Quarterly Progress Report   SRNL-STI-2019-00654

**Project Title: Kelvin Probe Force Microscopy for High-Resolution Imaging of Hydrogen
                  in Steel and Aluminum Alloys**

Project Period: 7/1/19 - 9/30/2019 (Q4)

Date of Report: 10/31/2019

Contacts: PI: Dr. Joy McNamara, Savannah River National Laboratory

Contributors: Dr. Andrew Duncan, DeWayne Dick, Prabhu Ganesan, Laken Inabinet, Anthony
McWilliams, and Tony Curtis, Savannah River National Laboratory

DOE Manager: Neha Rustagi, DOE HQ Technology Manager

Project Objective:
SRNL is working with Sandia NL, Pacific Northwest NL and Oak Ridge NL in the H-Mat consortium
with the objective of developing materials with a higher resistance to hydrogen attack.

Understanding the mechanism of hydrogen interactions in metal alloys is continually a topic of interest
for applications which involve the long-term storage of hydrogen. Atomic hydrogen segregates to regions
of extended defects, such as grain and phase boundaries, and can cause stress and premature cracking
through a process known as hydrogen embrittlement. Advanced microstructural imaging techniques, with
minimal sample preparation needs, that are capable of resolving hydrogen segregation at the nanometer
scale is needed. Current imaging technologies to aid in understanding the effects of hydrogen in metals
involve primarily fractography after mechanical testing.

Hydrogen segregated at the surface and particularly at surface defect sites changes the local work function
of the material. This can be measured by Kelvin Probe Force Microscopy, KPFM, a variant of atomic
force microscopy (AFM). KPFM produces surface potential images and is capable of measuring the local
change in work function of surfaces with very high spatial resolution. The spatial resolution of KPFM is
optimally ~5 nm, yielding very high hydrogen concentration/microstructure coloration capabilities. By
locating the presence of hydrogen and its relationship with extended defects, it may be possible to
develop microstructures less susceptible to hydrogen embrittlement. The objective of this effort is to
assess the utility of KPFM to determine the H_2 concentration profiles surrounding complex
microstructural features in high strength steel and aluminum alloys subjected to high pressure hydrogen
exposure.

Acronyms

- AFM: atomic force microscopy
- CV: cyclic voltammetry
- EC: electrochemical
- KPFM: Kelvin probe force microscopy
- SEM: scanning electron microscopy

Milestone Status:

Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
Complete KFPM of aluminum and ferrous alloy microstructures	Milestone	Q1		Q1	100%	Complete
Complete KFPM of H$_2$ charged of aluminum and ferrous alloy microstructures	Milestone	Q2	Q3	Q3	80%	In Progress
Complete KFPM of aluminum H$_2$+5μmol H$_2$O samples	Milestone	Q3	FY20		0%	Not started.
Complete KFPM of strained and H$_2$ charged ferrous alloy microstructures	Go/No-Go	Q4	FY20		0%	Not started.

Q1 – Q4 Summary:

The microstructures of several steel and Al samples, absent of noticeable hydrogen species, were characterized to provide a baseline and to understand the nature of hydrogen segregation after future hydrogen charging experiments. Samples of a pressure vessel steel (SA372, grade J), proprietary heat-treated steel (4340), and high strength aluminum alloy (2219) were supplied by SNL for evaluation. Various experimental techniques were used to explore the microstructures of these specimens and the preliminary results were reported in the Q1 and Q2 reports. Prior to characterization and examination, the alloys were metallurgically polished and some etched. Atomic force microscopy (AFM) in tandem with Kelvin probe force microscopy (KPFM) was used to evaluate the surface microstructures and corresponding surface potential difference. Understanding the nature of the surface work function for an uncharged sample is necessary to be able to compare with samples which have been hydrogen loaded. Q1 and Q2 results provide a basis for comparing uncharged specimens with hydrogen charged specimens. The Q2 milestone to perform hydrogen charging of the alloys was pushed to Q3 due to a work suspension at SRNL, and due to issues with the high-pressure charging vessel not passing leak tightness certification.

The revised goals for Q3 were to load the test samples with hydrogen and evaluate the hydrogen concentration at the surface of the sample with AFM and KPFM. This was accomplished via high pressure hydrogen loading in a high temperature pressure vessel, and through electrochemical charging in a solution. In Q3, the focus was primarily on the efforts of the electrochemical charging technique. The capability of electrochemically charging the alloys *in situ* while being investigated by the AFM is currently being developed in similar fashion to a system developed by researchers at MIT.[1] In Q4, the *in situ* electrochemical setup was fabricated and assembled to perform AFM measurements while charging a sample electrochemically. The results are that the system was successfully integrated into the AFM, but there were no noticeable hydrogen signatures on the surfaces of the samples. In this report, the experimental procedures and details are described and the possible reasons for not observing hydrogen signatures are discussed.

Hydrogen Charging by Electrochemical Methods

Hydrogen charging by electrochemical (EC) methods is accomplished by immersing the sample into an electrolyte and creating a voltage between the working electrode (sample) and a counter electrode (Pt wire). The current or voltage can be fixed, and cyclic voltammetry (CV) measurements can aid in determining the appropriate current or voltage values depending on the sample material and electrolyte resistance. By immersing the sample in an electrolyte, hydrogen formation and permeation can occur on all sides. While immersing the sample in electrolyte increases the probability of hydrogen permeation through all sides, it also makes it difficult to isolate the effects of surface oxide layers in trapping hydrogen directly and does not clearly demonstrate that hydrogen has diffused through the entire sample.

A custom-built EC cell was fabricated at SRNL to provide *in situ* hydrogen EC charging capabilities on our Park Systems AFM. The *in situ* EC cell is shown in **Figure 1** and can accommodate samples with approximate dimensions of 2.5 cm^2 and 0.075 cm thickness. For *in situ* hydrogen charging, one surface of the sample is exposed to hydrogen gas formation, and the opposite side is isolated from the solution and probed for hydrogen permeation and trapping at the surface. In this manner, an investigation of hydrogen diffusion through the bulk and surface trapping can be studied by KPFM. Hydrogen charging is accomplished in the typical manner except that only one side of the sample is immersed in the electrolyte while the other is kept dry via an O-ring seal. The small volume (~15 mL) of this cell necessitates that the electrolyte solution be refreshed during hydrogen charging. This is accomplished by using a peristaltic pump to pump the solution from a reservoir, through the cell, and back into the reservoir; this process also vents any off-gas that is generated during the charging process. Internal spacers and notches in the cell allow for varying sample sizes. This design was motivated by recent work performed at MIT.[1] In this work, we tested the custom built, *in situ* electrochemical charging cell with carbon steel alloy 4340, along with its austempered form AT40, and Al alloy 2219. A cursory search of the literature reveals efforts using KPFM to study other types of Al alloys, but none on Al 2219.[2,3,4,5,6,7]

Carbon steel samples (alloy 4340 and quenched and tempered AT40) were precisely machined to thickness of approximately 0.75mm using electric discharge machining (EDM), and lengths and widths of roughly 2.5 cm. The samples were polished to a mirror finish following standard metallographic procedures. At first, the samples were electrochemically charged by immersion in the electrolyte. A Pt counter-electrode and reversible hydrogen electrode (RHE) were employed during standard electrochemical measurements, such as cyclic voltammetry. These measurements provided information on the appropriate magnitude of current and voltage necessary to form hydrogen gas at the surface of the samples. The samples were then loaded into the EC cell (**Figure 1**) and sealed so that the top surface of the sample was isolated from the solution (**Figure 2**). To limit corrosion at the exposed sample surface, an Ar gas line was positioned close to the surface, and the set-up was monitored closely for any liquid leaks. A Pt wire mesh (with surface area comparable to the sample surface area) was used as the counter electrode and the sample was used as the working electrode. No reference electrode was used in the *in-situ* EC cell, since further design improvements will need to be made to accommodate a reference electrode. Solutions of 0.1 M NaOH + CH$_4$N$_2$S (thiourea) and 0.5 M H$_2$SO$_4$ + CH$_4$N$_2$S were circulated through the cell, and various current values (2 – 65mA) were applied for varying lengths of time (1 – 64 hrs). From CV studies, we found that current values as high as -65 mA/cm^2 (total current = -130mA) were necessary to form hydrogen at the bottom side of the sample which was exposed to the electrolyte.

Before taking AFM and KPFM measurements, the voltage being applied for electrochemical measurements must be switched off, in order to electrically ground the sample for KPFM measurements.
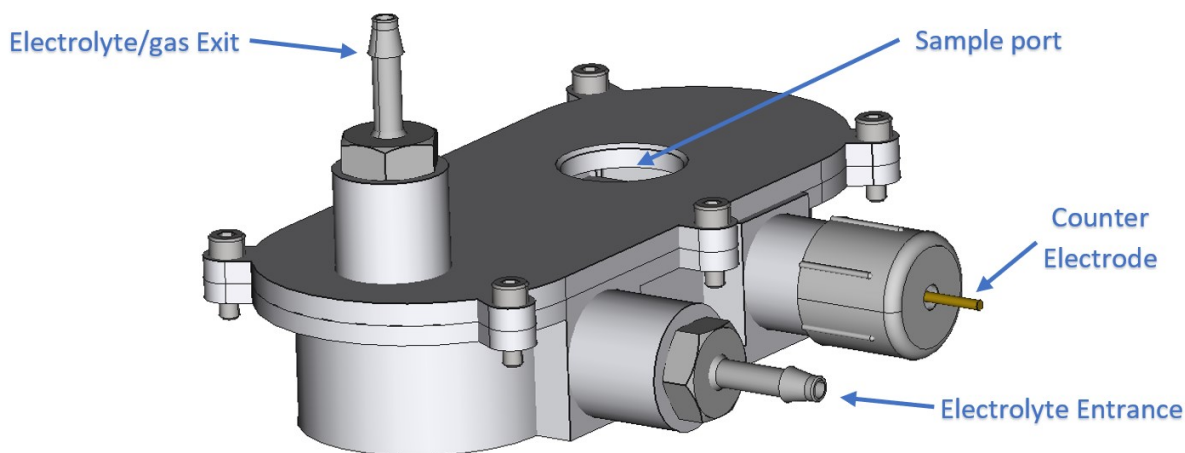

Figure 1: Drawing of EC cell designed specifically for our Park Systems AFM. The functions of each port are indicated.
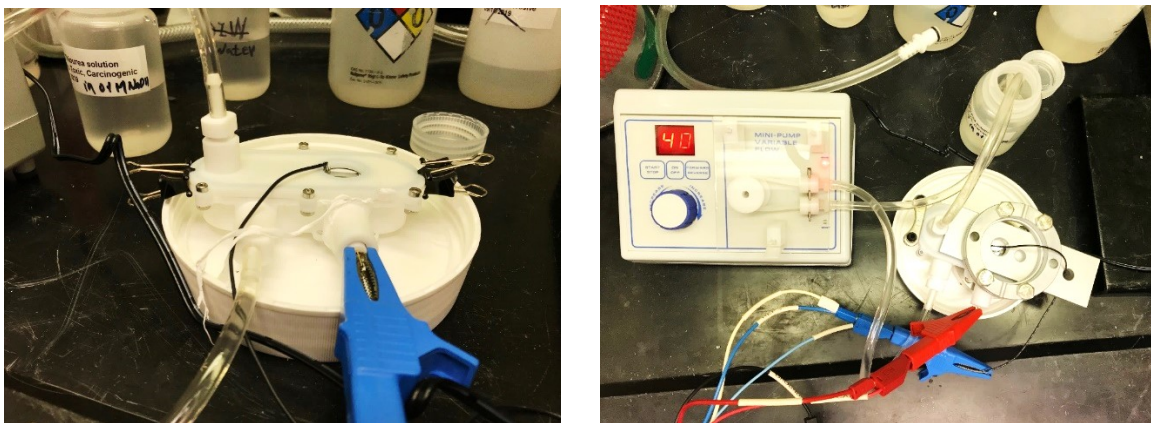

Figure 2: EC cell being used in electrochemical hydrogen charging experiments. The system was put in secondary containment and tested for leak-tightness before used with the AFM.

Figure 3 shows the difference between images acquired before and after hydrogen charging, for both topography and surface potential images. As hydrogen formation occurred at one side of the sample, it is expected that a diffusion gradient was established across the sample. It is well known that ferritic steel has a very high diffusivity rate and lower solubility for hydrogen than austenitic stainless steel. So without the presence of significant trapping sites, it is likely that atomic hydrogen species formed gaseous species at the surface and were desorbed into the atmosphere. If only trace amounts of hydrogen species are trapped at the surface or hydrogen is uniformly distributed across the surface, it is difficult for the KPFM technique to detect a change in surface work function, and a homogenous surface potential is measured across the scanned area.

This can be seen in **Figure 3**, since the surface potential images are not much different for the charged and uncharged conditions. To increase the chances of observing hydrogen at the surface of the sample, a duplex stainless-steel material with ferritic and austenitic phases, or a welded austenitic material with retained ferritic phases should be studied, since the two phases will provide a substantial difference in hydrogen diffusion and solubility characteristics. The *in situ* EC cell has the potential to provide visual insights into the phenomena of hydrogen diffusion through alloys of interest and to distinguish between surface charging effects (which may be present in gas charging and immersive EC charging) and bulk permeation. Future efforts will focus on studying materials with properties which are more suitable in showcasing these capabilities. Further modifications will also be made to the *in situ* EC setup to improve results.
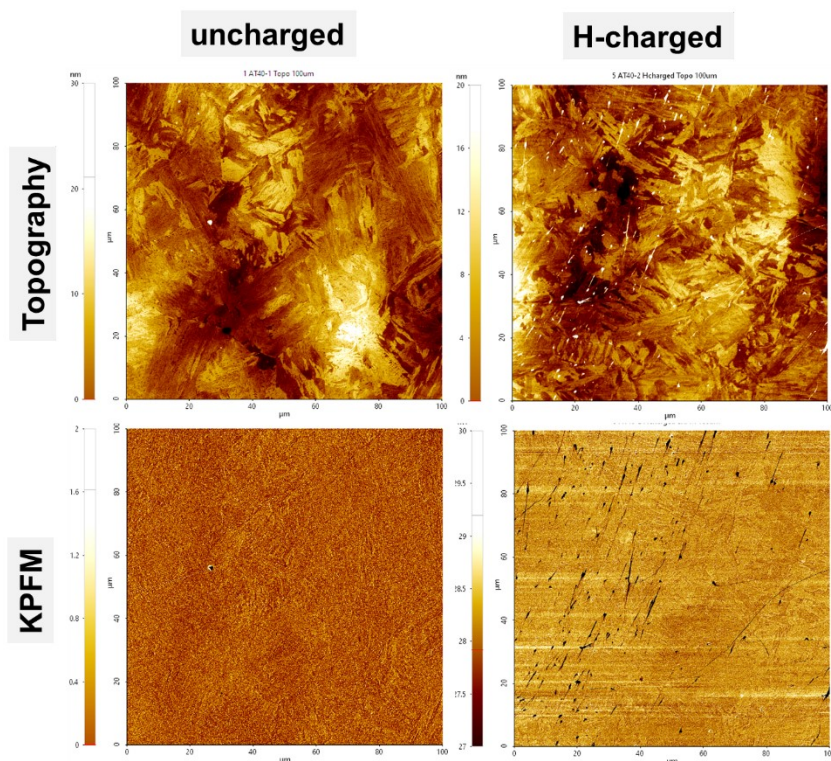

Figure 3: Topography (top) and surface potential images (bottom) of samples before (left) and after (right) charging. The subtle variation in surface potential is insufficient to demonstrate the presence of hydrogen trapped at the surface.

References:

[1] J. Kim, and C. C. Tasan, *Int. J. Hydrogen Energy*, **44** (2019) pp. 6333-6343.

[2] M. C. Lafouresse, M-L. de Bonfils-Lahovary, C. Charvillat, L. Oger, L. Laffont, C. Blanc, *J. Alloys and Compounds*, **722** (2017), pp. 760-766.

[3] C. Larignon, J. Alexis, E. Andrieu, L. Lacroix, G. Odemer, C. Blanc, *Electrochim. Acta*, **110** (2013), pp. 484-490.

[4] L. Oger, M. C. Lafouresse, G. Odemer, L. Peguet, C. Blanc, *Mat. Sci. Eng. A*, **706** (2017) pp. 126-135.

[5] C. Larignon, J. Alexis, E. Andrieu, L. Lacroix, G. Odemer, C. Blanc, *Scripta Materialia*, **68** (2013) pp. 479-482.

[6] N. Takamo, *Mat. Sci. Eng. A*, **483-484** (2008) pp. 336-339.

[7] P. Rozenak, E. Sirois, B. Ladna, H. K. Birnbaum, and S. Spooner, *J. Alloys and Compounds*, **387** (2005) pp. 201-216.