CAAP Annual Report

Date of Report: January, 2016

Contract Number: DTPH5614HCAP03

Prepared for: Government Agency: DOT

Project Title: Experimental Characterization and Monitoring of Early Stage Corrosion Degradation of Pipeline Steels

Prepared by: Iowa State University

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For quarterly period ending: December 31, 2015

Business and Activity Section

(a) Generated Commitments - None to report

(b) Status Update of Past Quarter Activities - The main objective of the proposed work is to enhance the pipeline safety through understanding the early corrosion mechanisms in high strength pipeline steels that lead to stress corrosion cracking with a focus on measurable degradation parameters that can guide the development of advanced NDE measurement procedures.

The focus of the fifth quarter was on establishing the residual stress build up during the corrosion process through monitoring the substrate curvature. All experimental testing will be conducted at the voltage peak where in the material is very susceptible to SCC. The main objective of the current effort is to arrive at physical understanding of the early SCC and how cracks are initiated. Within the experimental observation window, we have identified the following major aspect for the early stage of SCC:

1. The near surface layer experience compressive residual stress in nature.
2. A rapid rise in the residual compressive stress was observed, until a peak in the electrochemical cell current is reached. Then a modest rise in the residual stress compressive stress build up is reached.

3. The thickness of the formed oxide layer slow the continued progression of the SCC process.

b.1. Electrochemical Conditions:

All corrosion experiments were continued on X70 steel samples. The surface were ground with 600 and 1000 grit emery papers, followed by cleaning with deionized water and ethanol. A one molar bicarbonate solution (1M $NaHCO_3$) is utilized, representing high pH (>9) range for IGSCC. The peak potential of -0.521V on the voltage-current polarization curve is utilized of maximum SCC.

Prior to the experiments, the working electrode was cathodically polarized at -1 V (SCE) for 5 min to remove any oxides formed on the surface.

b.2. In Situ Measurement of Residual Stress Development During the Corrosion Process

Stress development during exposure of steel specimens to corrosion conditions that result in transgranular stress-corrosion cracking is being experimentally characterized. It has been speculated that anodic dissolution of the phase at the grain boundary is the crack mechanism of the IGSCC [1]. Additionally, solutions having a high pH caused the dissolution of grain boundaries when the stress is present [2]. The process is further exacerbated with applied cyclic stress as it would fracture the oxide film and further promote the IGSCC process [3]. Motivated by these mechanisms, we focused our attention on measurements of the residual stresses generated by the initial stage of the SCC process in the high pH solution. The present experiments employ a new technique, phase-shifting curvature interferometry, with significantly higher curvature resolution than cantilever defection methods typically used for electrochemical stress monitoring [4, 5].

Stress Measurement Principle was defined as the curvature changes in pipeline steel during exposure to a corrosive environment to measure stress and identify initial damage mechanism by using Stoney's equation for substrate curvature [6].

$$F = \left(\langle \sigma_{react} \rangle\right) h_{react} = \frac{E_s h_s^2}{6(1-\nu)} \Delta k$$

Where F is the in-plane force per unit width in the film, E_s Young's modulus of the substrate, h_s is the substrate thickness, ν is the Poisson's ratio, and k is substrate curvature. The enhanced curvature resolution of the utilized setup (shown in Fig.1) permits stress measurements in relatively thick sheet and foil samples, in contrast to thin metal films typically used for deflection techniques.

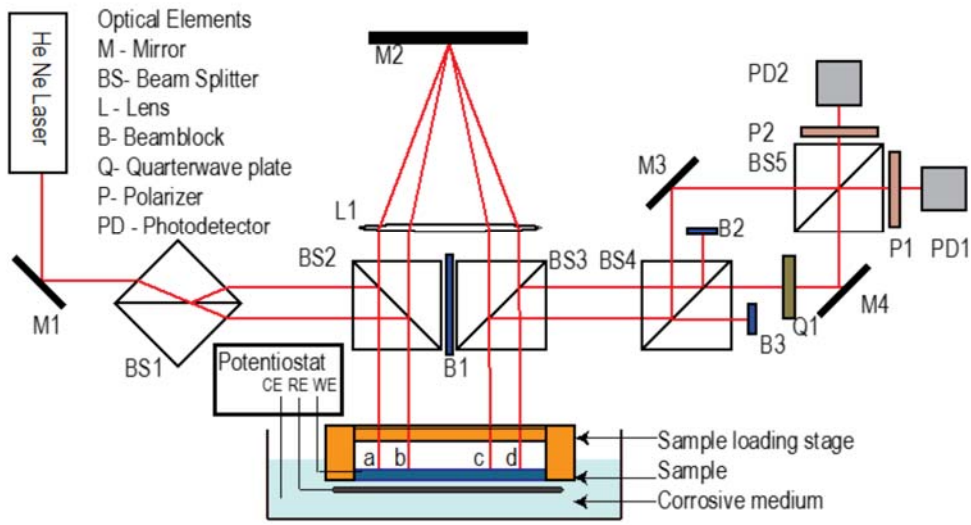

Figure 1: Schematic of the setup of interferometry system, which also shows the setup of the samples.

Specimens of X70 steels with dimensions of 30 mm length X 12 mm width and 0.6 mm thickness were cut from a pipeline specimen. The front surface of the sample is ground to remove machining grooves and to obtain a uniform surface roughness. The back surface of the specimens was mirror-polished to enable curvature measurements. The specimens were mounted in the electrochemical cells shown schematically in Figure 1 such that front surface is exposed to corrosion while the back surface is utilized for monitoring the stress development using phase-shifting curvature interferometry. Figure 2 shows atypical time evolution the dissolution current and the accompanied residual compressive stress builds up. During the initial short cathodic polarization to remove any native oxide, a small residual tensile stress builds up can be observed. Upon commencement of the anodic dissolution, the dissolution current reaches a peak level then starts to gradually drop. Consecutively, a sharp rise in the compressive stress builds up is observed. At the onset of the peak dissolution current, the compressive stress builds up continue at very modest rate, nearing a stationary level.

From the repeated stress measurements at different time intervals of 30, 60, 120 min, it can be concluded that upon the start of the process a strong anodic dissolution takes place, forming an oxide film over the surface. As such oxide layer thickened, the oxygen transport is imbedded and the anodic dissolution process is slowed down. Such progression of the oxide layer further impede the electrochemical dissolution process, leading to a decay of the dissolution current as well as stabilization of the compressive residual stress level.

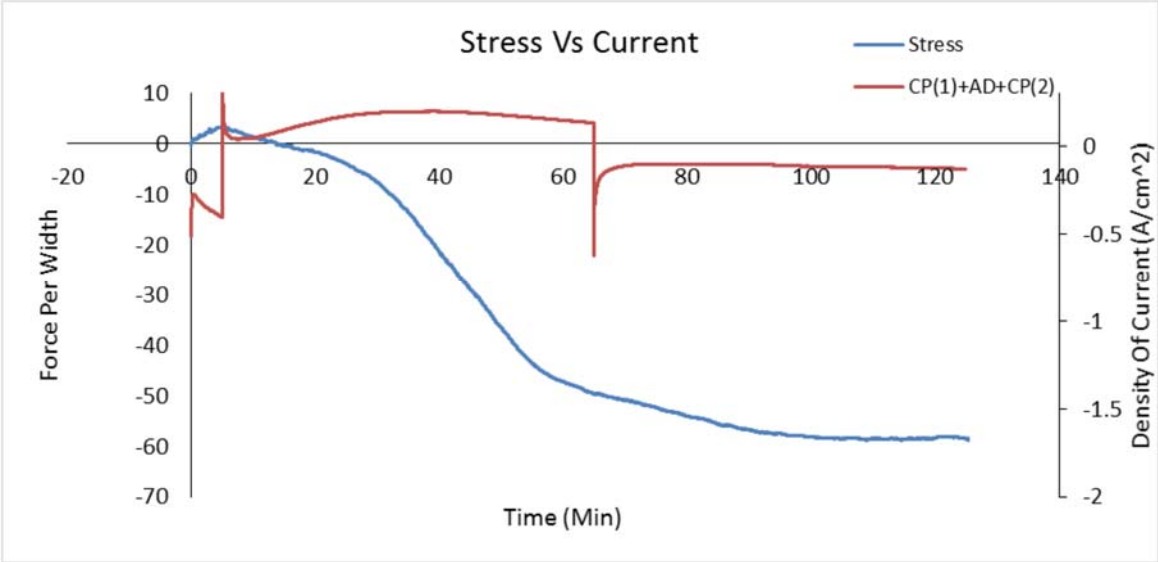

Figure 2: Measured residual stress builds up (N/m) and dissolution current density (A/cm^2) during the electrochemical process. A small tensile stress build up is observed during the initial cathodic polarization, then a strong residual compressive stress builds up during anodic dissolution.

b.3. Progress in Applying Tensile Stress During Residual Stress Measurements.

The key issue here is to understand the interplay between the tthickneing of the oxide film and the continued progression of the SCC process. We developed a loading device, shown in Figure 3, that would allow to fix-in an initail curvature of the tested sample, before being introduced to the electrochemical cell. Such fixture would allow to dial-in the level of intial tensile stress within the sample and how it would affect the SCC process kinetics.

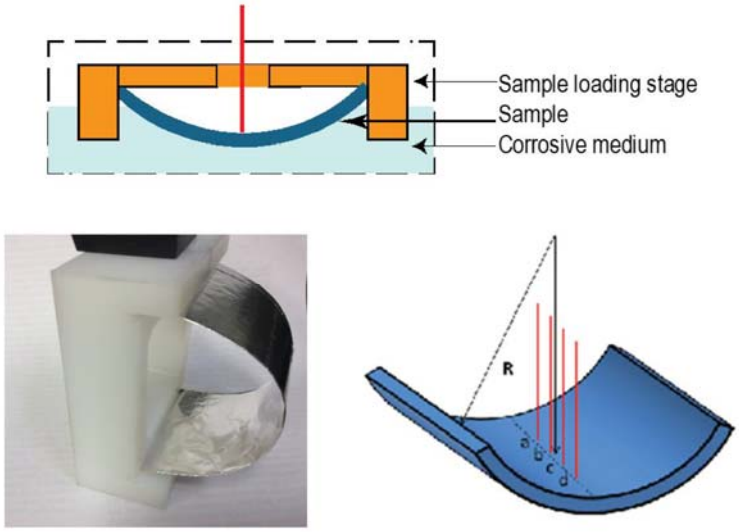

Figure 3: Schematic of the Lock-in applied stress fixture, to be used during residual stress measurement for SCC.

(c) Description of any Problems/Challenges – There are no major challenges, but rather issues to understand its role:

1. If the corrosion product play such an important role in controlling the progression of SCC; does that imply we have to change our testing protocol to further progress the SCC process? We will gain further understanding from the repeated testing under applied tensile stress level.
2. The addition of external tensile load proved to be slightly difficulty. Additional level of progressive sealing of the electrochemical chamber are needed with the curved sample. We are developing compliant seal that would not hinder the progressive curvature of the specimen during the electrochemical process and bias the measurements.

(d) Planned Activities for the Next Quarter - The main focus of the next phase of work will be on

1. Full cross sectional analysis of the oxide/substrate interface to identify the topological evolution of the corrosion process.
2. Detailed nano-indentation measurements of the near surface layer mechanical properties as it evolve during the electrochemical dissolution process.

(e) References Cited

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3. Parkins, R., E. Belhimer, and W. Blanchard Jr, *Stress corrosion cracking characteristics of a range of pipeline steels in carbonate-bicarbonate solution.* Corrosion, 1993. 49(12): p. 951-966.

4. Wang J., Shrotriya P., Kim K.S., *Surface residual stress measurement using curvature interferometry*, Exp Mech, 46, 39-46 (2006).

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6. Stoney, G.G., *The tension of metallic films deposited by electrolysis.* Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 1909. 82(553): p. 172-175.