Hydrogen Materials Compatibility

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Pacific Northwest National Laboratory

Monday, February 25, 2008

This presentation does not contain any proprietary or confidential information.

Outline

- Purpose of the Program
- Barriers
- Approach
- Performance Measures/Technical Accomplishments/Progress/Results
- Technology Transfer
- Publications/Patents
- Future Work
- Summary

Purpose of the Program

To develop materials, characterization techniques, and models to minimize Hydrogen Internal Combustion Engine injector leakage and wear in high pressure hydrogen, the #1 factor in Direct Inject H-ICE durability.

1. Characterize actuator material performance in high-pressure hydrogen; develop new materials & experimental methods.
   - Design and implement high-pressure hydrogen test chambers.
   - Conduct failure analysis – identify durability mechanisms.
   - Measure hydrogen diffusion in piezo materials.
   - Characterize the performance of new materials and piezo actuator designs.

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   - Design and implement high-pressure hydrogen test chambers.
   - Conduct failure analysis – identify durability mechanisms.
   - Measure hydrogen diffusion in piezo materials.
   - Characterize the performance of new materials and piezo actuator designs.
2. Measure the friction and wear characteristics of injector materials in hydrogen environments (*in-situ* and *ex-situ)*.
   - Expose materials to high-pressure/temperature hydrogen.
   - Measure friction and wear in *ex-situ* test apparatus.
   - Design, construct, test friction and wear of materials *in-situ.*
   - Develop new coating materials applicable to H2 – ICE systems.

Barriers

1. DI Hydrogen ICE requires precision actuation to accurately meter hydrogen injected into the cylinder cavity.
   - What is the rate of hydrogen diffusion into piezo ceramics?
   - What materials will minimize plastic deformation at the injector needle-nozzle interface?
   - What modeling methodology can be employed to design injectors with the requisite durability in a high-pressure 100% hydrogen environment?
2. Hydrogen has been shown to diffuse into PZT lattice forming OH^- groups; OH kills the internal dipole field and polarization.
   - What piezo-ceramics are suited for the hydrogen environment?
3. Hydrogen embrittlement is known; what is the most effective needle-nozzle design for hydrogen service?
   - What effect does hydrogen have on needle-nozzle impact?
   - Are there coatings that can be utilized to minimize sliding friction, deformation due to impact, and extend injector life?

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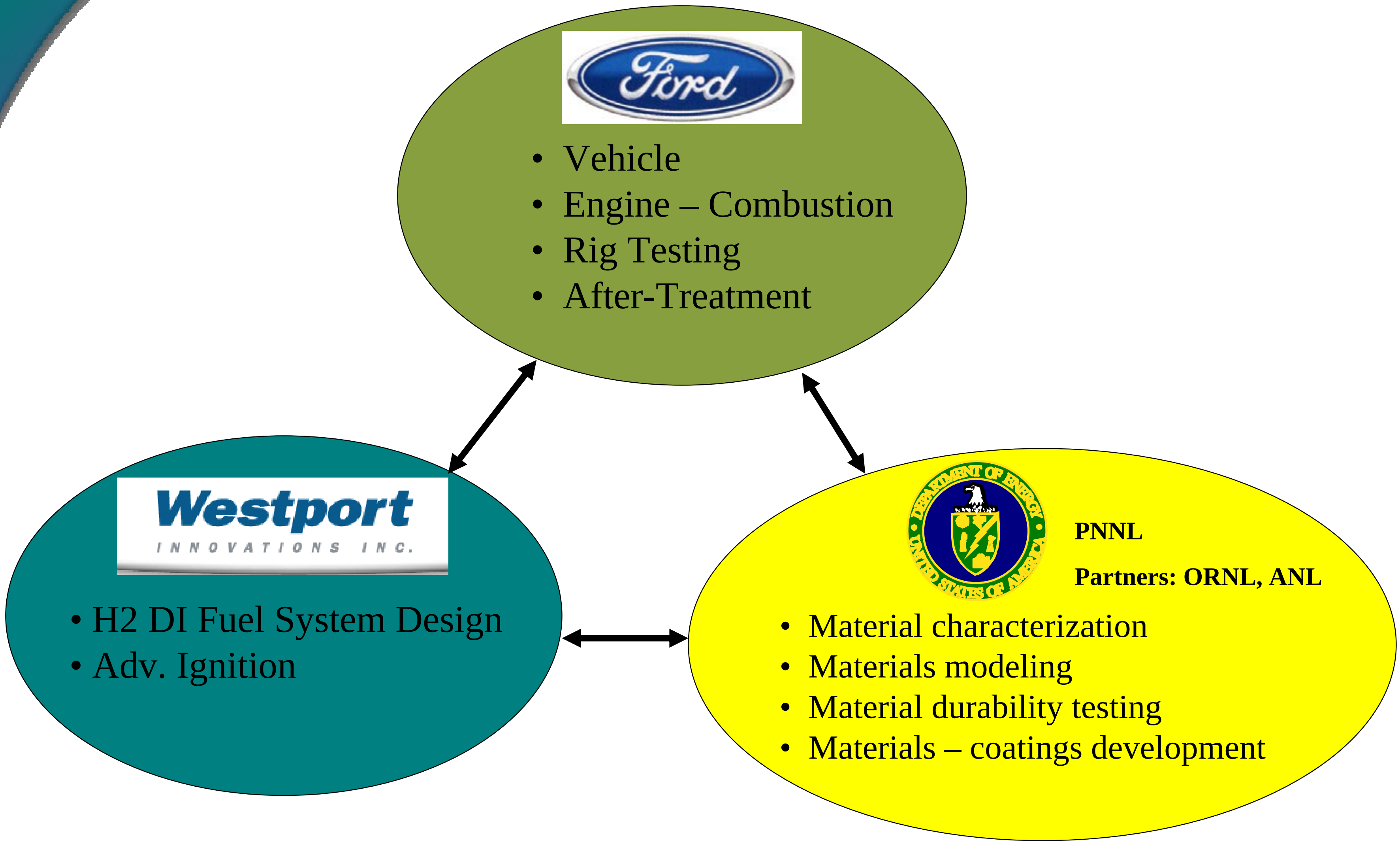
Program Approach



DOE Laboratory Cooperation

PNNL

- H2 Exposure Testing (350 Bar, 300°C capability)
- H2 Material Modeling
- Coating Development
- *In-Situ* Friction & Wear
- Material Analysis
  - NRA, TEM, AFM, XPS…

Coordination

ANL – Dr. Ali Erdemir

- DLC Coatings

ORNL – Dr. Peter Blau

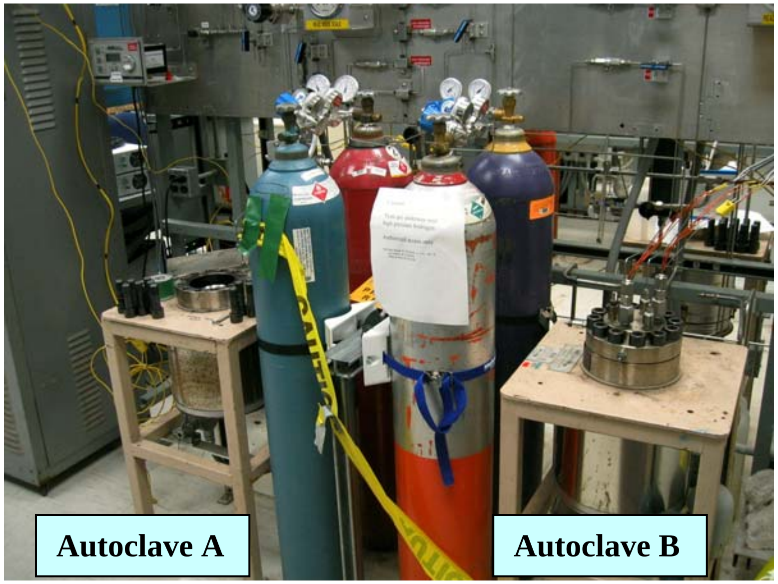
- Ex-Situ Friction & Wear

Performance Measures/Technical Accomplishments/Progress/Results
(FY08 Milestones – 50% Complete)

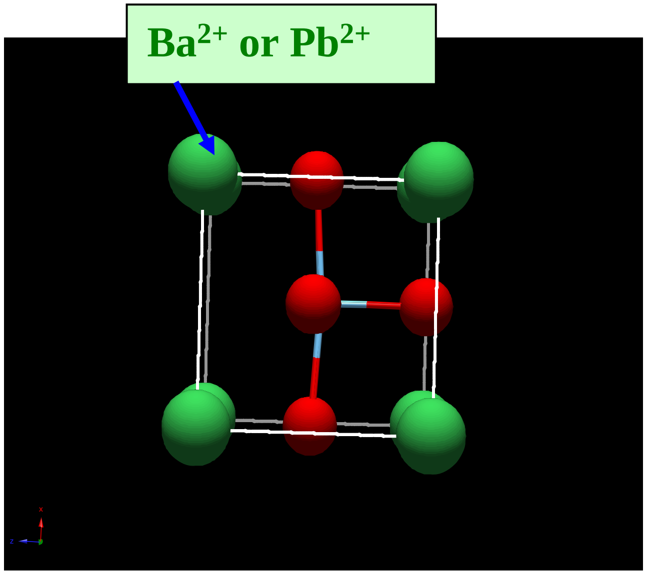
1. Piezo ceramic, M2 & J10 alloy diffusion experiments in process.
    1. NRA characterization in process, post-doc begins in March.

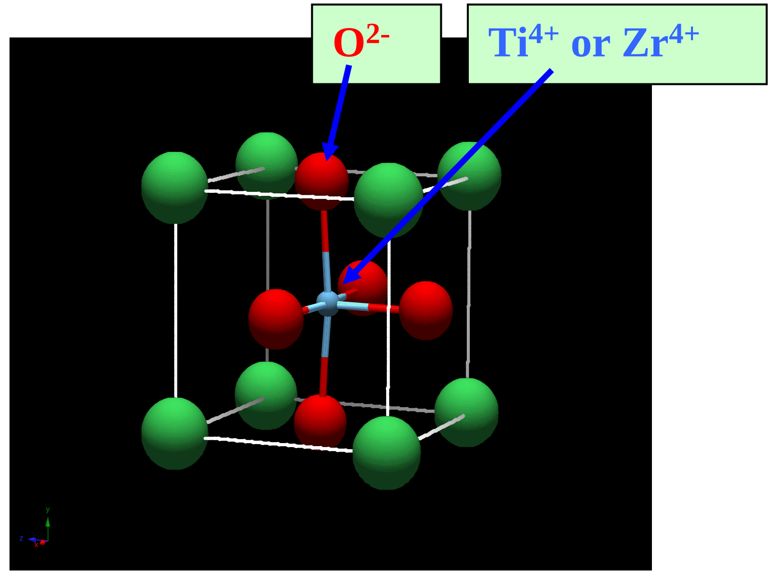
Hydrogen Test Facilities - PNNL

- **Two high-pressure autoclaves installed and operational.**
  - Pure H_2 4500 PSI (300 Bar).
  - 300˚C
- **Up to 4 simultaneous actuated injector tests.**
  - Computer-based data acquisition and control.

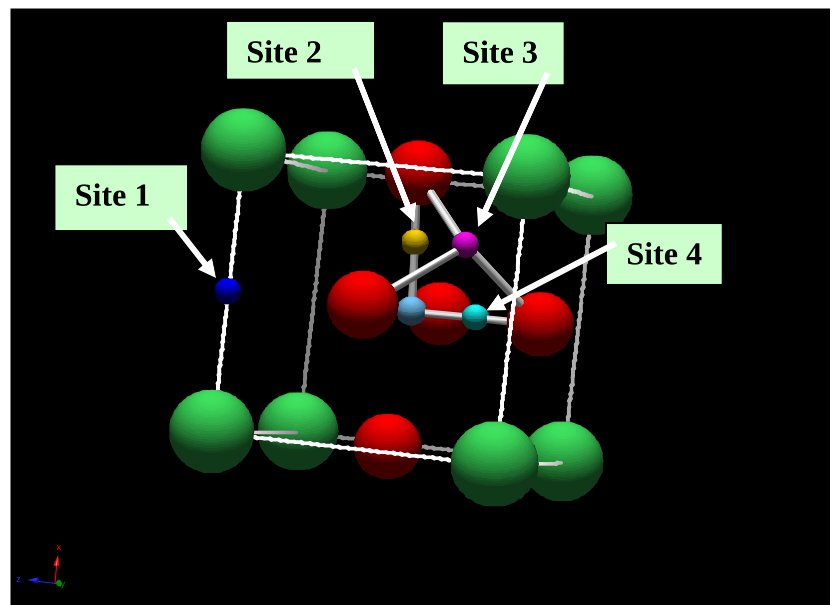


Hydrogen Effects in PZT





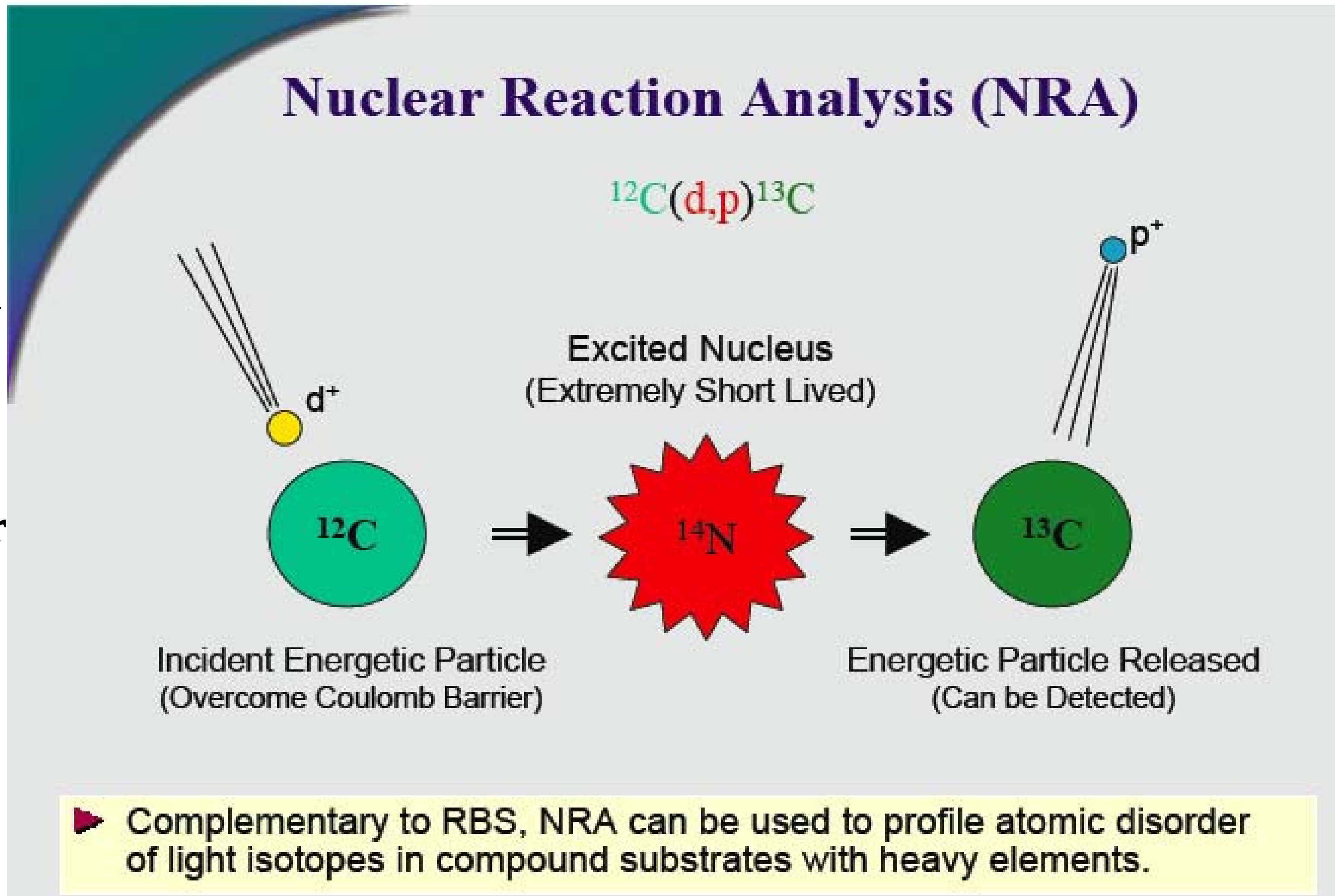
1. PZT tetragonal structure with dipole moment.
2. Hydrogen diffuses into structure and forms OH^- groups.
   - H_2 dissociation catalyzed by metallic electrodes.
   - OH^- kills internal dipole field and polarization.
3. Hydrogen uptake and transport is more fundamental.
   - What is hydrogen uptake rate?
   - What is the kinetics of hydrogen in PZT or metals?
   - Where is it trapped – what is lowest energy configuration?



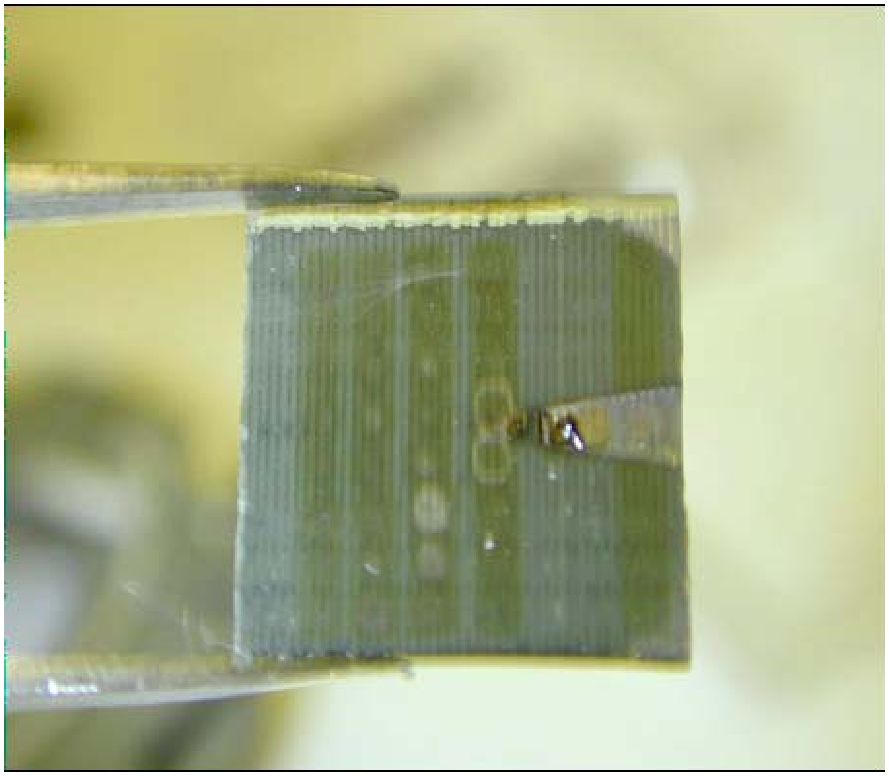
NRA

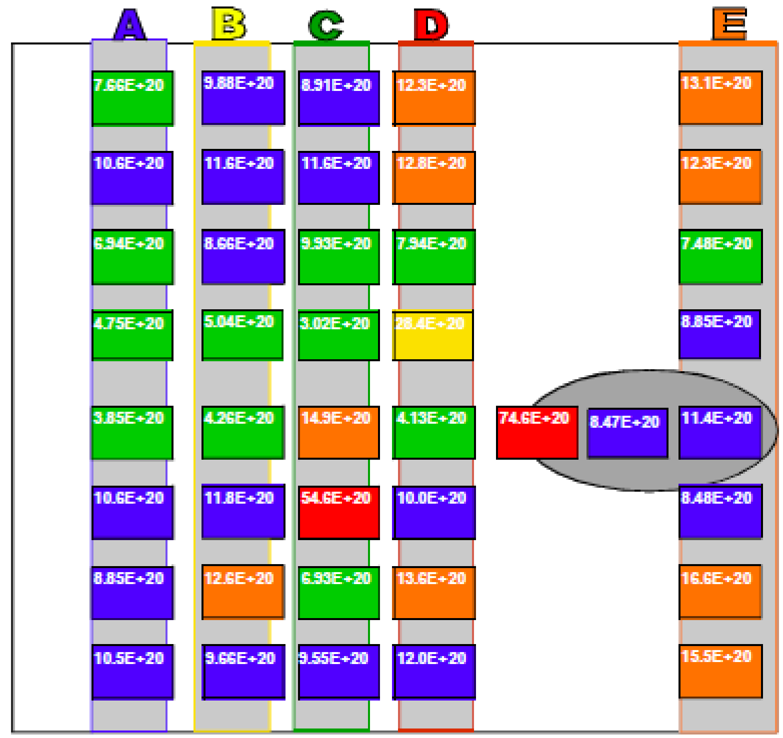
NRA is used to probe light elements with some depth selectivity.

Sensitivity for hydrogen is at a one percent level.



Fundamental Measurements



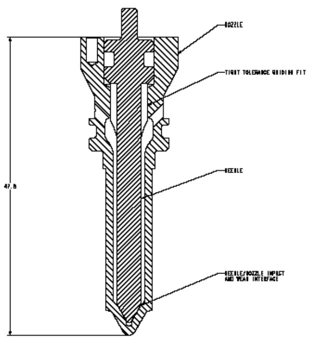


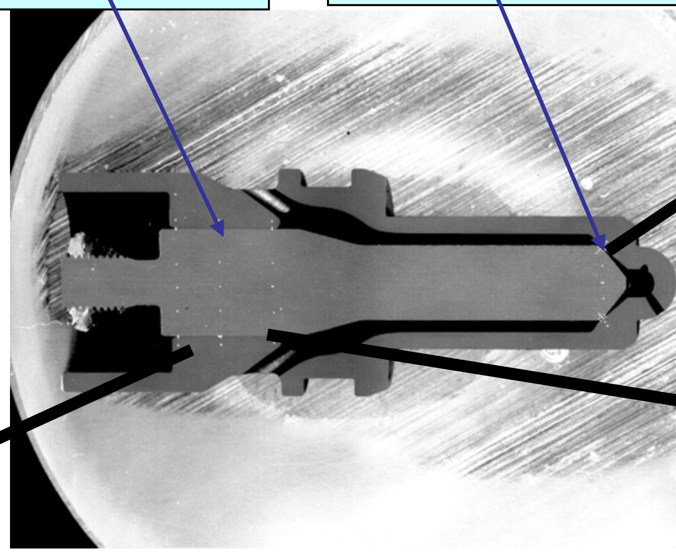
Open-core piezo was analyzed using NRA for total hydrogen content and mapped across sectioned piezo.

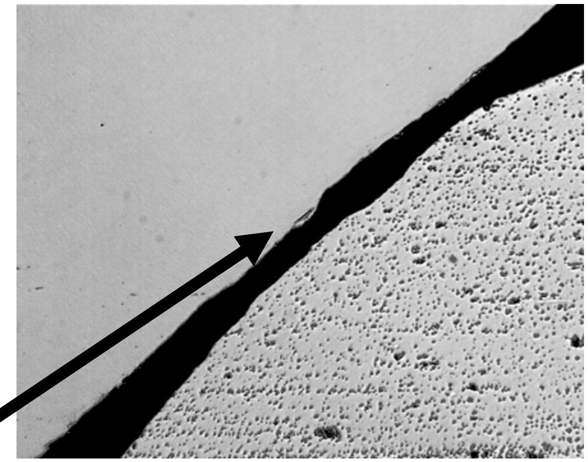
Performance Measures/Technical Accomplishments/Progress/Results
(FY08 Milestones – 50% Complete)

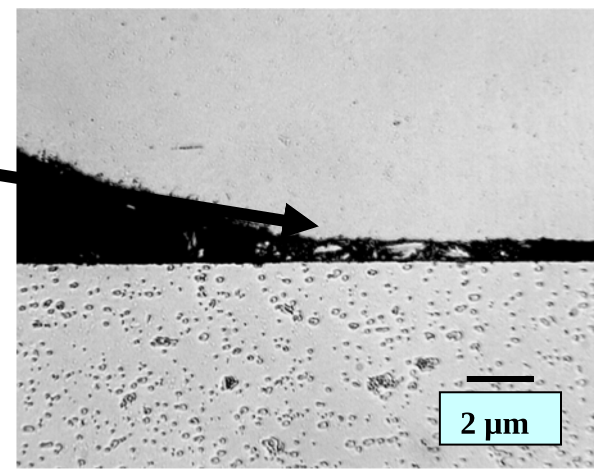
1. Piezo ceramic, M2 & J10 alloy diffusion experiments in process.
   1. NRA characterization in process, post-doc begins in March.
2. DLC-Nanolaminate coating development in process.
   1. DLC coating in process at ANL/commercial suppliers.
   2. PNNL nanolaminate material development underway.
   3. Raman spectroscopy technique quantified for DLC analysis.
   4. PNNL coating FEA modeling tool, Rev. 1 complete.

Analysis of Injector Failure

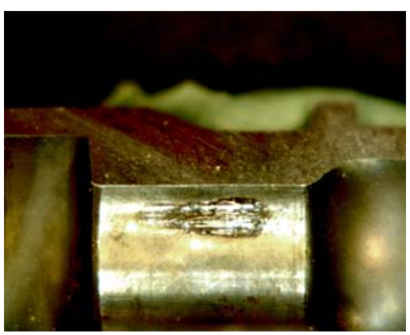




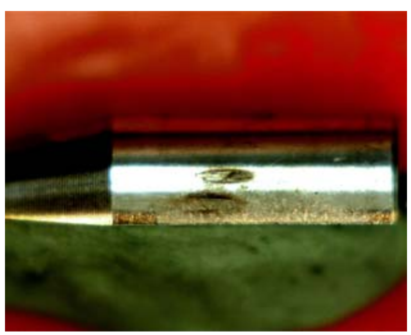




A



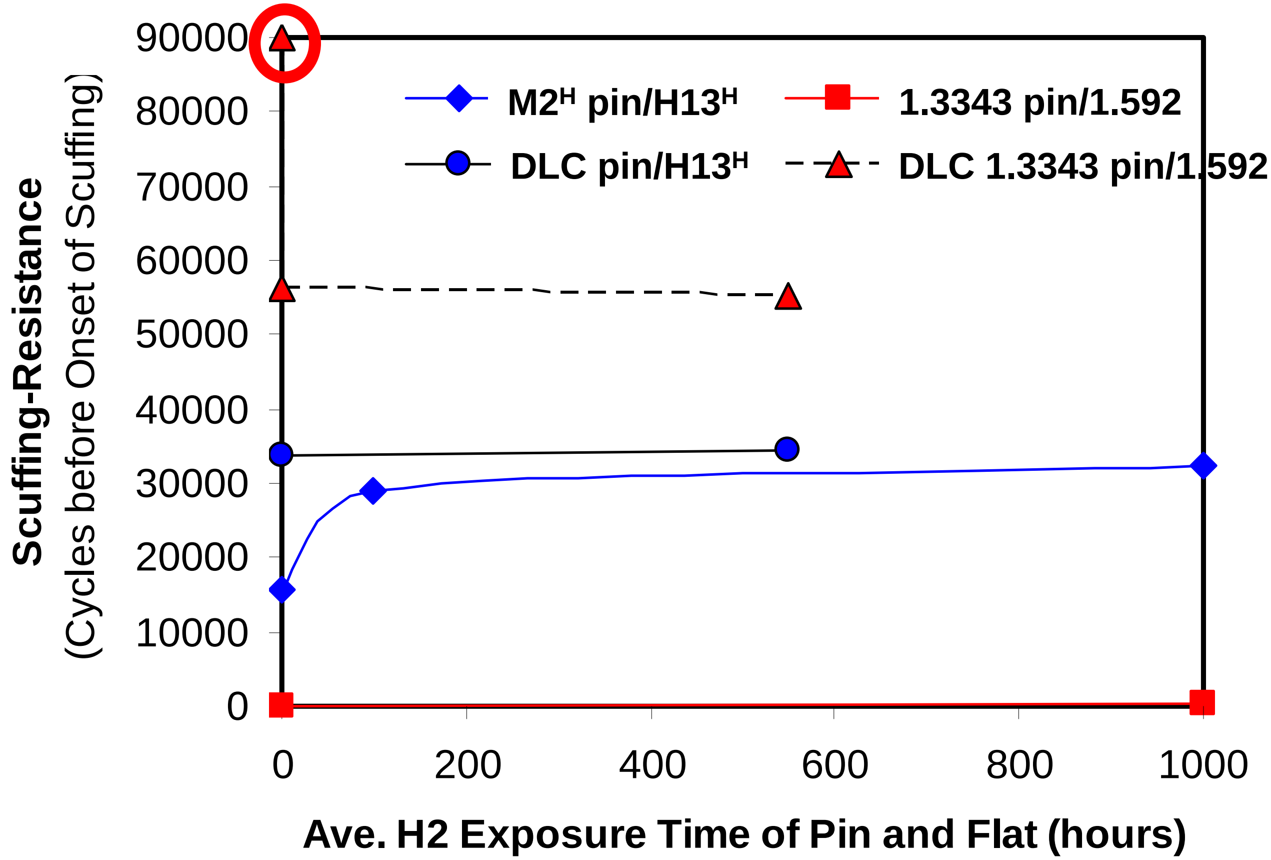
B



Wear marks and surface damage on (A) inner sliding nozzle portion and on (B) inner injector body.

Friction-Wear Results

(Argon, reciprocating, 530 MPa Pin Load)



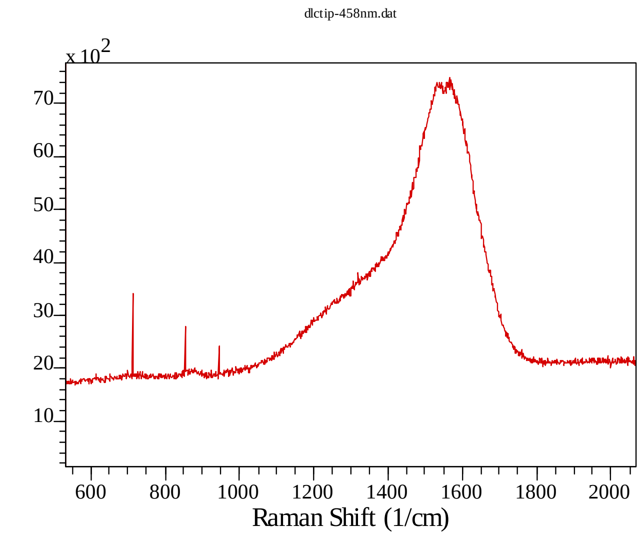
Summary of scuffing-resistance of four material combinations with various hydrogen exposure durations – DLC outperforms by 2-3x ++.

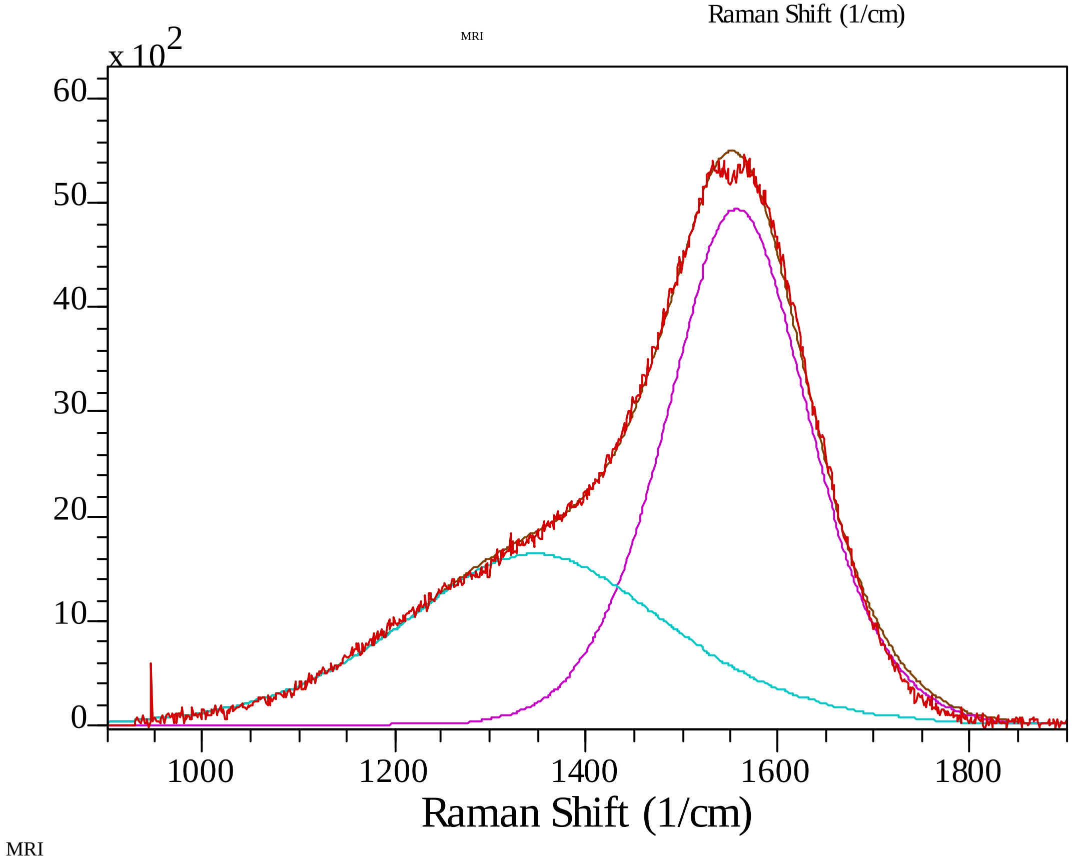
Battelle

Results developed with Peter Blau and Jun Qu/ORNL

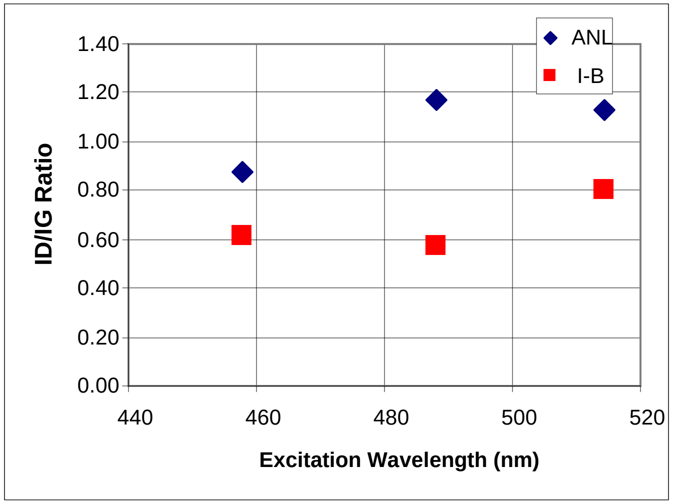
Pacific Northwest National Laboratory
U.S. Department of Energy

I-B DLC Pin
458nm

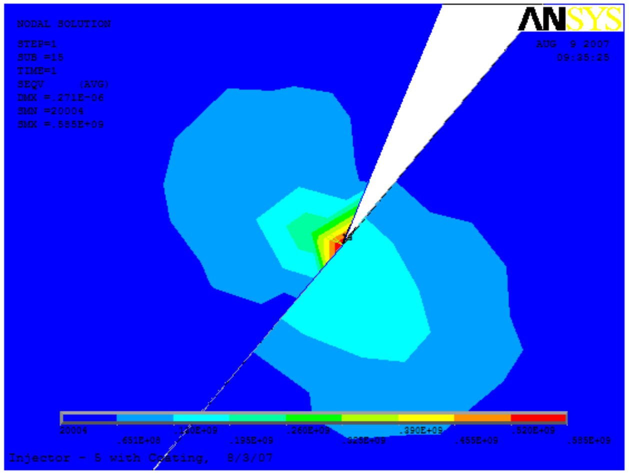


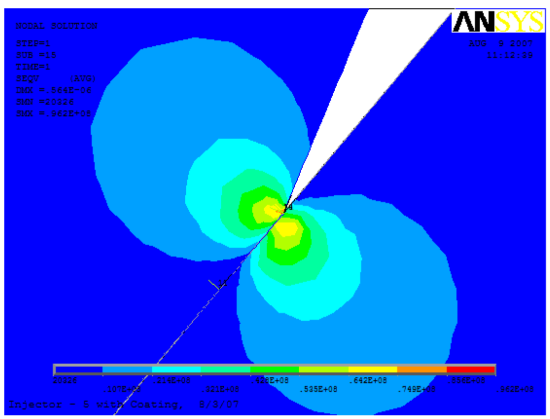


- G and D peaks (1560 and 1360) are due to sp2 sites. G peak: bond stretching of all pairs of sp2 atoms in both rings and chains. D peak: breathing modes of sp2 atoms in rings.
- Raman spectra depend on the following parameters:
  a. clustering of the sp2 phase
  b. bond disorder
  c. presence of sp2 rings or chains
  d. the sp2/sp3 ratio.

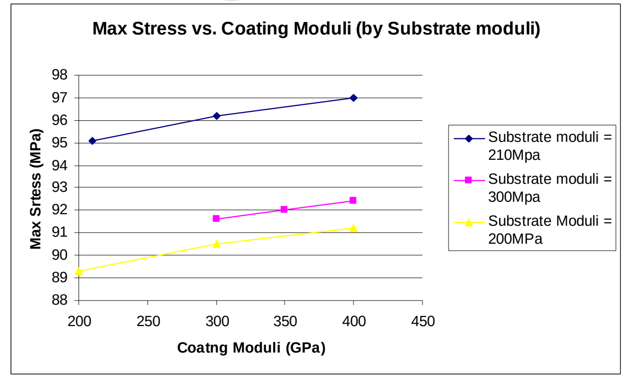


FEA Model to Predicting Performance

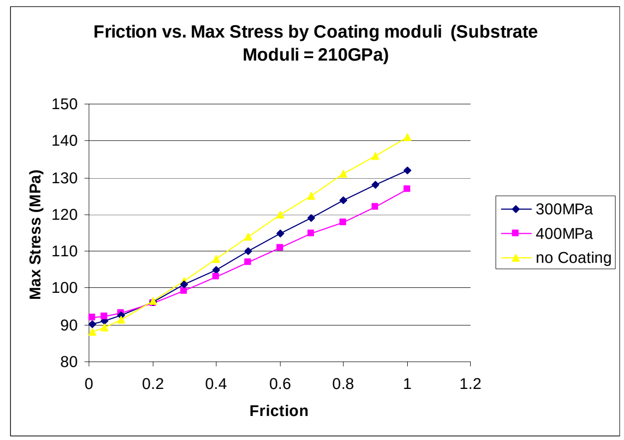




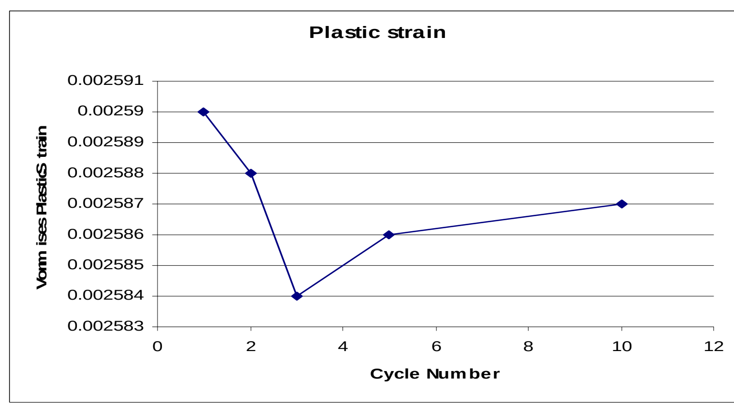
The elastic plastic distribution is defined by a yield stress, coating moduli is set to 300GPa. Maximum stress = 96.2Mpa



Maximum stress versus coating moduli as a function of substrate modulus.



Friction coefficient versus maximum stress as a function of coating property.



von Mises plastic strain versus number of cycles of a 200 MPa substrate.

GEM Student: L. Trinidad, U-Mass Amherst

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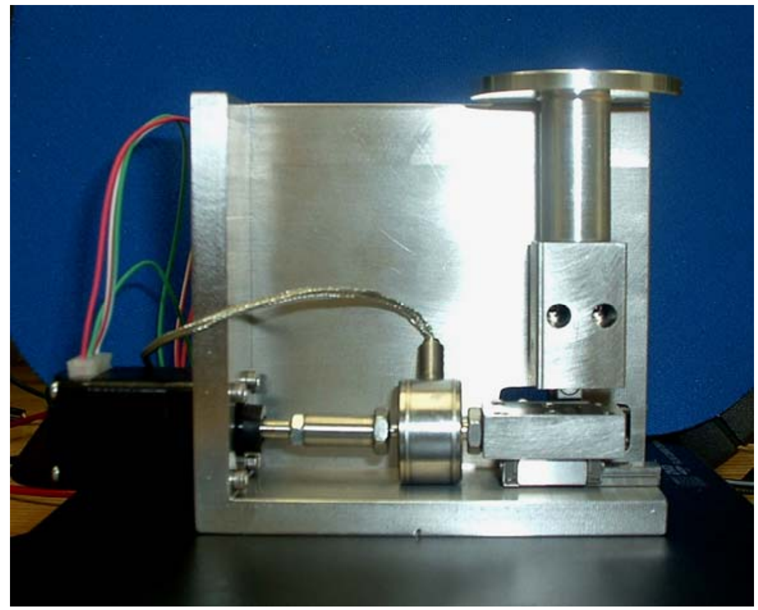
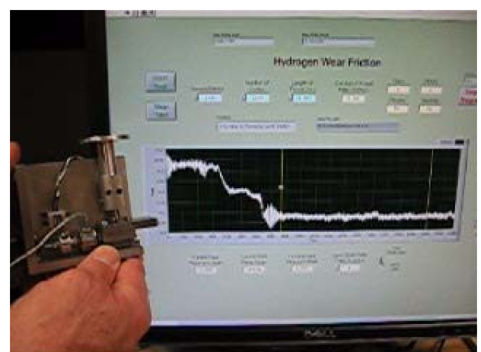
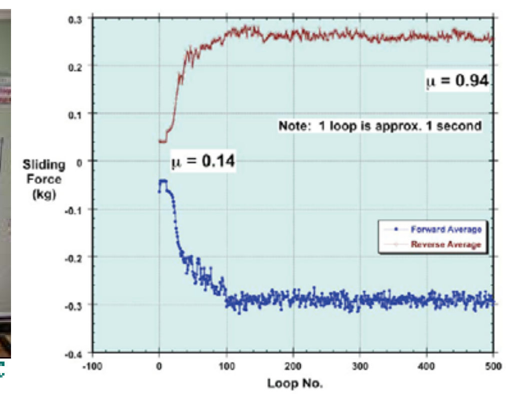
3. *In-situ* hydrogen friction measurements in process on standard materials.

PNNL *In-situ* Friction-Wear Test Instrument

- Measure lateral (frictional) force
- Maximum operating temperature 100C
- Maximum operating pressure: 300 Bar
- Stroke - minimum 0.05 mm, maximum 2.5 mm
- Radius of spherical surface 3 – 12.5 mm
- Applied normal force 100g – 10kg
- Frequency of tests – up to 10 cycles per second
- Device run continuously at 10 cycles per second for *many* days







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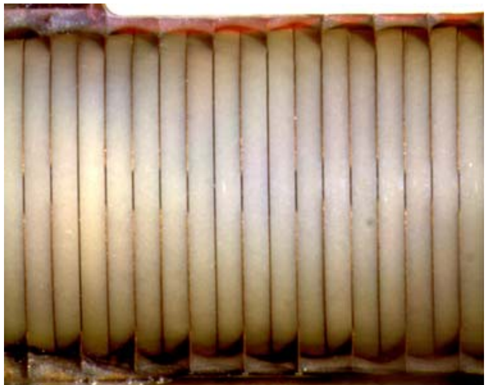
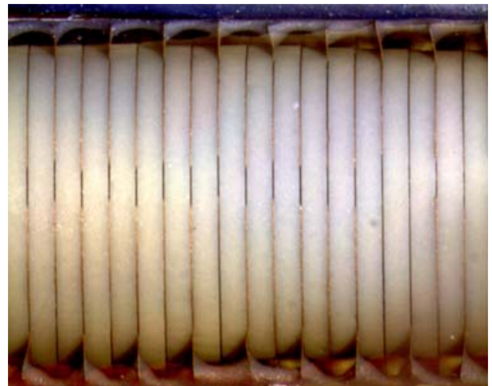
4. Alternative piezo materials development in process.
   1. Initiated collaboration with PI, Germany, samples received.
   2. Initiated collaboration with Morgan Ceramics, no samples.
   3. KCI and PI piezo ceramic diffusion studies in process.

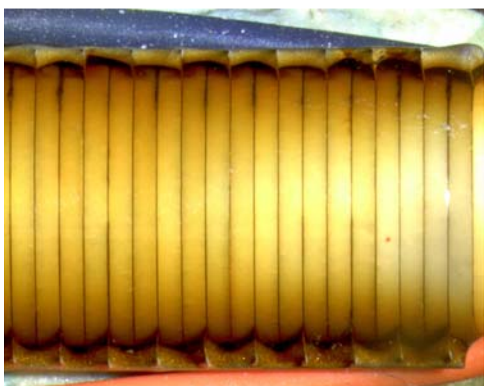
Optical Micrographs – KCI Piezo Actuators



06-5027: RT, N_2



06-5023: RT, H_2



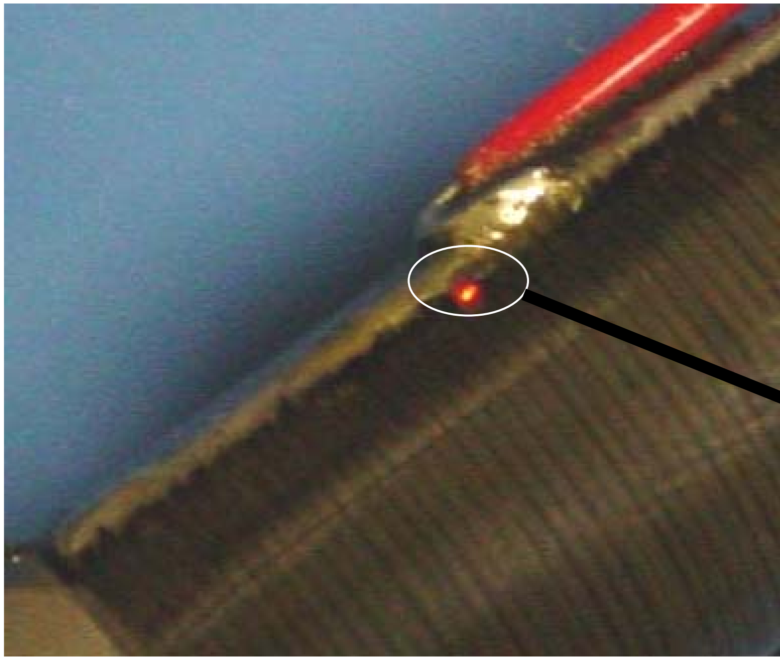
06-5028: 100C, N_2

06-5025: 100C, H_2

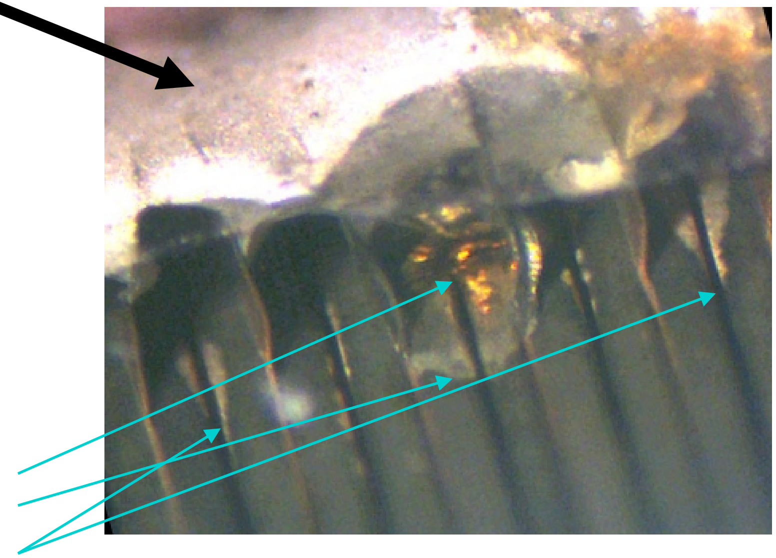
06-5040: 100C,
High Pressure (300 Bar) H_2

All actuators either ran or exposed for 1000 hours under the indicated conditions.

Failure Event/Site



Failure point glowing with 40 mA average input current.



Zone Near Arc Site - Two positive and one negative electrode

Smaller Delaminations starting at negative electrodes

Technology Transfer

1. Established working relationship with Ford Motor Company.
   - Full support of the FMC Alternative Fuels R&D Group.
   - Team meetings 1-2 times per year.
2. Closely coordinate a working relationship with Westport Innovations, Inc.
   - Westport visits PNNL at least 2x per year, monthly updates.
3. Established working relationship with US and International Companies.
   1. Kinetic Ceramics Inc., Hayward, CA. (NDA).
   2. Christopher Tool, OH (NDA).
   3. LE Jones, OH (NDA).
   4. Morgan Ceramics, OH (NDA in process).
   5. Physic Instrument Ceramics, Germany (NDA in process).
   6. DUAP, Switzerland.
   7. Ion-Bond, NY-Switzerland.

Publications, Presentations, Patents

1. Technical Presentations
   - TMS Annual Meeting: "Surface Engineering of Sliding Contacts in the Hydrogen Service Environment", Holbery, 2006.
   - Materials Research Society, Holbery, Fall 2006.
   - ASTM Annual Meeting, Blau, 2007.
2. Ford-DOE Laboratory Colloquium
   - Sandia National Lab, Feb. 11, 2008.
3. Publications
   - App. Phys. Letters, in process.

Future Work –Fiscal Year 2008

1. Complete materials diffusion studies.
   - "As-received" alloys, coated samples (April-May).
   - Piezo ceramic materials (May).
2. Complete coating development test plan.
   - Receive DLC coatings from outside suppliers (April).
   - Complete PNNL nanolaminate sample fabrication (April).
   - Conduct *in-situ* friction and wear studies on coated samples (July).
   - Complete coating structural analysis (August).
3. Input material test data to FEA Coating Modeling Tool (Rev. 2)
4. Complete sliding-impact samples, characterization at ORNL.
   - Samples completed at PNNL.
   - Conduct studies at ORNL – ILA underway (testing July-August).

Summary

1. Injector performance is critical to DI H-ICE performance
   - Potential for significant petroleum displacement via hydrogen exists.
   - DI H-ICE provides a measured approach to utilizing hydrogen as a fue source in the US.
2. PNNL research addresses critical technological challenges in support of H-ICE & DI H-ICE development
   - Materials modeling contributes to the reliability and accuracy in injector actuation to reduce leakage.
     - This applies to other hydrogen ICE parts and systems.
   - Needle-nozzle development has contributed to strategies that minimize the effect of a high-pressure hydrogen service environment.
   - System durability modeling and accelerated test development aid designers and manufactures.
3. Established commercial relationships to insure rapid technology insertion into the commercial sector.