

Contract No:

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

Project Period: 4/1/19 – 6/30/19 (Q3)

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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 H₂ 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 +5 μ mol H ₂ O samples	Milestone	Q3	Q4		0%	Not started.
Complete KFPM of strained and H ₂ charged ferrous alloy microstructures	Go/No-Go	Q4			0%	Not started.

Q1 and Q2 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.

Q3 Summary:

The revised goals for Q3 are to load the test samples with hydrogen and evaluate the hydrogen concentration at the surface of the sample with AFM and KPFM. This can be accomplished via high pressure hydrogen loading in a high temperature pressure vessel, or through electrochemical charging in a solution. In the first technique, hydrogen gas permeates through the surface of the material into the bulk at favorable temperatures and partial pressures. In the second technique, hydrogen gas is formed at the sample surface from an electrolytic solution when the sample is held at a constant voltage or current in respect to a reference electrode. This report will focus 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

Experimental Details and Results:

Samples representative of each alloy (SA372, 4340, and Al2219) were machined to 1 mm thickness, with approximately $2 \times 1 \text{ cm}^2$ length and width, respectively. These samples were polished with a mirror finish and wrapped carefully in chromel-alumel wire to protect the surfaces from being scratched. The samples were then loaded into a $\frac{1}{2}$ " stainless steel tube which had been pressure rated to 3500 PSI. The tube with samples was connected to a hydrogen overpressure of 2500 PSI and heated to 100°C . At the time of this report, the samples have been charging for 7 days, and it is expected that they will complete 2 full weeks of charging before being removed from the pressure vessel. The pressure vessel typically used for hydrogen charging is still undergoing service.

A more attractive alternative to high pressure hydrogen charging is electrochemical (EC) charging during which the sample is immersed into an electrolyte and a current is applied between the sample (working electrode) and a Pt wire (counter electrode). Either the current or the voltage can be held constant, and cyclic voltammetry (CV) measurements can aid in determining the appropriate current or voltage values depending on the sample material and electrolyte resistance. 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}

In this work, thin specimens of Al 2219 rolled plate material were cut into coupons with dimensions of approximately $10 \times 7 \times 1 \text{ mm}$ length, width, and thickness, respectively. To cathodically charge the samples with hydrogen, the coupons were immersed in 1M H_2SO_4 electrolyte at various current densities and durations. A Pt wire was used as the counter electrode, and a relative hydrogen electrode (RHE) for the reference electrode. Three runs, with a duration of 30 mins each, were conducted with 3 different coupons. The current density was varied from 0.5 mA/cm^2 to 2 mA/cm^2 . The samples were subsequently polished before imaging with AFM and KPFM. These results were inconclusive, and it was decided that the samples should be polished before hydrogen loading, and that the current should be increased. After using CV measurements to determine the appropriate voltage, one pre-polished sample was held at -0.8V for 30 minutes. The progressive appearance of bubbles at the surface of the charging face over time indicated that an initial oxygen reaction was replaced with hydrogen reduction and formation at the surface.

In no more than 20 minutes after being removed from the electrolytic solution, the sample was cleaned with high pressure CO_2 (known as "snow cleaning" ^[8]) under a blanket of nitrogen gas and loaded into the AFM environmental chamber. Figures 1 and 2 show the topography and surface potential measurements of the last sample which was kept at -0.8V for 30 minutes. Compared to previous surface potential measurements of Al 2219, there are significant changes in the surface potential at surface defects. More work is needed to clarify the role of hydrogen in these samples, as hydrogen is expected to increase the work function, thereby changing the local surface potential.

In addition to standard bath EC charging, we are building a system which will provide in situ hydrogen EC charging capabilities on our Park Systems AFM. The EC cell shown in Figure 3 allows for the bottom of a sample to be in situ hydrogen charged and its top surface probed for the presence of hydrogen using 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 allow for varying sample sizes.

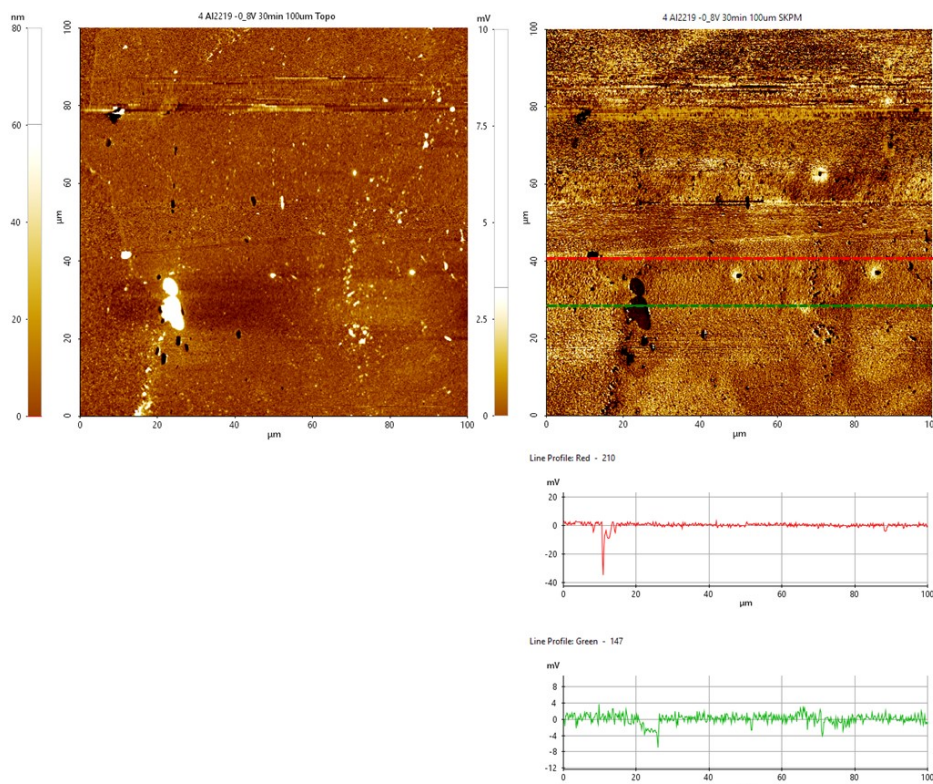


Figure 1: (left) Topography of Al 2219 after hydrogen loading at -0.8V in 1M H₂SO₄ for 30 min. (right) corresponding surface potential from KPFM measurement shows change in voltage in surface defects. (bottom right) surface potential line cross sections. AFM measurements were started 20 minutes after hydrogen loading and scanned from the bottom to the top.

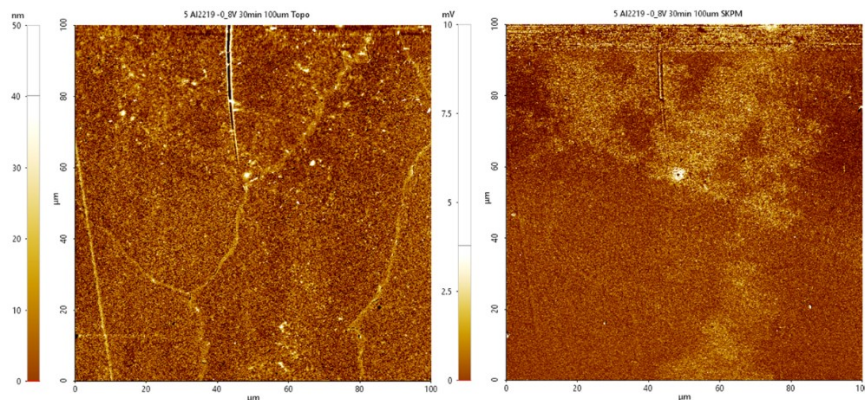


Figure 2: Topography (left) and surface potential (right) images of Al 2219 sample after hydrogen loading in 1M H₂SO₄ at -0.8V for 30 min. AFM measurements were started approximately 1 hour after hydrogen loading and scanned from the top to the bottom.

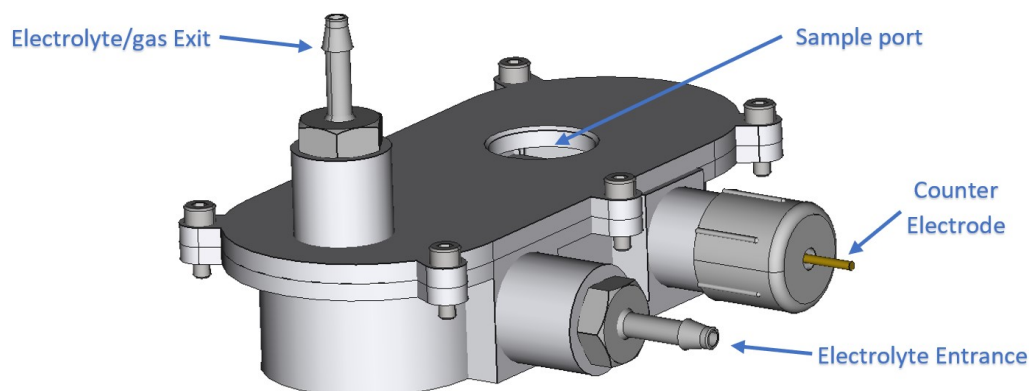


Figure 3: Drawing of EC cell designed specifically for our Park Systems AFM. The functions of each port are indicated.

References:

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