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Quantitative characterization by micro-electrochemical measurements of the synergism of hydrogen, stress and dissolution on near-neutral pH stress corrosion cracking of pipelines

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ABSTRACT

Occurrence of stress corrosion cracking of pipelines under a near-neutral pH condition depends on the synergism of stress, hydrogen and anodic dissolution at the crack tip of the steel. In this work, micro-electrochemical techniques, including localized electrochemical impedance spectroscopy and scanning vibrating electrode technique, were used to characterize quantitatively the synergistic effects of hydrogen and stress on local dissolution at crack-tip of a X70 pipeline steel in a near-neutral pH solution. Results demonstrate that, upon hydrogen-charging, the anodic dissolution of the steel is enhanced. The resistance of the deposited corrosion product layer depends on the charging current density. There is a non-uniform dissolution rate on the cracked steel specimen, with a highest dissolution current density measured at crack-tip. For a smooth steel specimen, the synergistic effect factor of hydrogen and stress is equal to 5.4, and the total effect of hydrogen and stress on anodic dissolution of the steel is 7.7. In the presence of a crack, the hydrogen effect factor, stress effect factor and the synergistic effect factor are approximately 4.3, 1.3 and 4.0, respectively. The total effect factor is up to 22.4, which is very close to the 20 times of difference of crack growth rate in pipelines in the presence and absence of the hydrogen involvement recorded in the field.

1. Introduction

There have been a significant number of experimental evidences demonstrating that hydrogen plays an important role in near-neutral pH stress corrosion cracking (SCC) of pipelines [1–10]. For example, Parkins [2] proposed that hydrogen is involved in stress corrosion crack initiation and growth under a near-neutral pH condition, accompanying anodic dissolution on crack wall and at the crack tip. Furthermore, Parkins et al. [7] reported that both dissolution and the ingress of hydrogen into the steel are involved in the crack propagation, and hydrogen facilitates crack growth by promoting reduced ductility. Gu et al. [11] used slow strain rate tests (SSRT) and secondary ion mass spectrometry (SIMS) to find that hydrogen diffused into the steels around the crack tip during the SCC process, and suggested that a local acidification was generated during anodic dissolution. The previous works performed by the authors' group [12–15] also found that the electrolytes extracted from soils with previous SCC history were always associated with the high hydrogen permeation current and sub-surface hydrogen concentration. Furthermore, the near-neutral pH environment is capable of generating a catalytic surface effect on hydrogen evolution.

The synergism of hydrogen and stress on the anodic dissolution of steel at crack-tip during SCC was proposed by Mao and Li [16]. Cheng [17] modified the relevant electrochemical reactions and thermodynamics, and proposed that the rate of crack growth in the hydrogen-charged, stressed steel depends on the determination of the effect of hydrogen on anodic dissolution in the absence of stress, the effect of stress on anodic dissolution in the absence of hydrogen, and the synergistic effect of hydrogen and stress on the anodic dissolution rate at the crack tip.

In this work, micro-electrochemical techniques, including scanning vibrating electrode technique (SVET) and localized electrochemical impedance spectroscopy (LEIS), were used to investigate and quantify the synergism of hydrogen and stress on local anodic dissolution at crack-tip of a X70 pipeline steel in a near-neutral pH solution, where both smooth and pre-cracked steel specimens were used. The effects of hydrogen-charging and stressing on local dissolution current density were determined, and the crack growth rate was predicted accurately.

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2. Experimental

Test specimens made of a sheet of X70 pipeline steel were identical to those used in the previous work [18]. The specimen preparation and treatment was also reported [18].

The test solution was a NS4 solution, containing 0.483 g/l $NaHCO_3$, 0.122 g/l KCl, 0.181 g/l $CaCl_2{\cdot}2H_2O$ and 0.131 g/l $MgSO_4{\cdot}7H_2O$. Prior to test, the solution was purged with 5% CO_2 balanced with N_2 gas for 1 h to achieve an anaerobic, near-neutral pH condition with a pH value of 6.8. The gas flow was maintained throughout the test.

All the tests were performed at ambient temperature (~22 °C).

The experimental apparatus, containing a PAR Model 370 scanning electrochemical workstation and a compressed spring force loader, as shown in Fig. 1. The tensile stress applied on the specimen was calculated based on the spring constant and the length change of the spring.

For micro-electrochemical measurements, the X-70 steel specimen was used as the working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum wire as an auxiliary electrode. The LEIS scanning microprobe was operated in two modes. The first mode was used for point-to-point local impedance measurements. The platinum microprobe with a 10 μm tip was set directly above the specimen, to measure the impedance responses at individual points. The distance between the probe tip and the specimen surface was 100 μm. During LEIS measurements, an AC disturbance signal of 20 mV was applied on the electrode. The measuring frequency ranged from 1,00,000 to 0.5 Hz. The point-to-point LEIS measurements were carried on the tensile specimen stressed at 525 MPa with various hydrogen charging current densities. The LEIS measurements were also performed on a pre-cracked specimen that was under a tensile force of 3000 N in NS4 solution with various hydrogen charging current densities.

The second mode of LEIS measurement was by local impedance mapping, where the microprobe was stepped over a designated area of the specimen. The scanning took the form of a raster in the *x*–*y* plane. The impedance distribution at a certain frequency within the scanning area was determined. All the LEIS measurements were conducted at corrosion potential.

The SVET measurements were conducted, with a 10 μm platinum tip microelectrode vibrating 100 μm above the specimen surface at an amplitude of 30 μm. In particular, the SVET measurement on the pre-cracked specimen shown in Fig. 2 were conducted within the lined area, and the LEIS was measured at four locations i.e., point A (800, 800 μm), point B (800, 1200 μm), point C (800, 1600 μm) and point D (0, 400 μm), as shown in Fig. 2.

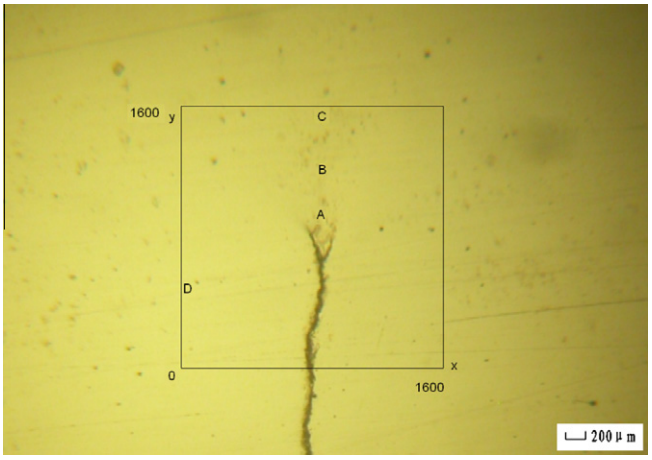

Fig. 2. Area for micro-electrode scanning on pre-cracked specimen.

3. Results

3.1. LEIS measurements on smooth specimen under various hydrogen-charging current densities

Fig. 3 shows the LEIS plots measured on the smooth steel specimen stressed at 525 MPa, which is close to yielding strength of the steel [18], under various hydrogen-charging current densities for 2 h. It is seen that there was a similar feature for the measured plots, i.e., two semicircles over the whole frequency range. Furthermore, the LEIS plots measured at uncharged and 0.1 mA/cm^2 charging current density were almost identical. With the charging current density increasing to 1 and 5 mA/cm^2, the size of both semicircles decreased. With the further increase of charging current density to 10 and 20 mA/cm^2, there were a significant increase and decrease of the sizes of high-frequency and low-frequency semicircles, respectively.

3.2. LEIS mapping on smooth specimen upon hydrogen-charging

Fig. 4 shows the LEIS map measured on the smooth specimen stressed at 525 MPa under a charging current density of 1 mA/cm^2 at 2 Hz, where both the impedance value and its contour are showed in the *x*–*y*–*z* three dimensional diagram. It is seen that there was an approximately uniform distribution of the impedance value (~750 Ω) on the specimen.

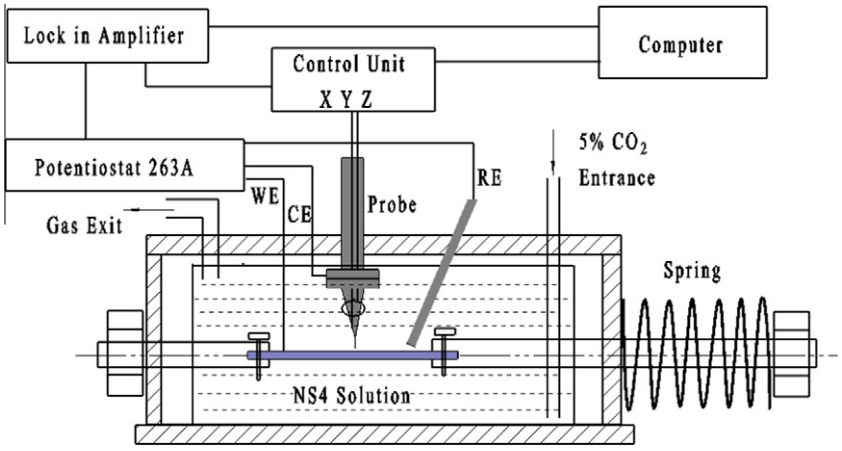

Fig. 1. Schematic diagram of the experimental set-up for micro-electrochemical measurements, where the reference electrode (RE) is a saturated calomel electrode (SCE), working electrode (WE) is X70 steel specimen and counter electrode (CE) is a platinum wire.