Effects of dissolved hydrogen and elastic and plastic deformation on active dissolution of pipeline steel in anaerobic groundwater of near-neutral pH

B.T. Lu\textsuperscript{a}, J.L. Luo\textsuperscript{a,*}, P.R. Norton\textsuperscript{b}, H.Y. Ma\textsuperscript{c}

\textsuperscript{a}Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alta., Canada T6G 2G6
\textsuperscript{b}Department of Chemistry, University of Western Ontario, London, Ont., Canada N6A 5B7
\textsuperscript{c}Department of Chemistry, Shandong University, Jinan, Shandong 250100, China

Received 6 January 2008; received in revised form 22 August 2008; accepted 23 August 2008
Available online 24 September 2008

Abstract

The mechano-electrochemical effects of deformation and hydrogen on active dissolution of pipeline steel in near-neutral pH groundwater are described. Thermodynamic analysis shows that the free energy increment due to elastic deformation is insufficient to alter active dissolution rate remarkably. The synergistic effect of stress field and dissolved hydrogen on active dissolution (corrosion) is negligible. The effect of plastic deformation on corrosion relies heavily on the heterogeneity of dislocation structures formed in the deformation. The plastic deformation cannot significantly change the corrosion rate at the open circuit potential. There is good agreement between these theoretical predictions and experimental observations, indicating that the stress corrosion cracking of pipeline steel in the anaerobic groundwater of near-neutral pH is unlikely to be related to the hydrogen-facilitated anodic dissolution mechanism.

Keywords: Deformation; Corrosion; Hydrogen; Stress; Dislocation

1. Introduction

Numerous models have been proposed to explain stress corrosion cracking (SCC) behavior of metals [1,2]. Basically, they can be summarized as hydrogen-induced cracking and anodic path cracking (or anodic dissolution). These proposed mechanisms have revealed that the complexity of SCC is related to certain mechano-electrochemical interaction at the crack tip.

The effects of elastic and plastic deformation on the electrochemical (corrosion) properties of metals have been investigated for over 50 years [3–6]. Although there has been intense experimental investigation, the mechanism behind SCC is still not well understood [5–10]. Recently, Sahal et al. [11,12] made a new attempt to explain the active dissolution (corrosion) behavior of nickel in 1 M \( \text{H}_2\text{SO}_4 \) solution based on thermodynamic analysis. In their thermodynamic analysis, the stored energy arising from plastic deformation of the metal is assumed to be equal to the work done during plastic deformation. However, it is known that up to 90% of plastic work will be dissipated to the environment in the form of heat [13–15].

Reduction of hydrogen ions is the most common cathodic half-reaction in localized corrosion processes:

\[ \text{H}^+ + \text{e}^- \rightarrow \text{H} \quad (1) \]

A part of the hydrogen so generated diffuses into the metal and is enriched around a crack tip under the action of local stress field [16,17]. It often plays an important role in cracking mechanism. For instance, SCC of pipelines in
near-neutral pH anaerobic groundwater [18,19] occurs at potentials close to or slightly lower than the open circuit potential (OCP) [18,19]. Pipeline steels display active dissolution behavior in groundwater and substantial active dissolution occurs on the crack side [18,20]. These experimental observations indicate that both the hydrogen dissolved in pipeline steel and active dissolution present on the surface may play important roles in the near-neutral pH SCC. According to Parkins [20], the crack growth rates experimentally observed in cathodically protected pipes in the potential range near the OCP were at least one order of magnitude higher than the prediction from Faraday’s law. To incorporate in the mechanism the contributions of dissolved hydrogen and active dissolution into the development of near-neutral pH SCC, Gu et al. [21] and Mao et al. [17] suggested that SCC was controlled by a hydrogen-facilitated anodic dissolution mechanism. The model for hydrogen-facilitated anodic dissolution was first proposed by Qiao et al. [22], based on their thermodynamic analysis. This model was originally developed to describe hydrogen-promoted corrosion in stainless steels. However, the theory is only applicable to an active dissolution system because the Butler–Volmer equation was used to describe the corrosion kinetics. According to this model, the local anodic dissolution rate at the crack tip is accelerated significantly because of a strong synergistic interaction between the dissolved hydrogen and the local stress field around the crack tip. However, such a strong synergistic effect was not supported by the experimental results for SCC under active dissolution conditions [23–26]. Therefore, the thermodynamic basis for the proposed model requires re-examination.

We will now describe quantification of the impacts of dissolved hydrogen and deformation caused by applied stress on the active dissolution of pipeline steel in a simulated near-neutral pH groundwater. A thermodynamic analysis is proposed to interpret the experimental observations, forming a basis for understanding of the near-neutral pH SCC mechanisms of pipelines.

2. Experimental procedures

The test material was X60 pipeline steel. Its yield strength was 436 MPa and ultimate tensile strength was 549 MPa. The size of specimens within the gauge was 85 mm × 20 mm × 1.2 mm. Before testing, the specimens were ground with SiC abrasive papers of grits up to #1200, then successively cleaned and rinsed with de-ionized water and acetone. All the test solutions were made with analytical reagents and de-ionized water. All the tests were conducted at room temperature, 22 ± 1 °C.

In order to demonstrate the effects of dissolved hydrogen and applied stress on active dissolution, the specimens were divided into four groups and the polarization curves and polarization resistance were measured under four different conditions: (1) no hydrogen charging and no stress; (2) hydrogen-charged; (3) cyclically loaded; and (4) hydrogen-charged and cyclically loaded. A modified Devanathan dual cell was used in the experiments (Fig. 1). A specimen with thickness 1.2 mm in the test section was inserted between the two cell compartments. In each side of the dual cell, a long platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. During electrochemical measurements, the stress on a specimen was applied with a material testing system under the action of a cyclic load of constant amplitude. The solution with the chemical composition (mmol l−1) of 1.64 KCl, 5.75 NaHCO₃, 1.23 CaCl₂ and 42 B.T. Lu et al. / Acta Materialia 57 (2009) 41–49

Fig. 1. A Devanathan dual cell.
0.74 MgSO₄ is commonly used to simulate trapped water on the pipe surface under a disbonded coating and is designated as NS4 solution [18]. The test solution was NS4 solution in the oxidizing side of the cell and an aqueous solution of 0.1 M H₂SO₄ + 250 ppm As₂O₃ in the hydrogen-charging side. Anaerobic conditions were established by continuously bubbling a mixture of 5% CO₂ + 95% N₂, leading to a solution with pH 6.7. All measurements were conducted at the oxidizing side in the anaerobic NS4 solution after the steady state hydrogen permeation condition was reached. Continuous hydrogen-charging with a charging current density \( i_{\text{H-charging}} \) of 100 A m\(^{-2}\) was utilized to create a high hydrogen concentration and to simulate the conditions at the crack tip. The dissolved hydrogen concentration under this condition measured by the secondary ion mass spectrometry (SIMS) technique was about 20 ppm [23]. Electrochemical measurements were conducted after 3 h of pre-charging and were completed within 2 h to avoid the impact of hydrogen damage, since blistering would occur if the total charging duration was more than 24 h. The potential resistance was measured in the potential range of \( E_{\text{corr}} \pm 0.01 \) V. The potential scanning rate used for measuring the polarization curves and the polarization resistance was \( 1.66 \times 10^{-4} \) V s\(^{-1}\). The maximum cyclic stress, \( \sigma_{\text{max}} \), applied during the polarization curve measurement was 462 MPa and those used in the measurements of polarization resistance were in the range between 0 and 545 MPa. The stress ratio of cyclic load, \( R \), was 0.5 and the loading frequency, \( f \), was 0.1 Hz.

3. Experimental observations

Fig. 2 shows that the hydrogen charging and action of cyclic tensile stress (\( \sigma_{\text{max}} = 462 \) MPa) do not significantly affect the polarization behavior except to bring about a slight decrease in OCP. A similar phenomenon has been observed by Qiao et al. [23–25]. Fig. 3 shows that the polarization resistance is reduced by about 40% by continuous hydrogen charging, but is almost unaffected by the action of cyclic stress. Since the OCP under the present experimental conditions was below the oxidation potential of hydrogen, the decrease in the polarization resistance is attributed to the change in corrosion current densities of X60 steel, since the corrosion current density at the OCP is inversely proportional to the polarization resistance. Under the action of a cyclic load with \( \sigma_{\text{max}} \) up to 545 MPa, which is close to the ultimate tensile strength of steel, sufficiently large plastic deformation occurred so that the specimen broke after a few tens of stress cycles. The approximately parallel curves of \( R_p \) vs. \( \sigma_{\text{max}} \) in Fig. 3 for the hydrogen-charged and uncharged specimens indicated that the synergism of the dissolved hydrogen and applied stress was very limited in spite of the coexistence of the high hydrogen concentration, high level of tensile stress and heavy plastic deformation.

The polarization curves in Fig. 2 indicate that the hydrogen charge and applied stress can affect the OCP. To demonstrate the effect of dissolved hydrogen and applied stress on the anodic current density, the anodic current densities at the potential of 0.7 V\(_{\text{SCE}}\) under the four different conditions were determined from the polarization curves in Fig. 2 and the results are shown in Fig. 4. The impacts of dissolved hydrogen, applied stress, synergistic effect of applied stress and dissolved hydrogen are assessed using the anodic current ratios as defined by the following equations. The hydrogen factor is

\[
k_H = \frac{i_a(H)}{i_a}
\]
The stress factor is

$$k_s = \frac{i_a(\sigma)}{i_a}$$

and the synergistic factor is

$$k_s = \frac{i_a(\sigma, H)}{k_{\text{HS}}i_a}$$

where $i_a$, $i_a(H)$, $i_a(\sigma)$, and $i_a(\sigma, H)$ are the anodic current densities of the specimens with no hydrogen charging/no stress, hydrogen-charged, cyclically loaded, and hydrogen-charged/cyclically loaded, respectively. Although the dissolved hydrogen and applied stress increased the anodic current density slightly, as demonstrated in Fig. 4, their effects are very limited. Especially, the synergistic effect of applied stress and dissolved hydrogen, which can be evaluated quantitatively with the synergistic factor, $k_s$, is negligible.

### 4. Thermodynamic analysis

Normally, the strain rates involved in the SCC process of pipelines are very low. Hence, the SCC can be considered as a pseudo-static deformation process and so application of equilibrium thermodynamics is an acceptable approximation. Therefore, in the following thermodynamic analysis, we will follow the same procedures as those adopted by Qiao et al. [22] and Pound and coworkers [27]. All equations, except the ones with the references cited, are our contributions. Let us consider two specimens of pipeline steel with unit molar mass and unit surface area. At the initial condition, both are free of dissolved hydrogen. When one of them, denoted as Specimen #1, is exposed to the anaerobic electrolyte, the corrosion process given by Eq. (2) will occur and give rise to a change in the free energy $\Delta G_1$. Another specimen, #2, is hydrogen-charged and subjected to an applied stress $\sigma$ first, and then it is immersed into the same electrolyte. This leads to a free energy change $\Delta G_2$. The difference between the changes in free energy for the two specimens caused by reaction (1) is given by [22,27]

$$\Delta G(\sigma, H) = \Delta G_2 - \Delta G_1 = \Delta U - T\Delta S + P\Delta V$$

(5)

where $\Delta U$ is the difference in the internal energy, $T$ is temperature, $\Delta S$ is the entropy increment, $P$ is the pressure and $\Delta V$ is the volume change. Obviously, $\Delta U$, $\Delta S$ and $\Delta V$ are the functions of dissolved hydrogen concentration, $C_{\text{H}_2}$ in the test material (mol H mol$^{-1}$), and applied stress, $\sigma$. In Eq. (5), the volume expansion is defined to be negative and $P = -\sigma$, where $\sigma$ is the hydrostatic stress and equals $(\sigma_1 + \sigma_2 + \sigma_3)/3$, where $\sigma_1$, $\sigma_2$ and $\sigma_3$ are the principal stresses. According to Qiao et al. [22], the volume increment $\Delta V$ of the electrode that is charged and loaded can be divided into two parts, $\Delta V_\sigma$ and $\Delta V_{\text{H}}$, the volume changes of metal with unit molar mass due to the applied stresses and the ingress of hydrogen, respectively.

$$\Delta V = \Delta V_\sigma + \Delta V_{\text{H}}$$

(6)

In the thermodynamic analysis given by Qiao et al. [22], only the contribution of elastic deformation has been considered and it has been assumed that the contribution of elastic deformation to the Gibbs free energy of the system was $P\Delta V_\sigma = V_M\Sigma_{i=1}^3\sigma_i^2/E$, where $E$ is the Young’s modulus and the molar volume of electrode $V_M = M/\rho$, $M$ and $\rho$ are the molar mass and the density of the electrode material, respectively. However, in the cracking process, both elastic and plastic deformations should be involved. Moreover, the elastic strain energy $V_M\Sigma_{i=1}^3\sigma_i^2/E$ is not always equal to $P\Delta V_\sigma$ because it includes the work done by the applied stresses other than just the volume expansion. To take the effect of plastic deformation into account, in the present study, the volume change due to applied stress $\Delta V_{\sigma}$ is further divided to $\Delta V_{\sigma}$ and $\Delta V_p$, denoting the components produced by the elastic and plastic deformation, respectively.

$$\Delta V_\sigma = \Delta V_{\sigma} + \Delta V_p$$

(7)

$\Delta V_\sigma$ can be formulated with the generalized Hooke’s law:

$$\Delta V_\sigma = V_M \sum_{i=1}^3 \sigma_i e_i = \frac{3(1-2v)s_i V_M}{E} = -\frac{3M(1-2v)s_i}{E\rho}$$

(8)

where $e_i = (i = 1, 2, 3)$ are the principal strains, $v$ the Poisson’s ratio.

In a polycrystalline metal, the interaction of dislocations during their movement may give rise to an increase in densities of flaws, including vacancies and dislocations, even micro-voids. This may lead to volume expansion. Hirth did some computer modeling of dislocation cores and concluded that there may be a small increase in volume with the formation of a dislocation, but this increase will be very small. It is a good approximation to ignore the contribution due to increasing dislocation density on the volume expansion [28]. Microvoids are an important form of dam-
age induced by the plastic deformation and the development of micro-voids can lead to the volume expansion [29]. Lapovok [30] measured the density change of aluminum alloy 6061 during plastic deformation. He used the equal channel angular extrusion technique to produce extremely heavy plastic deformation and found that the maximum density (or volume) change of plastically deformed metal (\( \bar{\rho}_{\text{p,max}} \)) is about 0.1%. Although it is still difficult to formulate the exact relationship between the values of \( \Delta V_p \) and plastic strain \( e_p \), a linear relation is believed to be a good approximation [30]. Hence we have:

\[
\Delta V_p = -\frac{M e_p}{\rho e} \bar{V}_{\text{p,max}}
\]

where \( e_p \) is the fracture strain.

For a specimen free of applied stress, \( \Delta U \) and \( \Delta S \) are state functions of chemical compositions, so that dissolved hydrogen will give rise to changes in both internal energy and entropy, denoted here as \( \Delta U_{\text{H}} \) and \( \Delta S_{\text{H}} \). If plastic deformation is caused by an applied stress, an increase in densities of crystalline defects, such as vacancies and dislocations, will also lead to changes in internal energy and entropy, denoted as \( \Delta U_{\sigma} \) and \( \Delta S_{\sigma} \). For a plastic deformation process under isothermal conditions, the value of \( \Delta U_{\sigma} + \Delta S_{\sigma} \) is assumed, in the present study, to be equal to the plastic strain energy stored in the metallic electrode with unit molar volume:

\[
\Delta U_{\sigma} + \Delta S_{\sigma} = e_p V_M = e_p M / \rho
\]

where \( e_p \) is the density of stored plastic strain energy. Then we have

\[
\Delta U - T \Delta S = (\Delta U_{\text{H}} + \Delta U_{\sigma}) - T(\Delta S_{\text{H}} + \Delta S_{\sigma})
= (\Delta U_{\text{H}} - T \Delta S_{\text{H}}) - e_p V_M
\]

In line with the principles of thermodynamics and electrochemical theory, the ratio of the anodic dissolution current densities of the hydrogen-charged/stressed electrode and the uncharged/unstressed electrode under an active condition can be approximately expressed as:

\[
\frac{i_a(\sigma, H)}{i_a} = \exp \left[ \frac{- \Delta U - T \Delta S + P \Delta V}{RT} \right]
= \exp \left[ \frac{- \Delta U_{\text{H}} - T \Delta S_{\text{H}}}{RT} \right]
\times \frac{- \Delta U - T \Delta S + P \Delta V}{RT}
\times \frac{- \Delta U - T \Delta S + P \Delta V}{RT}
= k_h k_e k_s
\]

where \( \Delta U - T \Delta S + P \Delta V \) is the Gibbs free energy of system. According to Eqs. (2), (3), (4), and (13), we have the following expressions for these coefficients. The hydrogen factor is

\[
k_h = \frac{i_a(\sigma, H)}{i_a} = \exp \left[ \frac{\Delta U_{\text{H}} - T \Delta S_{\text{H}}}{RT} \right]
\]

Eq. (14) is the same as the one given by Qiao et al. [22]. The stress factor is

\[
k_e = \frac{i_a(\sigma)}{i_a} = \exp \left[ \frac{3M(1 - 2\nu)\sigma^2}{E \rho RT} + \frac{M \sigma_{\text{H}} e_p \bar{V}_{\text{p,max}}}{e_p \rho RT} + \frac{M e_p}{\rho RT} \right]
= k_e k_p
\]

where \( k_e \) and \( k_p \) are the elastic and plastic deformation factors, respectively:

\[
k_e = \exp \left[ \frac{3M(1 - 2\nu)\sigma^2}{E \rho RT} \right] = \exp (\chi \lambda \sigma_h^2)
\]

\[
k_p = \exp \left[ \frac{\frac{M e_p}{\rho RT} + \frac{M \sigma_{\text{H}} e_p \bar{V}_{\text{p,max}}}{e_p \rho RT}}{\eta \sigma_e} \right] = \exp (\chi \lambda_p \sigma_h)
\]

The dependence of stored plastic strain energy on the stress and plastic strain is described in the Appendix. Inserting Eq. (A3) into Eq. (17), we have

\[
k_p = \exp \left[ \frac{M \bar{V}_{\text{p,max}}}{\rho RT} \left( 1 + \frac{(1 + n)\sigma_{\text{H}} \bar{V}_{\text{p,max}}}{\eta \sigma_e} \right) \right] = \exp (\chi \lambda_p \sigma_h)
\]

For a dilute solid solution of hydrogen, \( \Delta V_{\text{H}} \) can be expressed as:

\[
\Delta V_{\text{H}} = -C_H \bar{V}_{\text{H}}
\]

where \( \bar{V}_{\text{H}} \) is the partial molar volume of hydrogen in the test material. In the thermodynamic analysis conducted by Qiao et al. [17,21,22,24], they simply defined \( \Delta V_{\text{H}} = \bar{V}_{\text{H}} \). However, \( \Delta V_{\text{H}} \) and \( \bar{V}_{\text{H}} \) have different physical meanings. The former is the volume expansion of the metal with unit molar mass induced by the dissolved hydrogen, while the latter is the volume expansion of metal resulting from dissolving one mole of hydrogen. Note that the latter should be produced by a metallic material with mass much more than one mole because of the limited solubility of hydrogen. \( \bar{V}_{\text{H}} \) for a metallic material is independent of the hydrogen concentration when \( C_H \) is below the solubility of hydrogen in that material. For example, the value of \( \bar{V}_{\text{H}} \) for pipeline steels is \( 2 \times 10^{-6} \text{ m}^3 (\text{mol H})^{-1} \) [31]. Based on assumption of \( \Delta V_{\text{H}} = \bar{V}_{\text{H}} \), the contribution of interaction of applied stresses and dissolved hydrogen to the Gibbs free energy of system would be \( P \bar{V}_{\text{H}} \), which is independent of hydrogen concentration. This would be contradictory to the prediction of hydrogen-facilitated anodic dissolution model [22]. Therefore, the synergistic factor is

\[
k_s = \frac{i_a(\sigma, H)}{k_h k_e k_s} = \exp \left[ \frac{- \Delta P \Delta V_{\text{H}}}{RT} \right] = \exp \left[ \frac{\sigma_C H \bar{V}_{\text{H}}}{RT} \right]
\]

(19)
In Eqs. (16) and (19), the normalized hydrostatic stress $\sigma_h = \sigma / \sigma_y$, where $\sigma_y$ is the yield strength. In Eq. (18), the normalized plastic strain energy density $\varepsilon_p = \varepsilon_p / \varepsilon_{p,\text{max}}$ ($\leq 1$), where $\varepsilon_{p,\text{max}}$ is the maximum density of stored plastic strain energy in the metal, which is dependent on the stress conditions. The non-dimensional factors in Eqs. (16), (18), and (19) are:

$$\lambda_e = \frac{3M(1-2\nu)\sigma_y^2}{E\rho RT}$$

(20)

$$\lambda_p = \frac{Me_{p,\text{max}}}{\rho RT} \left[1 + \frac{(1+n)\sigma_h}{\eta\sigma_f}P_{p,\text{max}}\right]$$

(21)

$$\lambda_s = \frac{\sigma_c C_H V_{H,\text{max}}}{RT}$$

(22)

5. Effects of hydrogen, deformations and synergism on active dissolution

5.1. Dissolved hydrogen

Pound et al. [27] examined the effects of interstitial hydrogen. They concluded that it would be about an order of magnitude greater than the effects of hydrostatic strain on the potential of a metal or substitutional solid solution and that interstitial hydrogen was probably responsible for most of the reported observations of an effect of stress on potential. However, they also concluded it would still be very small (0.015 to 0.0015 mV MPa$^{-1}$). In this paper, we assess the effect of dissolved hydrogen on the anodic dissolution kinetics based on our experimental observation. According to the test results shown in Fig. 4, $k_H \approx 1.2$. Qiao et al. [24] measured corrosion rates for X52 steel in anaerobic NS4 solution and found the hydrogen charge did not significantly affect the active dissolution rate. Hu et al. [25] reported the real anodic dissolution rates of a low carbon steel under both hydrogen-charged ($C_H \approx 20$ ppm) and uncharged conditions by measuring iron ion concentrations in test solutions using the inductively coupled plasma technique, and they found the ratio of real anodic dissolution rates under these two condition was close to unity. These results indicate that there was only a very limited effect of dissolved hydrogen on active dissolution of pipeline steel in near-neutral pH solutions.

5.2. Elastic deformation

For pipeline steels at room temperature, the yield strength is within the range 350–700 MPa, $M$ is 55.85 g mol$^{-1}$, $\rho$ is 7.87 g cm$^{-3}$, $\nu = 0.3$, $E = 207$ GPa, $R = 8.314$ J K$^{-1}$ mol$^{-1}$, $T = 295$ K, so $\lambda_e \approx 2.1 \times 10^{-3}$ to $8.2 \times 10^{-3}$ according to Eq. (20). Based these values and Eq. (16), the correlation between $\lambda_e$ and $\sigma_h$ was determined and the results are shown in Fig. 5. According to the elastic–plastic fracture mechanics theory [32–34], the maximum non-dimensional hydrostatic stress ahead of a crack tip $\sigma_h \approx 5$ for a strain-hardened material. Therefore, the maximum value of $k_e$ is about 1.1, in agreement of experimental observations [35–37]. Despic et al. [6] found that the active dissolution rate of iron in 0.05 M H$_2$SO$_4$ aqueous solution was not affected by applied stress in the elastic deform regime.

5.3. Plastic deformation

For pipeline steels, $n \approx 0.1–0.15$, $\sigma_f = 900–1500$ MPa, and $\varepsilon_f = 0.8–1.2$ [17,38]. As a first approximation, we can take $P_{p,\text{max}} = 0.1\%$ [30] and $\eta \approx 0.15$ [13]. Under the uniaxial loading condition $\sigma_h = \sigma / 3$. Substituting these values into Eqs. (21) and (A4), we obtain $\lambda_p \approx 0.28–0.68$. According to Eq. (18), the dependence of $k_p$ on $\sigma_h$ was determined and the result is shown in Fig. 6. Under the condition of $\sigma_p = 1$, a maximum value of $k_p$ of about 1.41 is obtained.

The second term in blank of Eq. (21) represents the contribution due to the volume expansion caused by the plastic deformation. The calculation indicates that, under the uniaxial loading conditions, the contribution of the volume expansion to the stored plastic strain energy is less than 4%. Therefore, it is a good approximation to ignore the contribution of the volume expansion induced by the plastic deformation:

$$\lambda_p \approx \frac{Me_{p,\text{max}}}{\rho RT}$$

(23)

During initiation of SCC in pipelines, the applied stress is normally well below the yield strength of the material and the value of $\varepsilon_p$ of un-notched specimens is very small; hence the impact of applied stress or the pseudo-static deformation on the active dissolution is very limited. However, if a crack is present, significant local plastic deformation will be produced in the plastic zone ahead of the crack tip, so that the contribution of plastic deformation to the anodic dissolution should be taken into account. In this situation, the plastic deformation behavior will be affected by the multiaxial condition ahead of the crack tip. Under the plain strain condition, the maximum local stress at the crack tip can be up to $1.05\sigma_f$ but the fracture ductility is
only about 1/3 of that under the uniaxial tensile conditions [38]. As a result, the values of \( k_p \approx 1.05 \) to 1.13 are obtained.

In the above analysis, the dislocations are assumed to be uniformly distributed in the microstructure. Actually, the dislocations produced during plastic deformation tend to form heterogeneous structures such as pile-ups, patches, walls and cells. The heterogeneous distribution of dislocation structures will affect the active dissolution process [6,11]. It is well known that the anodic dissolution rate is non-uniform in micro-scale under active condition [6]. According to the TEM observations reported by Sahal et al. [11], we can divide the test surface of deformed electrode into two different zones: zone 1 has a high dislocation density and zone 2 has a low dislocation density. If the area fraction of zone 1 is denoted as \( \lambda \), the total stored strain energy density due to the plastic deformation \( e_p \) will be

\[
e_p = \lambda e_{p1} + (1 - \lambda) e_{p2} \tag{24}
\]

where \( e_{p1} \) and \( e_{p2} \) are the average values of stored strain energy in zones 1 and 2, respectively. The average active current density is approximately given by

\[
I_a = i_{a1} \lambda + i_{a2} (1 - \lambda) \tag{25}
\]

\( i_{a1} \) and \( i_{a2} \) are the local anodic current densities of zones 1 and 2, respectively. Obviously, \( i_{a1} > i_{a2} \). It is reasonable to correlate the local stored plastic strain energy to the local dislocation density. Gutman pointed out that the local stored plastic strain energy is approximately proportional to the square root of local dislocation density [8,9]. The dislocation density in zone 1, normally, is several magnitude orders higher than that in zone 2 [11]. Hence, we can further assume that the plastic strain energy stored in zone 2 is negligible and the plastic strain energy is mainly stored in zone 1 with high dislocation density to simplify our analysis. In line with Eq. (24), we have

\[
e_{p1} \approx \frac{e_p}{\lambda} \tag{26}
\]

The anodic current density in zone 2 should be very close to the anodic current density of an electrode free of plastic deformation. Therefore, we can estimate the average value of the plastic deformation factor for a plastically deformed electrode with the heterogeneous dislocation structures \( k_p \) as follows:

\[
k_p \approx 1 + \lambda (k_{p1} - 1) \tag{27}
\]

According to Eqs. (23) and (26), the plastic deformation factor of zone 1 is approximately given by

\[
k_{p1} \approx \exp \left( 2 \frac{Me_{p,\text{max}} e_{p1}}{\rho RT} \right) = \exp \left( \frac{\lambda_p e_p}{A e_{p1}} \right) \tag{28}
\]

\( A \) can be regarded as a parameter characterizing the heterogeneity of dislocation structures. When \( e_{p1} = 1 \), \( k_p = k_{p,\text{max}} \). The relation between \( k_{p,\text{max}} \) and \( \lambda \) determined according to Eq. (28), is shown in Fig. 7. It can be seen that the effect of plastic deformation on the active dissolution may be enhanced with increasing heterogeneity of dislocation structures. This prediction is in agreement with the experimental observations [5,6,11,39].

5.4. Synergistic effect of dissolved hydrogen and external stress field

The value of \( k_s \) can be estimated as follows. \( T_H \) is \( 2 \times 10^{-6} \) m\(^3\) (mol H\(^{-1}\)) for pipeline steels [31]. When a crack is present, hydrogen dissolved in steel will enrich at the crack tip under the action of local stress field ahead the crack tip. However, the maximum dissolved hydrogen concentration is limited by the solubility of hydrogen in the test materials. The dissolved hydrogen concentrates at crystalline defects, such as grain boundaries, when the hydrogen concentration exceeds the solubility. Assuming that the maximum hydrogen concentration at the crack tip is \( 1 \times 10^{-2} \) mol H mol\(^{-1}\) [40], a \( \lambda_s \) value in the range \( 2.9 \times 10^{-3} \) to \( 5.7 \times 10^{-3} \) is obtained according to Eq. (22). Based on Eq. (19), the dependence of \( k_s \) on \( \sigma_b \)
was determined and the result is shown in Fig. 8. The maximum value of $k_s$ is less than 1.02 when $\sigma_h = 5$, as shown in Fig. 8. The above analysis is based on the assumption that the dissolved hydrogen atoms are uniformly distributed in the crystal. Actually, a part of dissolved hydrogen is trapped in crystalline defects, such as dislocation lines and grain or subgrain boundaries. This will further reduce the interaction between the dissolved hydrogen atoms and external stress field on macro-scale. It is clear that the synergistic effect of dissolved hydrogen and external stress field on active dissolution is negligible. This prediction is in agreement with the test results shown in Figs. 2–4.

6. Implication for near-neutral pH SCC of pipeline steels

At a crack tip, the local stress level is very high and hydrogen is enriched under the action of a local stress field. To simplify our analysis, we assumed that hydrogen charging did not change the mechanical conditions of the crack tip. We can consider the crack side as a sample which is plastically deformed but unstressed, and the crack tip as another sample which is hydrogen-charged, plastically deformed and stressed. Then, the maximum ratio of anodic dissolution rates for these two samples is $k_{\text{tip}}k_{\text{side}} \approx 1.2 \times 1.1 \times 1.02 \approx 1.35$. If the hydrogen-facilitated anodic dissolution is the dominant mechanism for the SCC process, such a small difference in the anodic dissolution rates of the tip and wall of a crack cannot maintain crack propagation. Transmission electron microscope (TEM) in situ observations [41,42] indicated that, in certain situations, the crack tip during SCC remained sharp after dislocations were emitted from the crack tip where a dislocation-free zone (DFZ) formed. Selected area diffraction of the DFZ showed that the elastic strain in the DFZ ahead of the crack tip was about 0.1, indicating that the DFZ was a highly stressed region and the local stress had values up to the theoretical fracture stress of the material (0.1E).

Under this extreme condition, $\sigma_h \approx 0.1E/3 \approx 7000$ MPa because at the crack tip $\sigma_1 >> \sigma_2 > \sigma_3$. Substituting this $\sigma_h$ value into Eq. (19), we have $k_s = 1.03$ ($C_H = 0.01 \text{ mol H} \text{ mol}^{-1}$). Note that the elastic deformation dominated in this case, so that $k_s = 1.5$ was obtained. Under this extreme situation, the maximum ratio of anodic dissolution rates for the crack tip and crack wall was still less than 2. This value was not large enough to prevent the crack from losing its sharpness when the crack propagation was controlled by anodic dissolution at the crack tip. Because of the substantial lateral dissolution on the crack side walls, the crack tip became blunted. This reduced the stress concentration at the crack tip and, in turn, slowed down the anodic dissolution at the crack tip. Eventually, it is probable that propagation of the blunt crack would have stopped. The synergistic impact of dissolved hydrogen and applied stress was expected to be even less marked during crack initiation, because both lower hydrogen concentrations and lower levels of local stresses were involved.

Notably, the experimental evidence showing the hydrogen-facilitated anodic dissolution in stainless steels was obtained under transpassive conditions [16]. In this case, Eq. (13) was no longer suitable for use in formulating anodic dissolution kinetics. This phenomenon may be related to the hydrogen-induced passivity degradation [43,44]. The experimental results showed clearly that the hydrogen-loaded passive films were more defective and less protective, leading to a high passive current density and low resistances to the breakdown [43–45], especially when tensile stress coexisted [45]. However, the impact of hydrogen and applied stress on the active dissolution of carbon steels in near-neutral solutions was very limited [23–25]. Therefore, anodic dissolution must have affected the SCC of pipeline steel in near-neutral pH groundwater via some other mechanisms.

7. Conclusions

The following conclusions are drawn based on the thermodynamic analysis and experimental investigations.

(1) There is only very limited effect of dissolved hydrogen, elastic and plastic deformation on active dissolution of pipeline steel in near-neutral pH groundwater.

(2) The synergistic effect due to the interaction of dissolved hydrogen and local stress field on the active dissolution is negligible. This suggests that the near-neutral pH SCC is unlikely to be controlled by the hydrogen-facilitated anodic dissolution mechanism.

(3) The increment of free energy due to elastic and plastic deformation is not sufficient to alter the active dissolution kinetics substantially.

(4) The effect of plastic deformation on the active dissolution depends heavily on the corrosion mechanism and heterogeneity of dislocation structures.
Acknowledgements

This project was supported by a Strategic Project Grant of the Natural Sciences and Engineering Research Council of Canada, Syncrude Canada Ltd, Dow, IPSCO and NOVA.

Appendix A. Appendix: stored plastic deformation energy

To simplify our analysis, we first consider the plastic deformation process of an un-notched specimen under the action of uniaxial tensile stress at room temperature. Suppose the plastic deformation behavior obeys Hollomon’s law:

\[ \sigma = K \varepsilon_p^n \]  

(A1)

where \( \varepsilon_p \) is plastic strain, and \( K \) and \( n \) are the coefficient and exponent of strain-hardening, respectively. The plastic work done by the applied stress \( \sigma \) on the unit volume is

\[ w_p = \int_0^{\varepsilon_p} \sigma d\varepsilon_p = \int_0^{\varepsilon_p} K \varepsilon_p^n d\varepsilon_p = \frac{\sigma \varepsilon_p}{1+n} \]  

(A2)

It is known that only a small part of the plastic work can be stored in the deformed metal and the rest will be dissipated to the environment during the deformation processes [13]. So,

\[ \varepsilon_p = \eta w_p = \eta \frac{\sigma \varepsilon_p}{1+n} \]  

(A3)

where \( \eta (1<1) \) represents the fraction of plastic work stored in the deformed metal and its exact value depends on materials and loading procedure [13,15]. The fracture or cracking will happen when the local strain reaches the fracture ductility of the material \( \varepsilon_f (\varepsilon_f = -\ln(1-R/A)) \), where \( R/A \) is the reduction in area). Meanwhile, the local maximum stress will be \( \sigma_f = K \varepsilon_f^n \), the true fracture stress \( \sigma_f \) \( (\sigma_f \approx \sigma_u(1+R/A), \) where \( \sigma_u \) is the ultimate tensile strength) [38]. So, the maximum value of the stored plastic deformation energy in metal will be

\[ \varepsilon_{p,max} = \eta w_{p,max} = \eta \frac{\sigma_f \varepsilon_f}{1+n} \]  

(A4)

References
