2 in the range having length S as the individual crack on the pipe surface. We choose S as making quasi-Dirichlet energy minimum. That energy may be lower than that of figure 3a. Then, this solution is interpreted as the most probable cracking under the condition that there exists single crack in the range $[0, D]$. Note that S and strain energy E of the crack have the following relation:

$$E = \frac{1}{2} \int_0^S dx \frac{\varphi_x(x)^2}{1 + \beta\varphi_x(x)^2} = \frac{S}{8\beta}, \quad (12)$$

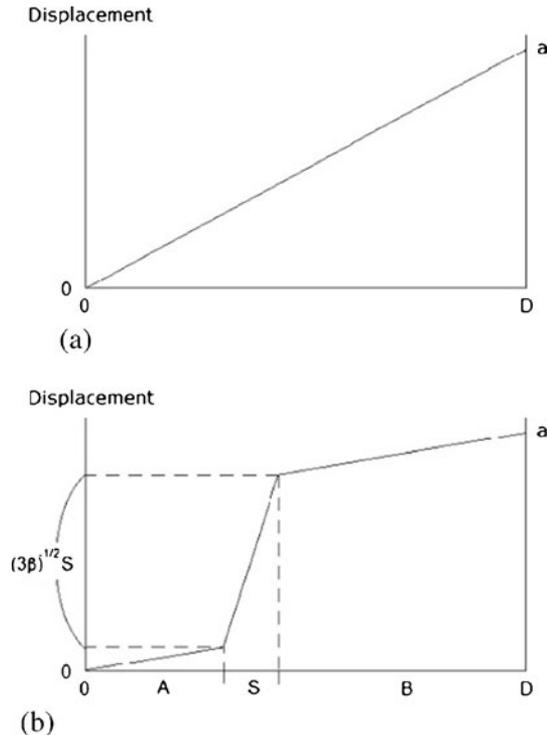


Figure 3. Two solutions for the stationary condition of quasi-Dirichlet energy $E_L[\varphi]$.

where $\varphi_x(x) = 1/\sqrt{3\beta}$. We assume that the displacement caused by cracking is proportional to crack's axial length and denote that factor as λ . Then the crack length L is written as $\lambda S/\sqrt{3\beta}$, and E is expressed with the crack length L as

$$E = \frac{\lambda S/\sqrt{3\beta}}{8\lambda\beta/\sqrt{3\beta}} = \frac{L}{8\lambda}\sqrt{\frac{3}{\beta}}. \tag{13}$$

3. Crack distribution

Although the second model mentioned tells how much energy is stored around the crack, it is unable to predict how cracks distribute because that model is applicable only to single crack. As most of SCC form crack colony, it is important to deal with the ensemble of SCC in order to describe the distribution of cracks in the crack colony.

To deal with multiple cracks, we consider the decomposition of the above crack on the range having length S by keeping the quasi-Dirichlet energy minimum. First we assume ideal isotropy and homogeneity for the material of the pipe wall. Now we decompose the crack into n subcracks as seen in figures 4a and 4b satisfying the minimum quasi-Dirichlet energy $E_L[\varphi]$ which is equal to that shown in figure 3b. The events corresponding to the solutions shown in figures 3b, 4a and 4b seem to have the probability

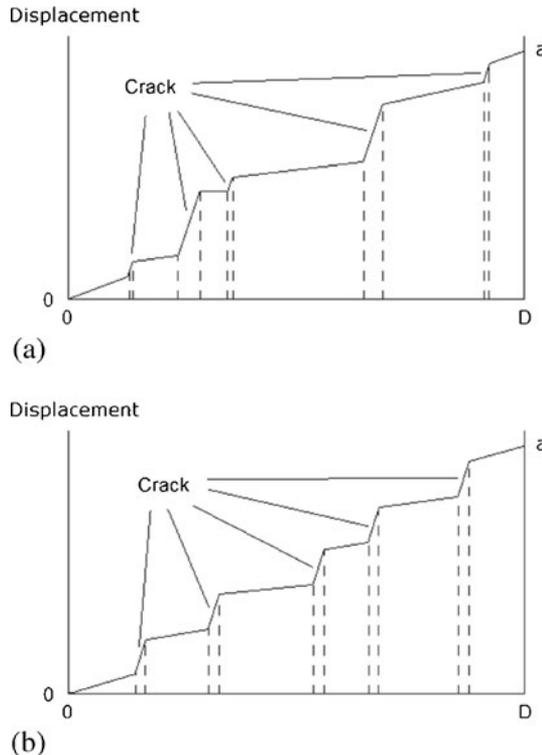


Figure 4. Decomposition of the crack.

equal to each other since their quasi-Dirichlet energy is equal to each other. However, actually the event shown in figure 4b where every subcrack has the same energy and length is thermodynamically more probable than figure 4a according to the maximum entropy principle. Intuitively it is comprehended as we do not have any *a priori* reason that one of those n cracks is longer than the others. Thus, under the condition that the crack is divided into n subcracks in thermal equilibrium, the probability of division into n equi-length subcracks is almost 1. That is, the crack length L is discretized and expressed as

$$L_n = \frac{\lambda S}{n\sqrt{3\beta}} \quad (n: 1, 2, 3, \dots) \quad (14)$$

namely,

$$L_n = \frac{L_1}{n} \quad (n: 1, 2, 3, \dots). \quad (15)$$

Following the discretization of crack length, the energy level of crack E is also discretized and expressed using the relation (13) as

$$E_n = \frac{L_n}{8\lambda} \sqrt{\frac{3}{\beta}} \quad (n: 1, 2, 3, \dots) \quad (16)$$

namely,

$$E_n = \frac{E_1}{n} \quad (n: 1, 2, 3, \dots). \quad (17)$$

The above discretization of crack implies that the crack has a nature of ‘particle’ under ideal thermal equilibrium, and the probability $f(E_j)$ that the crack has the energy E_j would be proportional to the Boltzmann factor, i.e.

$$f(E_j) = c_N \cdot \exp\left(\frac{\mu - E_j}{kT}\right), \quad (18)$$

where k is the Boltzmann constant, T is the temperature, μ is the chemical potential and c_N is the normalization factor.

Therefore, we can estimate the mean number of cracks having the energy E_n under the temperature T as

$$\begin{aligned} m(E_n) &= \frac{\sum_{j=1}^n j \cdot \exp\left(\frac{j(\mu - E_n)}{kT}\right)}{\sum_{j=1}^n \exp\left(\frac{j(\mu - E_n)}{kT}\right)} \\ &= \frac{1}{\exp\left(\frac{(E_n - \mu)}{kT}\right) - 1} + \frac{\exp\left(\frac{n(E_n - \mu)}{kT}\right) - n - 1}{\exp\left(\frac{n(E_n - \mu)}{kT}\right) - 1}, \end{aligned} \quad (19)$$

where the upper bound n in the summation is equal to the number of divisions in the range having length S since the sum of the subcrack’s strain energy cannot exceed the original single crack’s energy $E_1 (= T/8\beta)$.

As mentioned in Introduction, we have assumed SCC to be thermally stable in a certain short period and the crack growth is negligible. Then SCC is independent of the change of Gibbs free energy because the cracks can neither diffuse nor move. That is, the chemical potential μ is null. Thus, the crack distribution (19) is rewritten as

$$\begin{aligned}
 m(E_n) &= \frac{1}{\exp(E_n/kT) - 1} + \frac{\exp(nE_n/kT) - n - 1}{\exp(nE_n/kT) - 1} \\
 &= \frac{1}{\exp(E_n/kT) - 1} + \frac{\exp(E_1/kT) - n - 1}{\exp(E_1/kT) - 1}.
 \end{aligned}
 \tag{20}$$

In figure 5 the behaviours of $m(E_n)$ under three different conditions are illustrated. When E_n/kT is sufficiently small, $\exp(E_n/kT)$ is approximated as

$$\exp\left(\frac{E_n}{kT}\right) \approx 1 + \frac{E_n}{kT}.
 \tag{21}$$

Using (21), (20) is approximated as

$$m(E_n) \approx n.
 \tag{22}$$

It is also expressed with (15) and (17) as

$$m(E_n) \approx \frac{L_1}{L_n} = \frac{E_1}{E_n}.
 \tag{23}$$

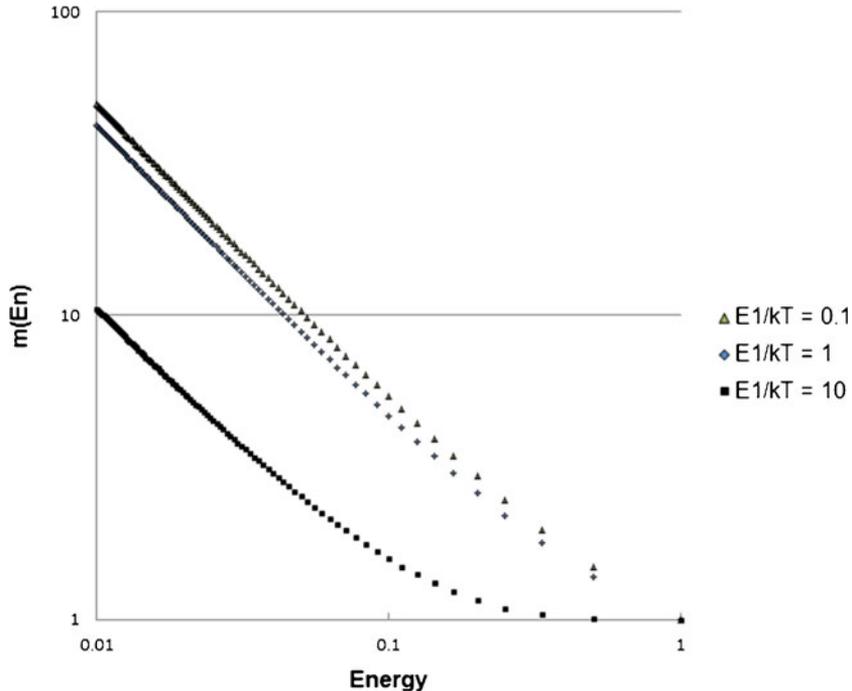


Figure 5. Mean crack numbers as a function of crack energy.



Figure 6. SCC colony.

That is, the mean number of cracks having energy E_n (or length L_n) is inversely proportional to E_n (or L_n) approximately at sufficiently high temperature or small crack energy.

An example of the SCC colony on the pipe surface is shown in figure 6. It is unlikely that the SCC colony was created at once. Actually, most of the cracks shown in that

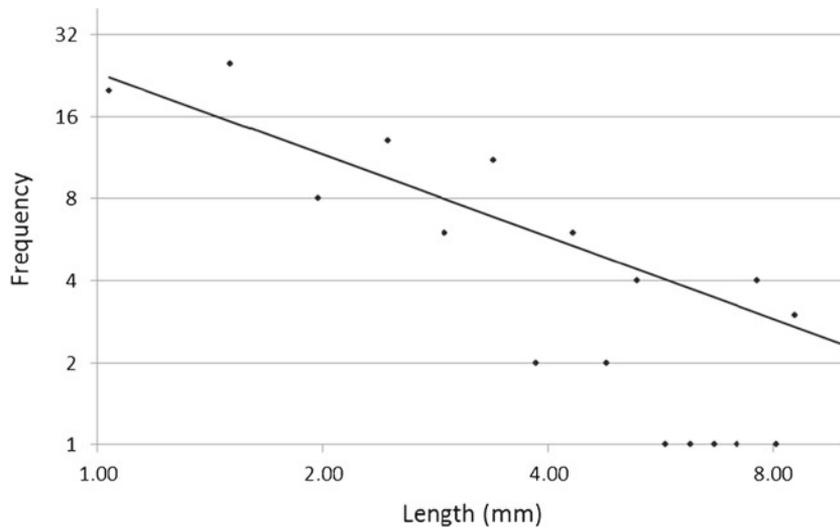


Figure 7. The frequency of crack length as an inversely proportional function of crack length.

picture would have grown gradually for years and eventually aggregated into the colony. In that process some of them might have combined and formed larger cracks because adjacent cracks tend to link each other. Therefore, it seems difficult to apply the previous assumptions, i.e. thermodynamical stability and null chemical potential, to such example. Further, as seen in the picture, each crack is not exactly parallel to the pipe axis owing to microstructural anisotropy of the material. However, for sufficiently small cracks, those assumptions are thought still applicable since we can estimate a small crack as having created at a single incident, and eliminate the effect of crack growth and reduce the influence of stress caused by the anisotropy of the materials.

In figure 7, the frequency of crack length on the above example was fitted by inversely proportional function of crack length. Figure 7 indicates that the assumptions mentioned above are applicable to the cracks having length less than around 3 mm, i.e. such cracks are thought to have been created in a single incident. As threshold of length depends not only on temperature, but also on the material properties, the length of 3 mm as the threshold is specific to that example.

4. Summary

Although SCC, or stress corrosion cracking, is thermodynamically unstable, dealing with it as approximately stable phenomenon in sufficiently short period is thought plausible. Then it would take the minimum energy state in thermodynamically closed system. According to the variational principle, it approximately satisfies the stationary condition of Dirichlet energy. In order to induce from the variational principle the displacement on pipe surface including SCC under high tensile stress, we discuss to extend Dirichlet energy that derives multiple solutions under stationary condition. One of those solutions coincides with that of the ordinary Laplace equation. The other one is independent of the boundary conditions but depends on the internal parameter introduced in the extended Dirichlet energy. The latter solution represents the displacement on pipe surface caused by SCC.

As most of the SCC form a colony, we need to deal with the ensemble of SCC statistically to discuss the nature of SCC colony. For that purpose, first we decompose virtually the largest single crack caused by SCC into multiple subcracks. Then, by applying the maximum entropy principle, we induce that each subcrack has the discrete energy and length which are determined by the extent of the largest crack under ideal thermal equilibrium. The nature of those subcracks is similar to that of a particle, and the frequency of their length is expected to be inversely proportional to the length itself when the length of each subcrack is small enough. It was verified using the example of an actual SCC colony.

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