Enabling hydrogen energy infrastructure through surface passivation of structural materials

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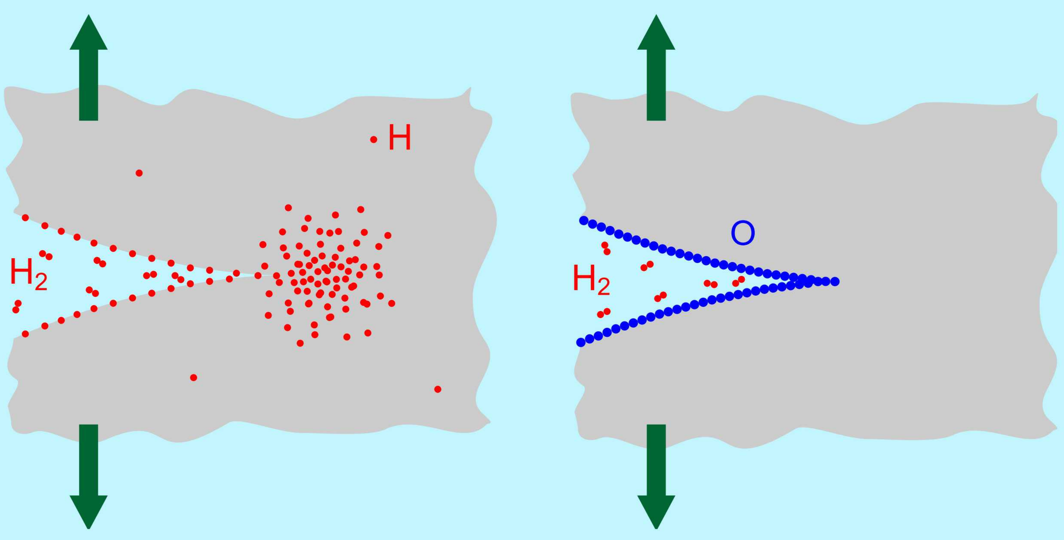
Can a monolayer of adsorbed oxygen eliminate H-assisted fatigue in pipeline steels?

The primary technology challenges for hydrogen as a transportation fuel have increasingly focused on infrastructure. Pipeline steels are susceptible to hydrogen embrittlement. Cyclic loading leads to hydrogen-accelerated fatigue, where crack-growth rates can increase tenfold. This has led to conservative design standards for hydrogen pipelines, dramatically increasing materials cost.

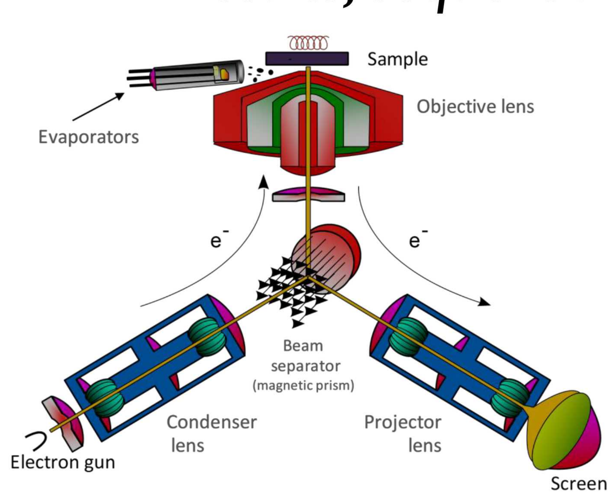


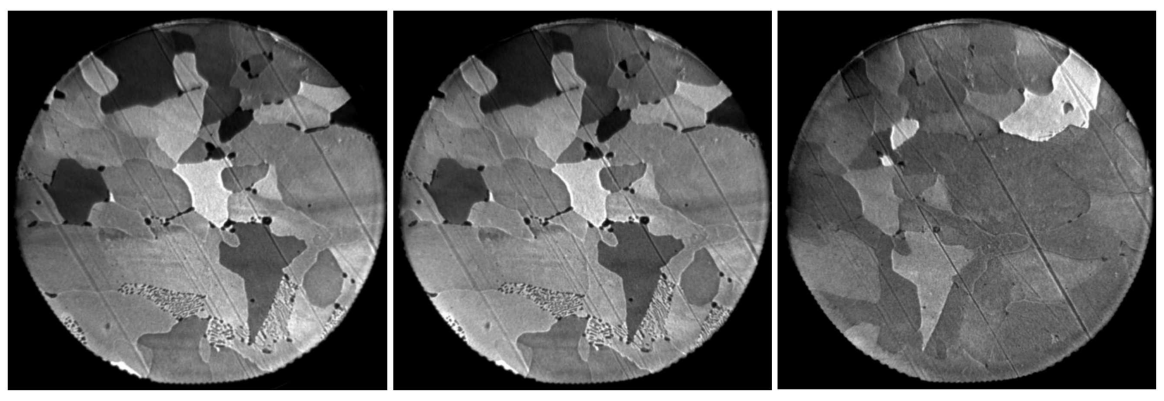
Recent evidence reveals a potential solution: under appropriate conditions, ppm concentrations of oxygen almost completely suppress hydrogen-induced material damage. The proposed underlying mechanism is that oxygen displaces hydrogen and chemisorbs on the crack tip surface freshly exposed during load cycling, forming a barrier that prevents H_2 from entering the material. The details of this passivation are unknown and adjustable parameters are used to fit the mechanical data. To make the model predictive, we have undertaken experiments in which we expose iron and steel surfaces hydrogen and precisely-controlled amounts of O_2 and H_2.

Technical Challenge: Applying surface science techniques to non-ideal systems / environments

Employing surface analysis techniques with molecular-layer resolution, we have measured how impurities reduce the hydrogen adsorption and uptake. We are using these data to develop a quantitative understanding of the passivation mechanism. Making the needed measurements required extending surface analysis tools beyond their traditional applications. As an example, low energy electron microscopy (LEEM), typically used to monitor the dynamics of thin film growth on single crystals, is applied here to image technical steel surfaces. With this approach, it is possible to monitor work function changes in individual grains as a result of adsorption and impurity segregation to grain boundaries in real time.

LEEM results, sequential H_2 and O_2 exposure





Sputtered for 1 h before exposure | After H_2 exposure 10^{-5} Torr for 2 h | After O_2 exposure 10^{-7} Torr for 5 min

- O_2 chemisorption reduces contrast between grains, work function becomes more uniform over entire surface
- No definitive change observed due to H_2 adsorption

Research Highlights

Low energy electron microscopy enables real time imaging of O_2 chemisorption on technical X52 / X100 steel surfaces

- Directly observed work function changes due to chemisorption
- Stability of the oxide determined, migration of C to grain boundaries can be directly imaged

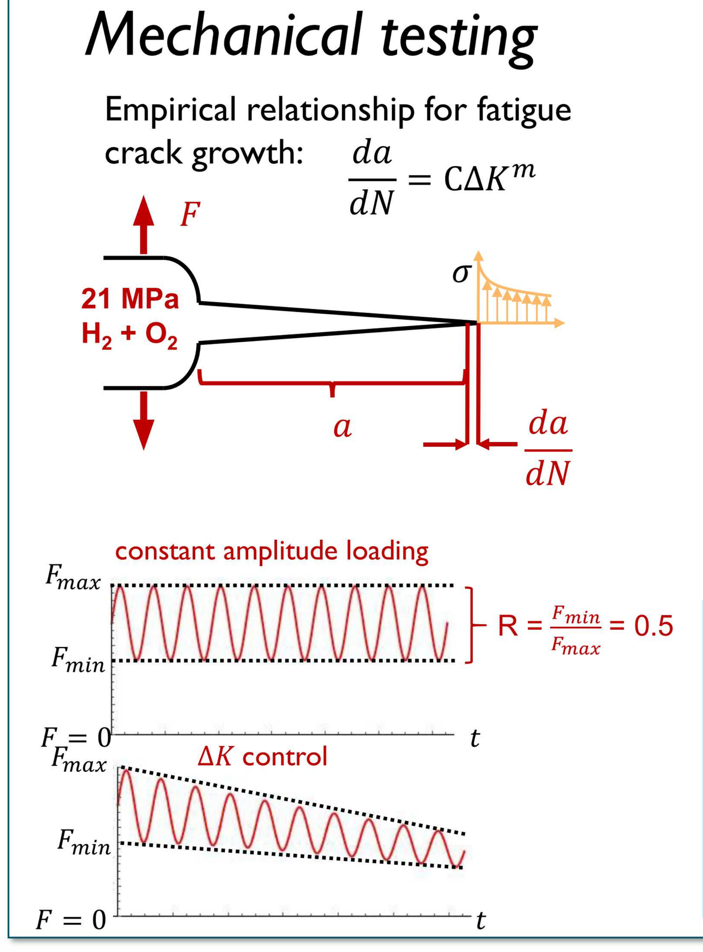
Ion scattering spectroscopy (ISS): sub-monolayer detection of hydrogen on surfaces

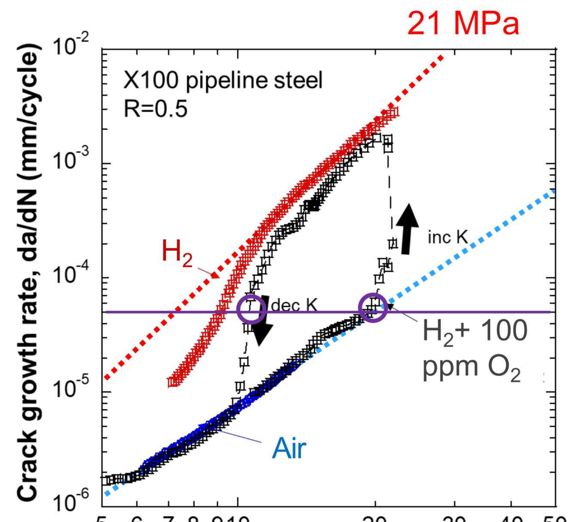
- Characterization of H_2 chemisorption kinetics / H binding structure

Mechanical testing using high-pressure hydrogen testing capabilities at Sandia

- Demonstrates passivation effect on high-strength X100 steel
- Effects explored: H_2 pressure dependence (1.4 – 21 MPa), embrittlement onset as a function of absolute crack growth rate

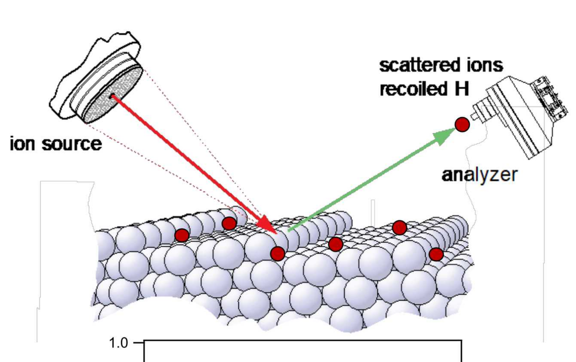
Mechanical testing

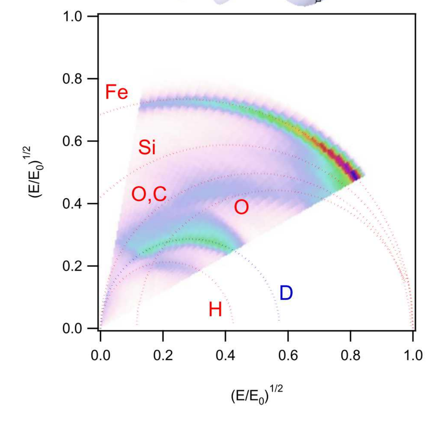




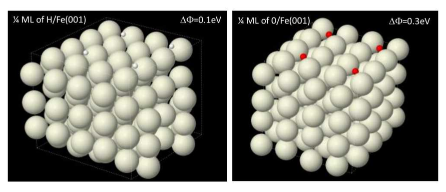
- Return to inert crack growth rate occurs at same critical da/dN
- Dependence on new crack surface area exposed per cycle, not on stress state at crack tip

Surface Analysis

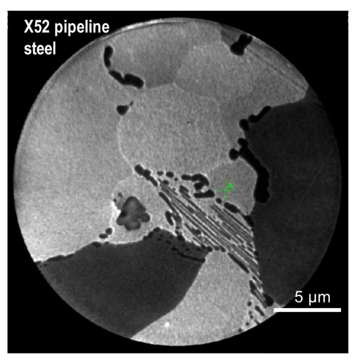




ISS: collision circles showing D on X52 steel surface



DFT work function calculations complement LEEM/LEIS results



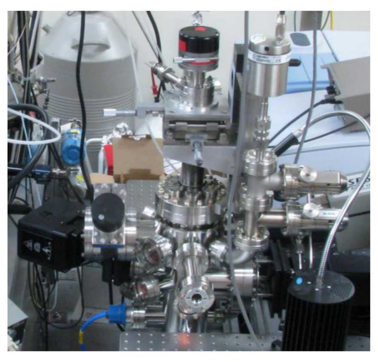
LEEM image showing pearlite phase, and carbide at grain boundaries

New capabilities developed

Optical spectroscopies:

Fourier transform infrared spectroscopy (FTIR) and ellipsometry systems added to bridge the divide between UHV and high-pressure testing:

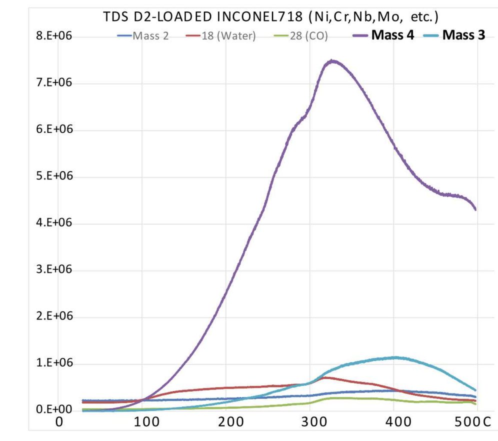
- FTIR vibrational spectroscopy (1 Pa – 10^2 Pa)
- Ellipsometry measures oxide thickness, 1 nm resolution (10^4 – 10^5 Pa)

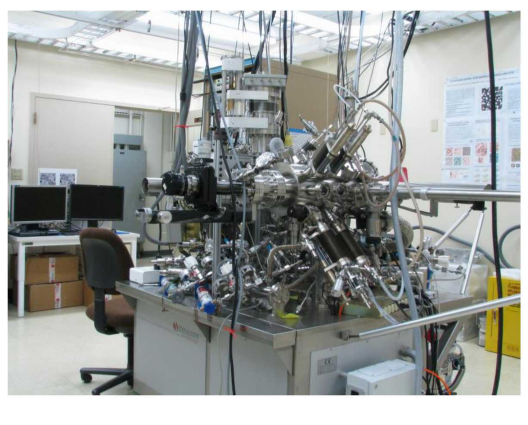


Temperature programmed desorption:

Enables quantification of surface-to-bulk transport of H in Fe surfaces

- New system allows for 10^3 higher sensitivity than conventional mass spectrometry





Summary & Impact

Our surface analysis and mechanical experiments test different aspects of the passivation mechanism, enabling us to replace adjustable model parameters with values measured directly with atomic precision. This is allowing us to develop a robust capability to predict how impurities inhibit fatigue crack growth in commercial materials. We envision this effort will help justify adopting natural gas standards for hydrogen pipeline design, reducing cost without compromising safety and service life.

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