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Thermodynamically modeling the interactions of hydrogen, stress and anodic dissolution at crack-tip during near-neutral pH SCC in pipelines

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Abstract A thermodynamic model was developed to clarify the interactions of hydrogen, stress and anodic dissolution at crack-tip during near-neutral pH stress corrosion cracking in pipelines by comprehensively considering the electrochemical reactions occurring in the pipeline steel in deoxygenated, near-neutral pH solution. By analyzing the change of the free-energy of steel due to the presence of hydrogen and stress, it is demonstrated that a synergism of hydrogen and stress promotes the cracking of steel. The enhanced hydrogen concentration in the stressed steel significantly accelerates the crack growth. An exact expression of the hydrogen concentration factor, i.e., the dependence of anodic dissolution rate of steel at crack-tip on the hydrogen concentration, is essential at the quantitative prediction of the crack growth rate.

Introduction

Stress corrosion cracking (SCC) is a known integrity threat to the safe operation of the natural gas pipelines. The great majority of pipeline failures have involved high pH (~9.0) SCC [1]. Near-neutral pH SCC on pipelines, cracking at pH of about 6.5, was initially recorded in Canada during the mid-1980s, and has been responsible for an increasing number of pipeline failures in recent years in Canada [2]. High pH SCC, engendered by concentrated bicarbonate or carbonate–bicarbonate solutions, has usually an intergranular morphology, and the cracks are sharp, with little lateral corrosion. Near-neutral pH SCC, engendered by anaerobic, dilute ground water, has a transgranular, quasi-cleavage crack morphology with appreciable lateral corrosion of the crack sides.

Whereas high pH SCC of pipelines has been studied extensively to develop the well-accepted mechanism, i.e., high pH SCC being attributed to anodic dissolution resulting from selective dissolution at the grain boundaries and repeated rupture of passive films that form over the crack tip [1, 3], there has been relatively little work performed to study near-neutral pH SCC. To date, there is no precise mechanism identified to understand the crack initiation, and there is no predictive model developed to define the rate of crack growth in the line pipe steels [4].

Previous work showed [5] that hydrogen could play an important role in near-neutral pH SCC in pipeline steels, altering the dissolution at and ahead of the crack-tip. The experimental results have indicated that the extracted soil solutions with more SCC susceptibility are always associated with higher hydrogen permeation current and sub-surface hydrogen concentration. Parkins [1] analyzed the potential-pH range where high pH SCC and near-neutral pH SCC occurred, and found that in the near-neutral pH solution, hydrogen discharge is possible. He concluded that some synergistic effects between the hydrogen and the anodic dissolution exist during the growth of near-neutral pH SCC of pipelines.

There is a considerable amount of evidence [6–8] that hydrogen plays a critical role in the near-neutral

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pH SCC of pipelines. However, the precise mechanism has not been identified. Gu et al. [9] deduced an equation for the synergistic effect of hydrogen and stress on the anodic dissolution rate. They suggested a local acidification generating during anodic dissolution, and thus thought that near-neutral pH SCC is dominated by the mechanism of hydrogen-facilitated dissolution. However, there is no further evidence to support this theory. Mao and Li [10] developed a thermodynamic model to explain the interaction between the hydrogen and the stress at the crack-tip. In this model, they ignored the fact that the main cathodic reaction occurring in deoxygenated, near-neutral pH solution is the reduction of water molecules, not the hydrogen ions. Furthermore, they did not take account into the effect of applied stress and the presence of cracks on the concentration of hydrogen atoms diffusing in the steels, and thus, over-simplified the thermodynamic consideration.

In this work, a thermodynamic model was developed to analyze the interactions of hydrogen, stress and anodic dissolution at crack-tip during near-neutral pH SCC in pipelines. By comprehensively considering the electrochemical reactions occurring outside and inside the cracks, the alternation of free-energy of the steel in the presence of stress and the absence of hydrogen was analyzed. It is aimed at clarifying the synergism of hydrogen, stress and anodic dissolution during the near-neutral pH SCC in pipeline steel.

Corrosion electrochemistry of steel in deoxygenated, near-neutral pH solution

The electrochemical reactions of a steel specimen without applied stress in deoxygenated, near-neutral pH solution can be described as

$$\text{Anodic reaction}: \mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e} \tag{1}$$

$$\text{Cathodic reaction}: \mathrm{H_2O} + \mathrm{e} \rightarrow \mathrm{H_{ads}} + \mathrm{OH^-} \tag{2}$$

The hydrogen atoms adsorpted on the steel surface may combine into hydrogen molecules by the chemical reaction:

$$2\mathrm{H_{ads}} \rightarrow \mathrm{H_2} \tag{3}$$

or the electrochemical reaction:

$$\mathrm{H_{ads}} + \mathrm{H_2O} + \mathrm{e} \rightarrow \mathrm{H_2} + \mathrm{OH^-} \tag{4}$$

The hydrogen atoms generated from the cathodic reaction may also penetrate into the steel surface and become absorbed hydrogen atoms by

$$\mathrm{H_{ads}} \rightarrow \mathrm{H_{abs}} \tag{5}$$

Apparently, only some of the adsorpted hydrogen atoms generated from the cathodic reaction (2) will recombine to be the hydrogen molecules, and the others will permeate into the steel.

It has been established [11] that, in near-neutral pH solutions without added hydrogen-permeation promoters, the electrochemical reaction (4) predominates the hydrogen recombination process. Therefore, the whole electrode reaction for the steel in deoxygenated, near-neutral pH solution can be described as:

$$\mathrm{Fe}(x\mathrm{H}) + 2\mathrm{H_2O} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{OH^-} + \frac{2(1-x)}{2-x}\mathrm{H_2} + \frac{2x}{2-x}\mathrm{H_{abs}} \tag{6}$$

where x is the amount of hydrogen atoms permeating into the steel and Fe(xH) means the steel specimen containing hydrogen atoms with the amount of x.

For a stressed, line pipe steel specimen with the presence of cracks in the deoxygenated near-neutral pH solution, there are separated sites for cathodic and anodic reactions, i.e., the anodic reaction—Fe dissolution—occurs mainly inside the crack and the cathodic reaction—reduction of water molecules—occurs outside the crack. The hydrogen atoms generated from the cathodic reaction may recombine into hydrogen molecules, and may also penetrate into the steel and become the absorbed hydrogen atoms, which will then diffuse towards the crack-tip, where a high tri-axial stress concentration exists [12]. The hydrogen atoms nearby the crack-tip are accumulated in the plastic zone, according to Yokobori et al.'s work [13], as shown in Fig. 1.

It has been acknowledged [14] that the high dissociation energy of the hydrogen is applied by a deforming steel specimen. For this reason, the hydrogen in a tension-stress field can penetrate into the steel lattice much more easily than into an intact tension-free specimen. Therefore, there will be more hydrogen atoms diffusing into the deformed steel specimen, preferably accumulating in the site with a high stress concentration, such as crack-tip. The whole electrochemical reaction for the stressed steel with cracks in deoxygenated, near-neutral pH solution is described as:

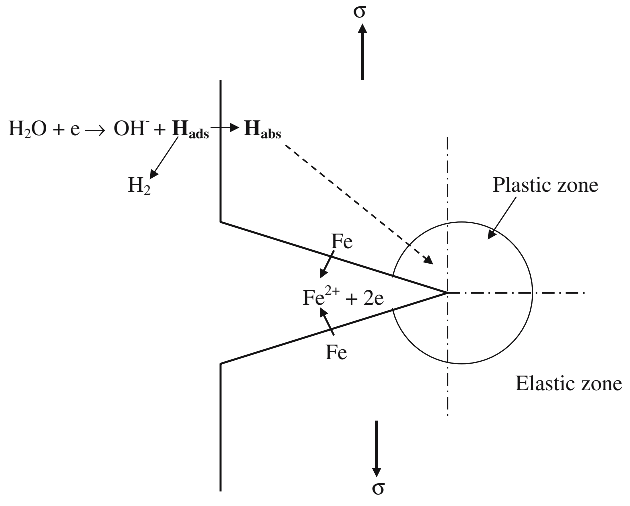

Fig. 1 Model for hydrogen diffusion and dissolution reaction at the crack-tip for a stressed steel specimen in deoxygenated, near-neutral pH solution

$$\mathrm{Fe}(\sigma, y\mathrm{H}) + 2\mathrm{H_2O} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{OH}^- + \frac{2(1-y)}{2-y}\mathrm{H_2} + \frac{2y}{2-y}\mathrm{H_{abs}} \tag{7}$$

where y is the amount of hydrogen atoms permeating into the stressed steel, and $y > x$. Fe(yH) means the steel specimen containing hydrogen atoms with the amount of y.

Thermodynamics of the interactions of hydrogen, stress and anodic dissolution

Equations (6) and (7) are the electrochemical reactions occurring in the steel without and with applied stress in deoxygenated, near-neutral pH solution, respectively. With respect of the identical products, the difference of electrochemical potentials between reaction (6) and (7) is caused by both the free-energy change between the stressed steel and the unstressed steel and the different amount of hydrogen atoms penetrating into the steel. If the free-energy changes and the electrochemical potentials in reactions (6) and (7) are denoted as ΔG_1 and ΔG_2, E_1 and E_2, respectively, then

$$\Delta G_1 = G_{\mathrm{Fe}^{2+}} + 2G_{\mathrm{OH}^-} + \frac{2(1-x)}{2-x}G_{\mathrm{H_2}} + \frac{2x}{2-x}G_{\mathrm{H_{abs}}} - \mathrm{G_{Fe}}(x\mathrm{H}) - 2G_{\mathrm{H_2O}} = -nFE_1 \tag{8}$$

$$\begin{aligned}\Delta G_2 &= G_{\mathrm{Fe}^{2+}} + 2G_{\mathrm{OH}^-} + \frac{2(1-y)}{2-y}G_{\mathrm{H_2}} + \frac{2y}{2-y}G_{\mathrm{H_{abs}}} - G_{\mathrm{Fe}}(\sigma, y\mathrm{H}) - 2G_{\mathrm{H_2O}} \\ &= \Delta G_1 - \frac{2(y-x)}{(2-y)(2-x)}\left[G_{\mathrm{H_2}} - 2G_{\mathrm{H_{abs}}}\right] - \Delta G_{\mathrm{Fe}}(\sigma, H) = -nFE_2\end{aligned} \tag{9}$$

where G represents the formation free-energy of the individual species, n is the number of electrons exchanged in the reaction, F is Faraday's constant and $\Delta G_{\mathrm{Fe}}(\sigma, \mathrm{H}) = G_{\mathrm{Fe}}(\sigma, y\mathrm{H}) - G_{\mathrm{Fe}}(x\mathrm{H})$ is due to the presence of stress and the different concentrations of hydrogen atoms in the steels.

The anodic dissolution current density i_1 in reaction (6) is

$$i_1 = i_0 \exp\left[-\frac{\Delta G_1}{RT}\beta\right] = i_0 \exp\left[\frac{nFE_1}{RT}\beta\right] \tag{10}$$

where i_0 is the exchange current density and β is the charge transfer coefficient. The dissolution current density i_2 at the crack-tip in reaction (7) is

$$\begin{aligned}i_2 &= i_0(\sigma, yH)\exp\left[-\frac{\Delta G_2}{RT}\beta\right] \\ &= i_0(\sigma, yH) \\ &\quad \times \exp\left[-\frac{\Delta G_1 - \frac{2(y-x)}{(2-y)(2-x)}(G_{\mathrm{H_2}} - 2G_{\mathrm{H_{abs}}}) - \Delta G_{\mathrm{Fe}}(\sigma, H)}{RT}\beta\right]\end{aligned} \tag{11}$$

If it is assumed that the exchange current density keeps constant, then

$$i_2 = i_1 \exp\left[\frac{\frac{2(y-x)}{(2-y)(2-x)}(G_{\mathrm{H_2}} - 2G_{\mathrm{H_{abs}}}) + \Delta G_{\mathrm{Fe}}(\sigma, H)}{RT}\beta\right] \tag{12}$$

When the steel specimen is free of stress ($\sigma = 0$), it is expected that there is no SCC crack initiating in the steel, and the steel corrodes in the deoxygenated, near-neutral pH solution following Eq. (6). The amount of hydrogen atoms penetrating into the steel, x, is approximately equal to y. Since there is no difference with respect of the free-energy change for Eqs. (6) and (7), $i_2 = i_1$.

In case of applied stress resulting in the generation of cracks in the steel, when the amount of hydrogen penetrating into the steel is not sufficiently enough to be involved in SCC of the steel, i.e., the concentration of hydrogen atoms in the steel is too low to affect the cracking process of the steel, the difference in free-energy change mainly comes from the effect of stress. The SCC of the steel follows the anodic dissolution mechanism, that is, the interaction between anodic dissolution reaction and stress dominates the crack growth. Equation (12) can then be described as

$$i_2 = i_1 \exp\left[\frac{\Delta G_{\mathrm{Fe}}(\sigma, \mathrm{H} = 0)}{RT}\beta\right] \tag{13}$$

According to Mao and Li [10], the change of free-energy $_{\mathrm{Fe}}(\sigma, \mathrm{H})$ can be given at constant pressure and constant temperature as

$$\Delta G_{\mathrm{Fe}}(\sigma, \mathrm{H}) = \Delta U - T\Delta S + (U_1 + U_2) \tag{14}$$

where ΔU is the internal energy change, ΔS is the entropy change, U_1 is the strain energy density, and U_2 is the interaction energy between the lattice strain induced by hydrogen atoms and external stress field. For the case with stress and no hydrogen, ΔU, ΔS and U_2 are zero. $\Delta G_{\mathrm{Fe}}(\sigma, \mathrm{H} = 0)$ is simply the strain energy density, and can be described as

$$\Delta G_{\mathrm{Fe}}(\sigma, \mathrm{H} = 0) = U_1 = \frac{W(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)}{2E\rho} \tag{15}$$

where W is the molar weight, σ_1, σ_2 and σ_3 are the principal stresses, ρ is the density and E is the Young's modulus. Equation (13) is then given as

$$i_2 = i_1 \exp\left[\frac{W(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)}{2E\rho RT}\beta\right] = k_{\sigma_1} k_{\sigma_2} k_{\sigma_3} i_1 = k_\sigma i_1 \tag{16}$$

where k_σ is stress factor.

In case of both hydrogen atoms and stress contributing to the cracking process of the steel, the interaction energy U_2 has been established as [15]

$$U_2 = \frac{(\sigma_1 + \sigma_2 + \sigma_3)V_{\mathrm{H}}^-}{3} = \sigma_h V_{\mathrm{H}}^- \tag{17}$$

where σ_{h} is a volume stress. The synergistic effect of hydrogen and stress on anodic dissolution can be given as

$$\begin{aligned} i_2 = i_1 \exp\left[\frac{\frac{2(y-x)}{(2-y)(2-x)}(G_{\mathrm{H}_2} - 2G_{\mathrm{H_{abs}}})}{RT}\beta\right] \times \exp\left[\frac{\Delta U - T\Delta S}{RT}\beta\right] \\ \times \exp\left[\frac{W(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)}{2E\rho RT}\beta\right] \\ \times \exp\left[\frac{\sigma_h V_{\mathrm{H}}^-}{RT}\beta\right] = k_{\Delta\mathrm{CH}} k_{\mathrm{H}} k_\sigma k_{\mathrm{H}\sigma} i_1 \end{aligned} \tag{18}$$

k_{H} is the effect of hydrogen on the anodic dissolution rate in the absence of stress, i.e., the free corrosion rate of Fe in deoxygenated, near-neutral pH solution. k_σ is the effect of stress on the anodic dissolution in the absence of hydrogen, i.e., a pure anodic dissolution-based cracking mechanism. $k_{\mathrm{H\backslash sigma}}$ reflects the synergistic effect of hydrogen and stress on the anodic dissolution at crack-tip, and $k_{\Delta\ \mathrm{CH}}$ is the effect of the concentration difference of hydrogen atoms between the stressed steel and unstressed steel on the anodic dissolution reaction.

According to slip-oxidation model, the crack growth rate (CGR) by anodic dissolution mechanism can be represented as

$$\mathrm{CGR} = \frac{iW}{nF\rho} \tag{19}$$

Thus, the CGR in the presence of hydrogen and stress can be given as

$$\begin{aligned} \mathrm{CGR}(\sigma, \mathrm{H}) &= k_{\Delta\mathrm{CH}} k_{\mathrm{H}} k_{\mathrm{H}_\sigma} i_1 \frac{W}{nF\rho} \\ &= k_{\Delta\mathrm{CH}} k_{\mathrm{H}} k_\sigma k_{\mathrm{H}\sigma} \mathrm{CGR}(\sigma, \mathrm{H} = 0) \end{aligned} \tag{20}$$

where CGR(σ, H = 0) is the crack growth rate without the effect of hydrogen. Therefore, a quantitative prediction of the rate of crack growth in the pipeline steel in deoxygenated, near-neutral pH solution depends on the determination of these four affecting factors.

Summary

A thermodynamic model was developed to clarify the interactions of hydrogen, stress and anodic dissolution at crack-tip during near-neutral pH SCC in pipelines by comprehensively considering the electrochemical reactions occurring on the line pipe steel in deoxygenated, near-neutral pH solution and by analyzing the changes of free-energy of the steel. It is shown that a synergism of hydrogen and stress exists to promote crack growth by changing the free-energy of the steel. Furthermore, the hydrogen concentration in the stressed steel significantly affects the crack growth rate. The quantitative prediction of the rate of crack growth in the pipeline steel will depend on the determination of the dependence of anodic dissolution rate of steel at crack-tip on the hydrogen concentration.

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