CAAP Quarterly Report

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

Prepared by: Iowa State University

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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.

An experimental protocol will be developed to characterize the residual stress buildup using in situ substrate curvature measurements. The accompanying material property changes (modulus and flow stress) of the near surface layer will be probed by nano-indentation and nano-scratch experiment. A 4-point AC/DC probe will be also incorporated to measure the changes in electrical resistance of near surface layer as a function of the corrosion environment and history to enable further development of NDE corrosion detection techniques.

The focus of this quarter was on Electrochemical Experiments, surface topological evolution and testing of the mechanical properties of the near surface layer after corrosion.

1. Electrochemical Experiments:
Corrosion of steel occurs via electrochemical reactions. Electrochemical experiments were done to mimic and accelerate the environmentally occurring corrosion processes in pipeline steel, to gain insight into the behavior of steel under different system variables. A schematic drawing of the electrochemical cell is shown in Fig. 1. Potential vs. current curves, also called polarization curves, were generated to identify the susceptibility potential range for the steel. Figure 2 shows the potential vs. current density in Carbonate-Bicarbonate Chloride Solution on X-70 steel sample. We identified the condition of the highest corrosion susceptibility. At such identified applied potential, constant voltage

corrosion experiments were carried out for different set time to understand the evolution of the oxide layer. Figure 3 shows the recorded current vs. time curves for these experiments.

We have arrived at the following preliminary results from the electrochemical experiments:

(a) Bicarbonate Solution:

- Maximum current density of polarization curves was in the range -0.5V to -0.4V and zero current in the range -0.75 to -0.7V, both in agreement with literature. The polarization curves were reproducible with the same set of conditions. The maximum current density identifies the potential range of susceptibility to transgranular SCC.
- Crevice corrosion is eliminated by applying sealant. No pitting is observed. Uniform corrosion in the exposed area produces a uniform coverage of iron oxide/carbonate particles. After long exposures, the particles form a dense compacted layer.
- Uniform corrosion is favorable for near surface mechanical testing by nano-indentation measurements.

(b) Carbonate-Bicarbonate-Cloride Solution:

- Maximum current density of polarization curves was in the range -0.6V to -0.5V and zero current in the range -0.8 to -0.75V, both in agreement with literature. The polarization curve was reproducible with the same set of experimental conditions.

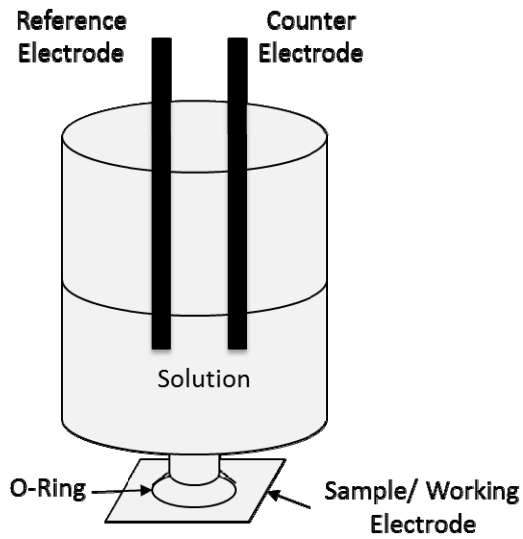

Fig 1. Schematic drawing of the Electrochemical cell used in the corrosion experiments. Gamry Reference 3000 potentiostat/galvanostat was used as the power source.

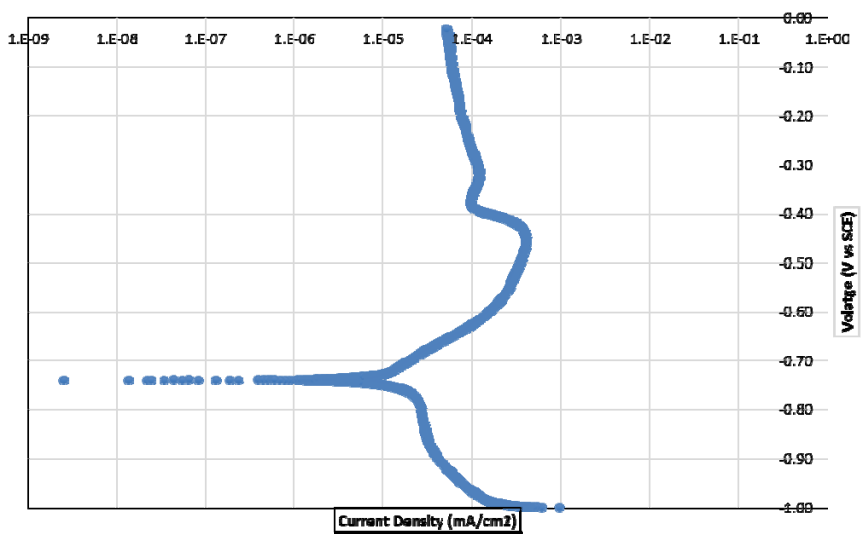

Fig. 2. Polarization Experiment in Bicarbonate Solution (1M $NaHCO_3$). A scan rate of 0.1 mV/sec. Sealant applied beneath the o-ring.

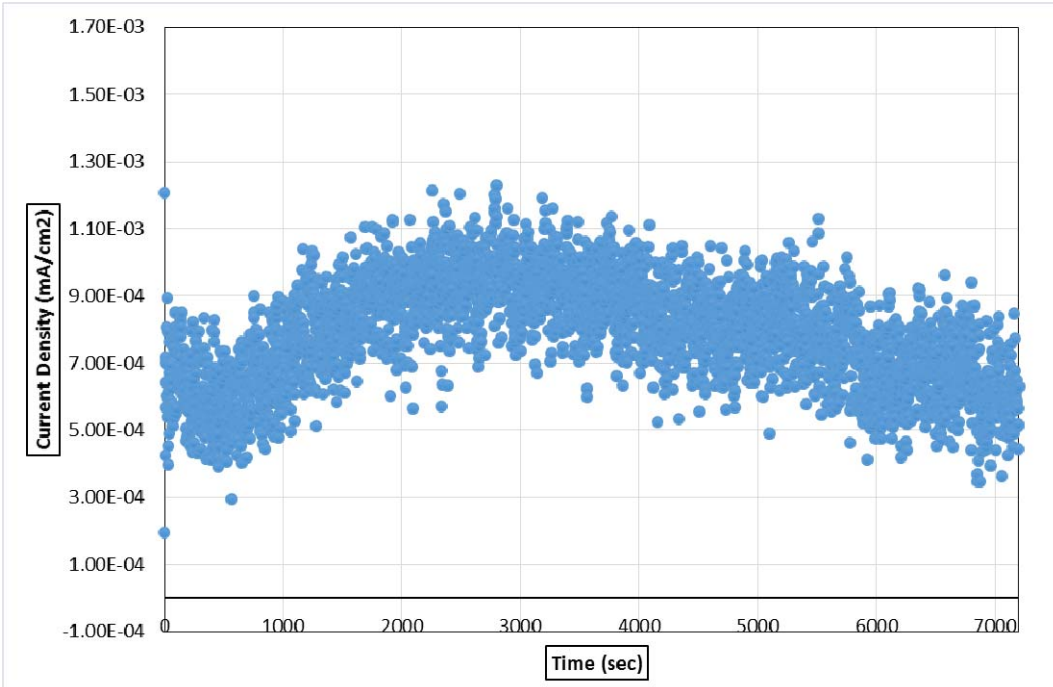

Fig. 3. Constant Potential Experiment in Bicarbonate Solution (1M $NaHCO_3$). Current density vs. time for the constant potential of -0.5V (vs. SCE) for 2 hours. Sealant applied beneath the o-ring. The potential is at the maximum current density of polarization curve, corresponding to the condition of highest TGSCC susceptibility.

2. Surface Topological Evolution:

The topological evolution of the corroded surface was examined by a non-contact optical interferometer after each electrochemical experiment. Figure 4 and 5 show the topological evolution of the corroded surface, after a polarization experiment in bicarbonate Solution (1M $NaHCO_3$). The corrosion product were deposited on the surface. Since the iron oxide is porous, it has a higher volumetric expansion compared to the unexposed surface. Figure 6 and 7 shows the corrosion deposits formation under constant applied potential for 30 min and 120 min. As the exposure time increase a denser multilayer of what could be identified as scallops could be observed.

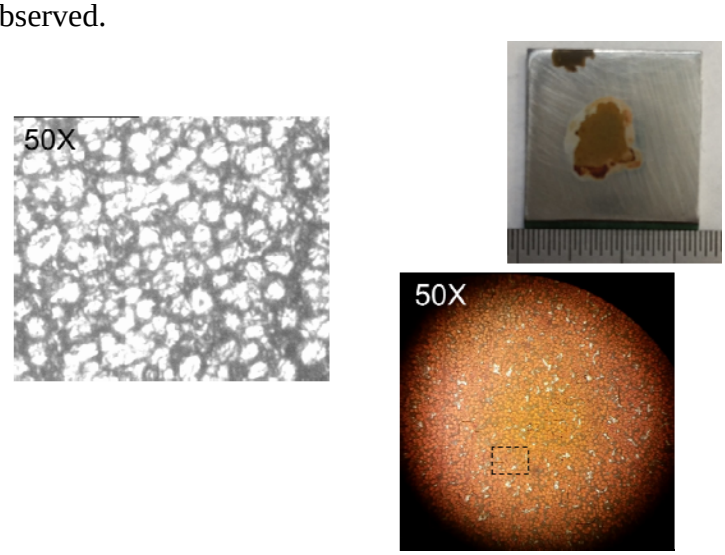

Fig 4. Optical images of the X70 steel after Polarization Experiment in Bicarbonate Solution (1M $NaHCO_3$). The corrosion products were deposited on the corrosion regions in what could be identified as scallops (X70-sample-061115-1).

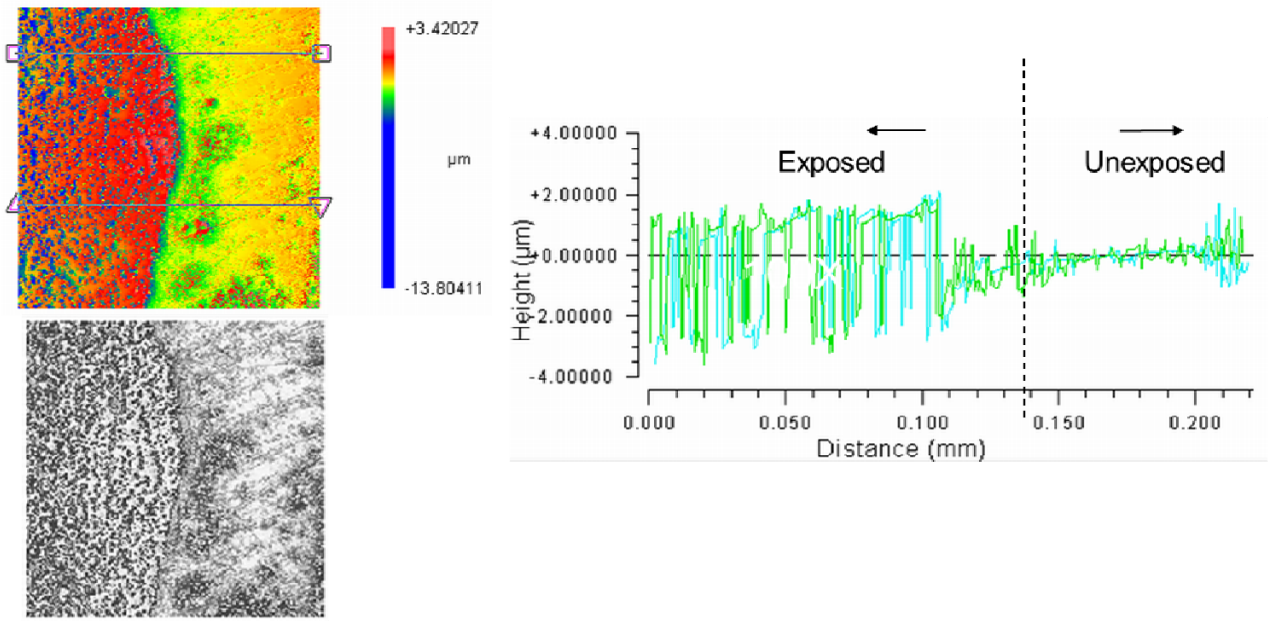

Fig. 5. Surface topological evaluation for sample of Fig. 3, examined by non-contact optical interferometry showing the corrosion product scale and periodicity (X70-sample-061115-1).

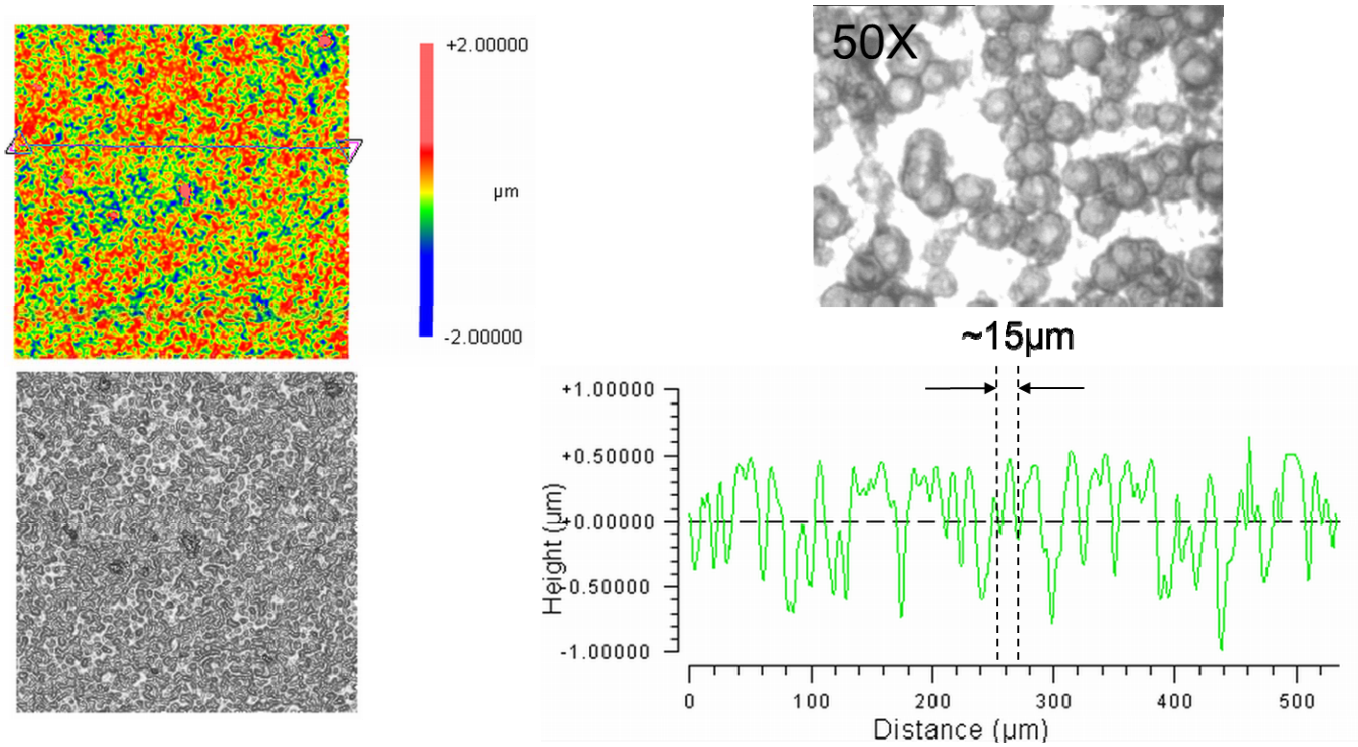

Fig. 6. Surface topological evaluation for a constant potential electrochemical experiment for 30 min, showing partial coverage of the corrosion products, (X70-sample-061515-2).

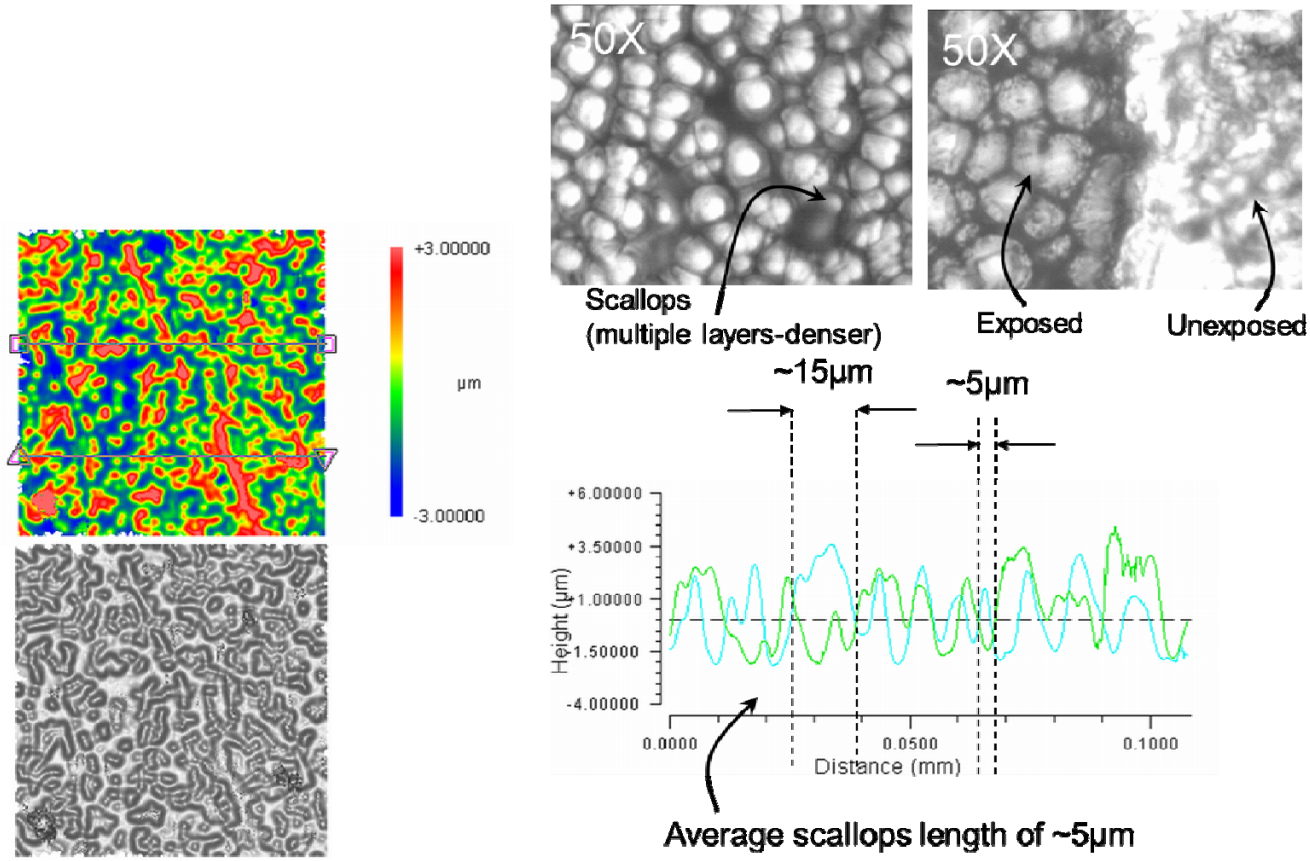

Fig. 7. Surface topological evaluation for a constant potential electrochemical experiment for 120 min, showing multiple layer of the corrosion products coverage, (X70-sample-061515-1).

3. Near Surface Mechanical Property Assessment:

The reference and electrochemically corroded X70 samples were tested by nano-indentaion to establish variance of its subsurface mechanical properties and the depth extent of such variance. All measurement were carried out in the dynamic nano-indentation mode to allow depth profiling of the measured properties. Nano-DMA mode on a Hysitron TI-950 Tribo Indentor was utilized with a Berkovich nano-indentation pyramidal tip. Figure 8 shows a representative continuous hardness measurements on the reference (no corrosion) and corroded (X70-Sample-051415-1) samples as a function of indentation depth. Corresponding indentation imprint patterns are also presented. Here, corroded sample exhibits lower hardness; at least two times lower than the reference value and extend to a depth of about 150 nm. After 150 nm indentation depth, both samples show the same H.

These measurements would enable the development of nondestructive evaluation protocols that might explore the depth and the level of mechanical property degradation to assess the extent of the initial state of stress corrosion cracking.

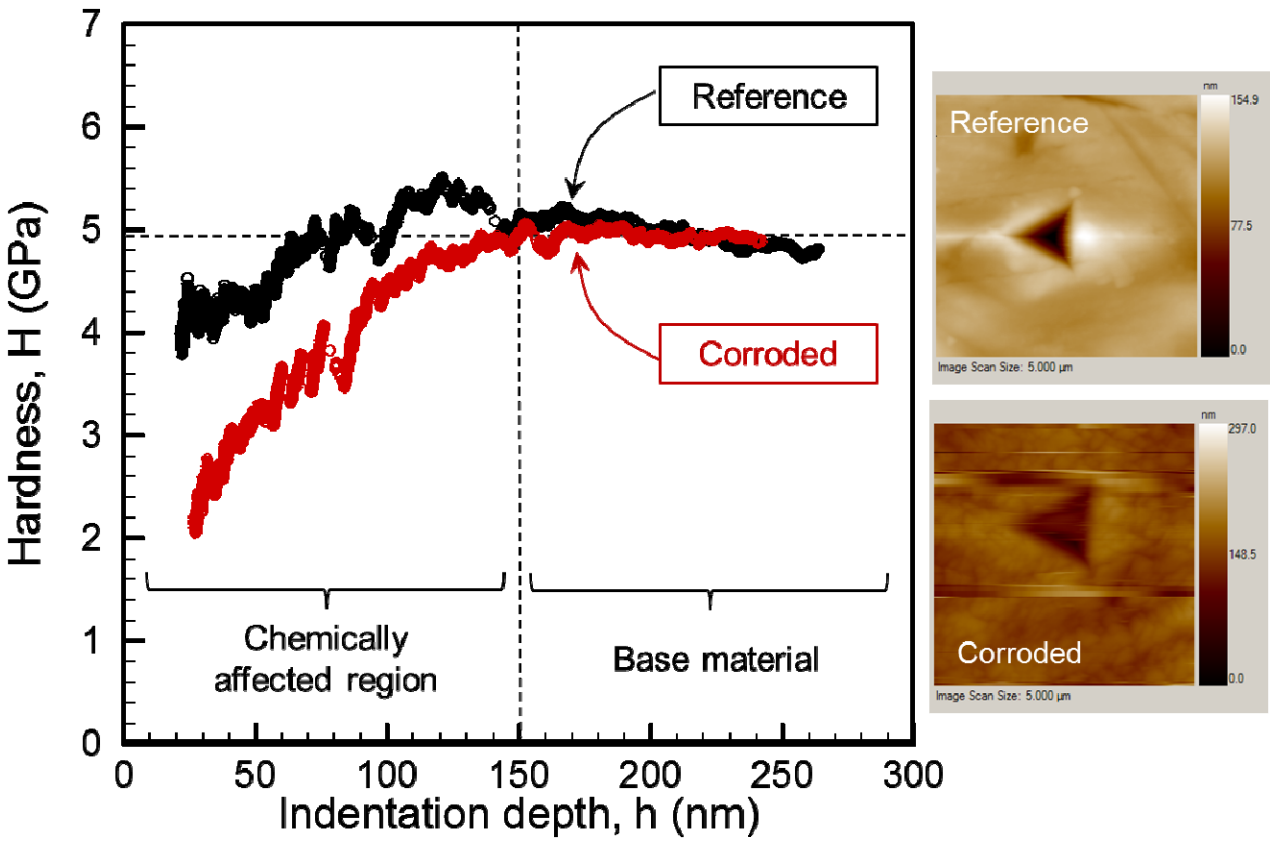

Fig. 8. Near surface mechanical properties characterization by nano-indentation for unexposed and corroded X70 steel that were undergone an electrochemical polarization experiment in Carbonate-bicarbonate-chloride solution (0.05M Na2CO3+ 0.1M NaHCO3+ 0.1M NaCl). Variation of hardness through the depth of the sample. The corroded area showed almost two

(c) Description of any Problems/Challenges – Two key challenges were faced during this period:

1. Crevice corrosion and pitting corrosion: In the first set of electrochemical experiments we observed crevice and pitting corrosion that produce high steel corrosion in a localized area and can alter the corrosion rates substantially. Figure 9 shows example of the early testing for both Crevice and pitting corrosion. We have overcome that by adjusting the experimental conditions, such as the electrochemical solution, as well as the use of vacuum lubricant to eliminate them.

2. Thick Oxide Layer: The extended electrochemical corrosion experiment at constant voltage showed the continuous evolution and growth of the corrosion products (iron oxide). When tested by nano- indentation (Fig. 10), we found that this layer extends to more than 2µm deep. Our plan is to use a combined chemical and mechanical procedure to remove such oxide layer. Chemically, we will utilize Clark 'solution with different concentration to remove the oxide layer in low ultrasonic agitating path. Mechanically, we will perform a nano-scratch sweep test and measure the change of the properties as a function of the depth. Such test would provide a full depth-wise profiling of the mechanical properties variation as well as the prospective extent of the oxide layer and the subsurface damage layer.

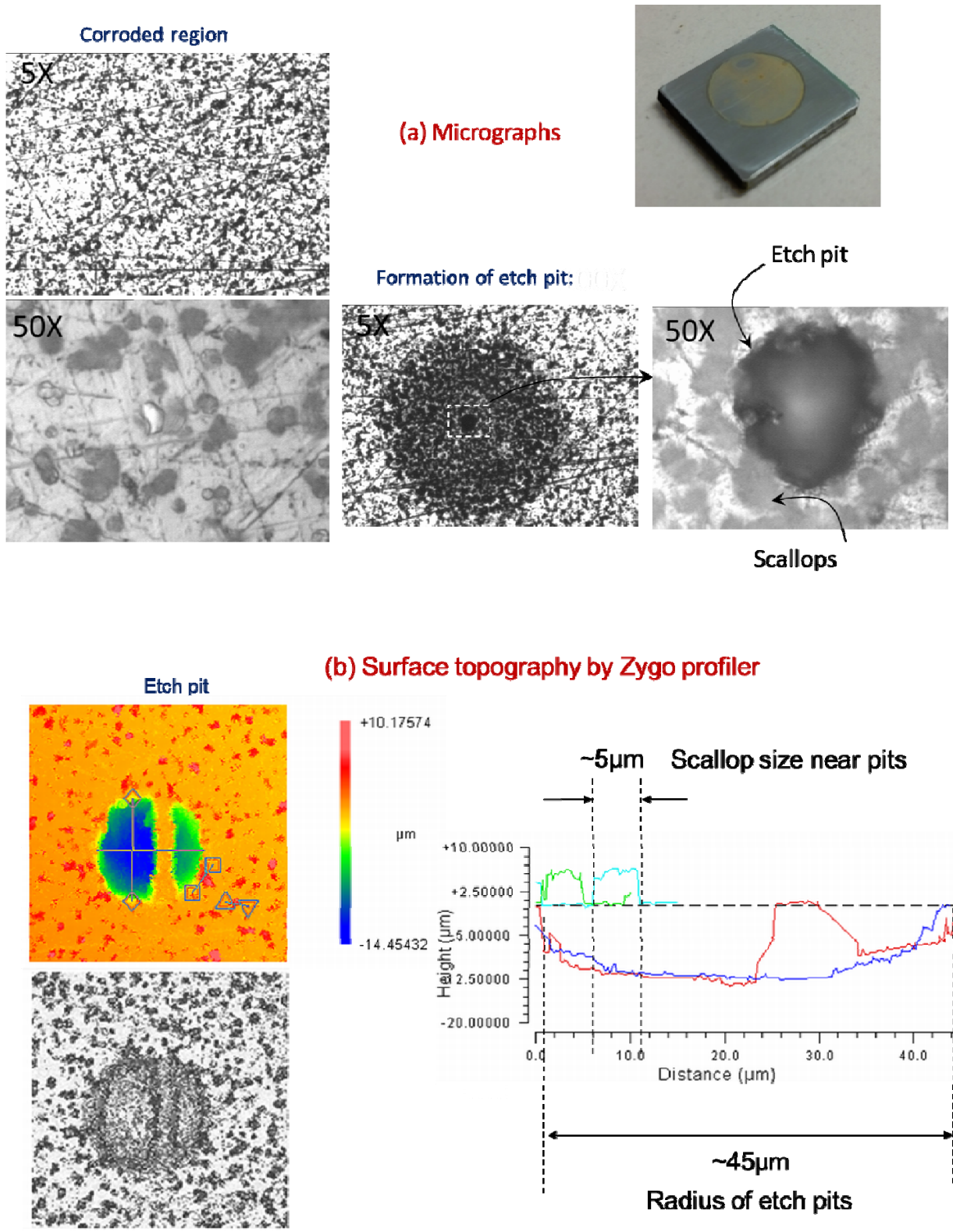

Fig. 9. An early issue of corrosion pitting was observed, (X70-sample-051414-1). By adjusting the experimental conditions, such as the electrochemical solution, as well as the use of vacuum lubricant, such issue was eliminated.

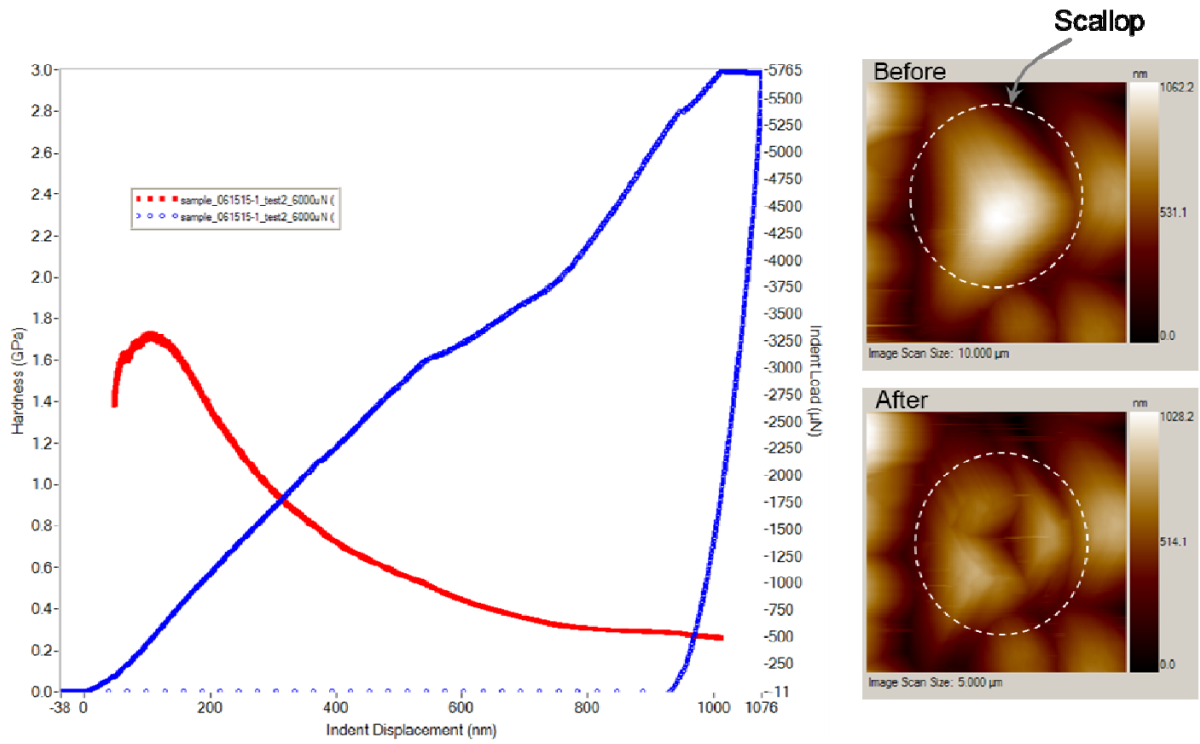

Fig. 10. Variation of the surface hardness for the prolonged exposed sample (120min) in a Bicarbonate Solution (1M $NaHCO_3$). The preliminary nano-indentation measurements on one of the formed scallops show that the extent of the oxide product layer has a less than 5% the hardness of the parent steel and extend to a depth of more than 2µm. different methods will be attempted to remove the oxide layer before the nano-indentation testing to expose the subsurface layer of interest, (X70-sample-061515-1).

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

1. Continue the parametric study for the electrochemical corrosion experiment
2. Identification of the mechanical properties and the extent of the damage layer due to the early stage of corrosion by nanoindentation.
3. Perform preliminary assessment of the in situ measurements of the corrosion induced stresses.