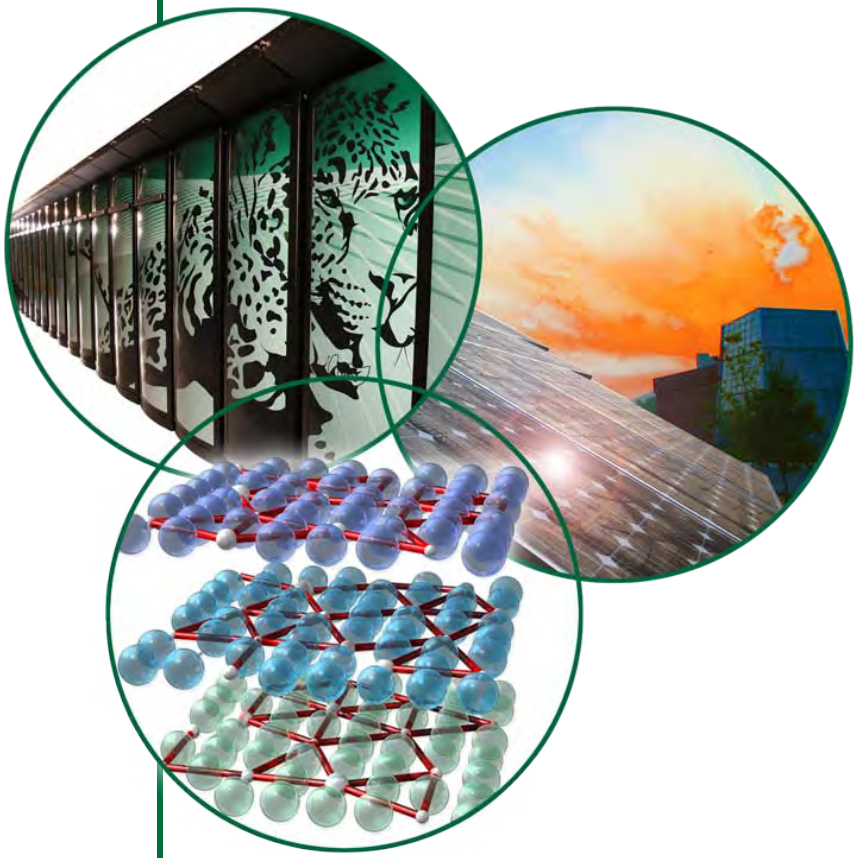
Materials Characterization Capabilities at the High Temperature Materials Laboratory and HTML User Program Success Stories

Project ID: LM028

DOE 2011 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

Edgar Lara-Curzio
HTML User Program
Materials Science and Technology Division
Oak Ridge National Laboratory

Washington, DC
May 13, 2011



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The HTML User Program – Objectives & Relevance

- The HTML is a DOE Designated National User Facility. The Vehicle Technologies Program funds the operation of the HTML User Program to maintain **world-class expertise and instrumentation capabilities for materials characterization** to work with industry, universities and national laboratories to address critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program.
- The HTML User Program capabilities are also being utilized to support Vehicle Technologies Program projects at ORNL in the program's technology areas of Lightweight Materials, Propulsion Materials, Energy Storage, Power Electronics & Electric Motors, Emission Controls and Solid State Energy Conversion.

Overview

Timeline

Project Start Date: 1987
Project End Date: -

Barriers

HTML user projects address cost and technical barriers in most of the Vehicle Technologies Program technology areas.

Partners

During FY2010, the HTML User Program collaborated with 18 companies, 25 universities, and 6 national laboratories on 68 user projects addressing critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program. There were 96 researchers, 63% of them first-time users, who visited the HTML for a total of 716 research days.

The HTML also supports the education and preparation of the next generation of scientists and engineers. During FY2010, students and professors from 25 universities participated in the HTML User Program. **Five** of those students earned their Ph.D. degree and **one** earned her M.S. degree based in part on research they conducted through the HTML User Program.

Budget

The FY2010 budget for the HTML was $5,312,400

- $881,959 for capital equipment purchases
- $4,430,441 for the operation of user program

Users cost-share user projects through:

1. direct involvement with HTML staff members during the development of the user project;
2. funding their time and travel to the HTML
3. costs of materials provided by the user and the research performed prior to the user project;
4. subsequent collaboration with HTML staff members to analyze and publish the results.

HTML User Program – FY2010 Participating Organizations

Industry	Universities		National Labs
• Applied Sciences, Inc. • Atriax Components, Inc. • Btechcorp. • Capstone Turbine Corp. • Chromalloy • Corning Incorporated • Cummins, Inc. • Fiberforge • General Motors R&D • GrafTech Int'l Holdings • Hans Tech • II-VI Incorporated • Magnesium Elektron NA • Marlow Industries, Inc. • Metalsa Roanoke, Inc. • The Timken Company • Triton • UOP, LLC	• Columbia • Georgia Tech • MIT • Michigan State • New Jersey Tech • Ohio State • Pennsylvania State • Purdue • SUNY, Stony Brook • Tennessee Tech • Virginia Commonwealth • Worcester Polytechnic	**University of:** • Alabama-Birmingham • Connecticut • Florida • Kentucky • Massachusetts-Amherst • Michigan • Minnesota • Missouri-St. Louis • New Mexico • Tennessee-Knoxville • Texas-Austin • Texas-San Antonio • Wyoming	• ORNL • BNL • NREL • National Res. Council, Canada • PNNL • Sandia Nat. Laboratories

2010: 18 industry, 25 university, 6 nat. labs

Approach

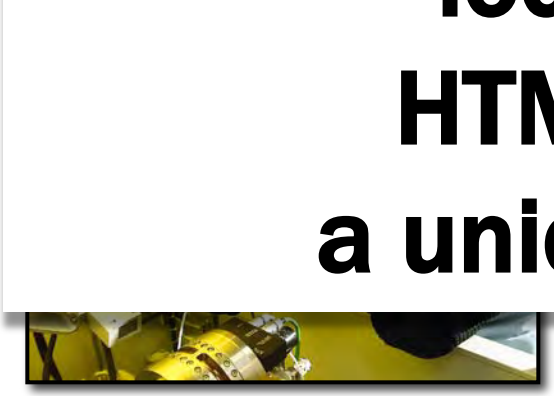
The HTML is organized into 6 User Centers,

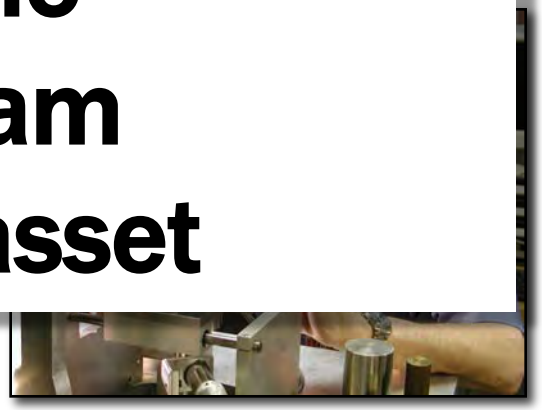
which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization



The concentration of these capabilities and expertise in one location make the HTML User Program a unique national asset

on



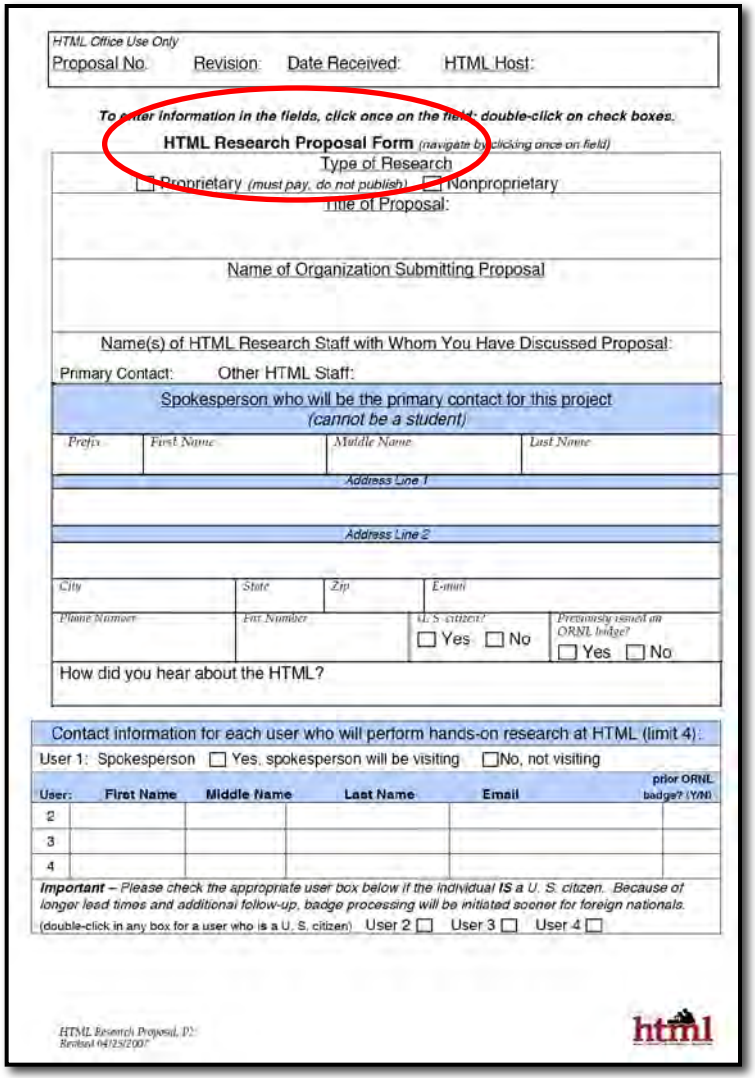


Residual Stresses

Thermography & Thermophysical Properties

Tribology Research

Approach: Access to the HTML



HTML Office Use Only
Proposal No. Revision: Date Received: HTML Host:

To enter information in the fields, click once on the field; double-click on check boxes.

HTML Research Proposal Form (navigate by clicking once on field)

Type of Research
☐ Proprietary (must pay, do not publish) ☐ Nonproprietary

Title of Proposal:

Name of Organization Submitting Proposal

Name(s) of HTML Research Staff with Whom You Have Discussed Proposal:

Primary Contact: Other HTML Staff:

Spokesperson who will be the primary contact for this project (cannot be a student)

Prefix	First Name	Middle Name	Last Name

Address Line 1

Address Line 2

City	State	Zip	E-mail

Phone Number	Fax Number	U.S. citizen?	Previously issued an ORNL badge?
		☐ Yes ☐ No	☐ Yes ☐ No

How did you hear about the HTML?

Contact information for each user who will perform hands-on research at HTML (limit 4):

User 1: Spokesperson ☐ Yes, spokesperson will be visiting ☐ No, not visiting

User:	First Name	Middle Name	Last Name	Email	prior ORNL badge? (Y/N)
2					
3					
4					

Important – Please check the appropriate user box below if the individual IS a U. S. citizen. Because of longer lead times and additional follow-up, badge processing will be initiated sooner for foreign nationals.

(double-click in any box for a user who is a U. S. citizen) User 2 ☐ User 3 ☐ User 4 ☐

HTML Research Proposal, P2:
Revised 04/25/2007

html

- Access to the HTML User Program is provided through a formal proposal process. Proposals are reviewed by an internal review committee and evaluated based on
  - Technical merit
  - Relevance of the proposed research to the mission of the Vehicle Technologies Program
  - Non-competition with the private sector
  - Organizations based in the U.S.
- Research is completed within 24 months, and it involves one or more user visits to the HTML.

A user agreement (proprietary or non-proprietary) is required prior to starting a user project.

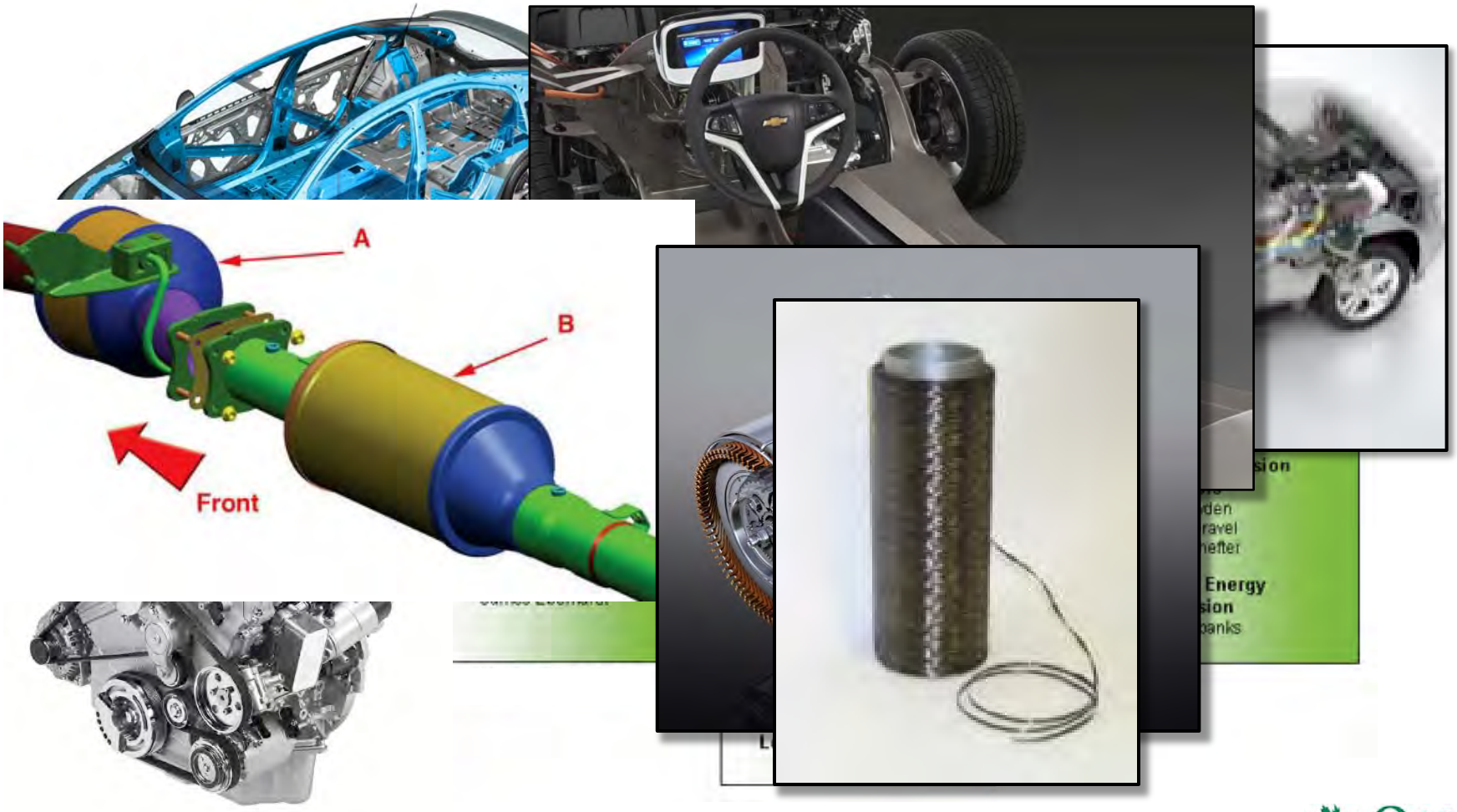
Performance Goals and Milestones

Milestone for FY10		
1	Perform characterization of catalytic materials at elevated temperatures using the HTML's Aberration Corrected Electron Microscope.	✓

One milestone for the HTML User Program in FY2011 is to complete three user projects on the characterization of lightweight and lightweighting materials.

Project ID	Organization	Project	Status	
2010-018	Atriax Components Inc.	Characterization of corrosion in heavy vehicle compressor components: Mg and Al casting and Al-MMC cylinder liner interface	Completed	✓
2010-027	Virginia Commonwealth University	Characterization of lightweight materials for automotive applications	Completed	✓
2010-028	University of Alabama-Birmingham	Effect of chemistry on the transformation characteristics of metastable austenite in intercritically austempered ductile iron for automotive applications	Completed	✓

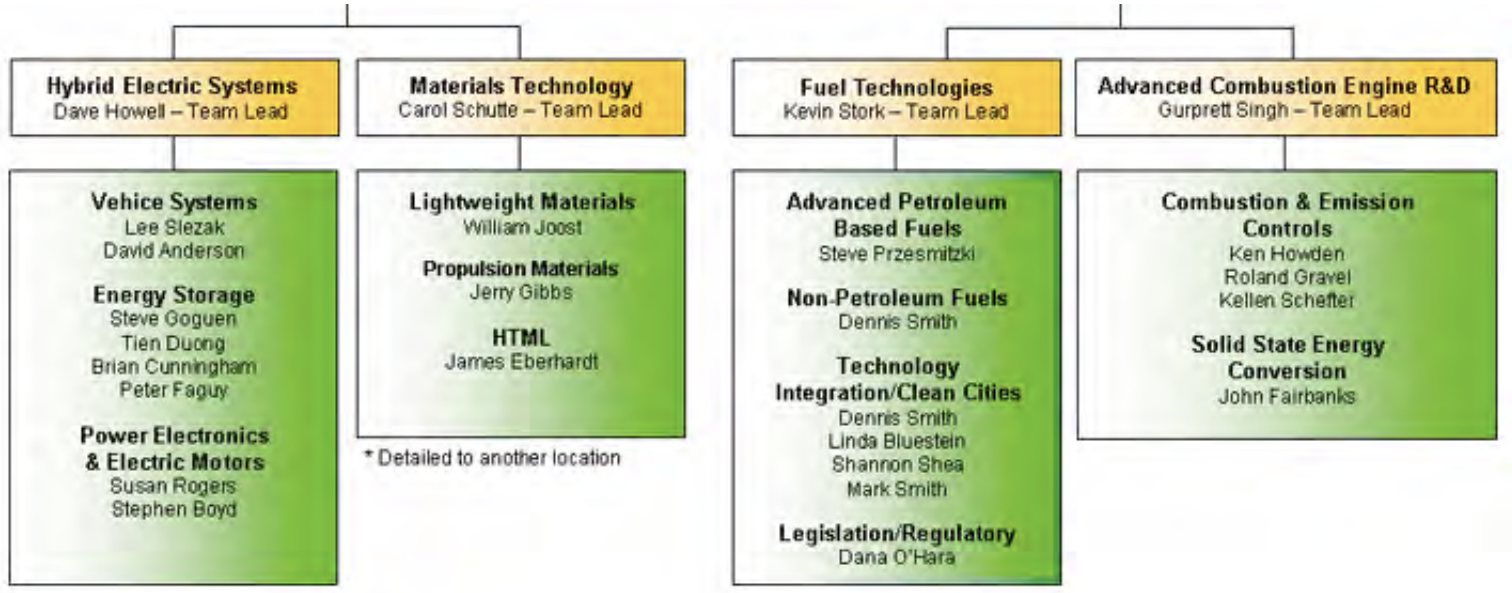
The HTML User Program - Accomplishments



The HTML User Program - Accomplishments

Examples of User Projects

Vehicle Technologies Program



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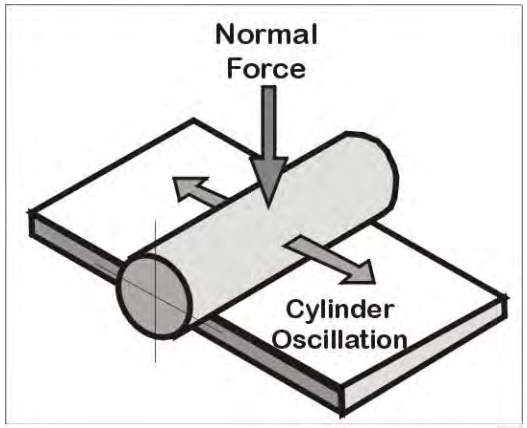
User Project with Virginia Commonwealth University "Surface treatment of dies for high strength steel forming"

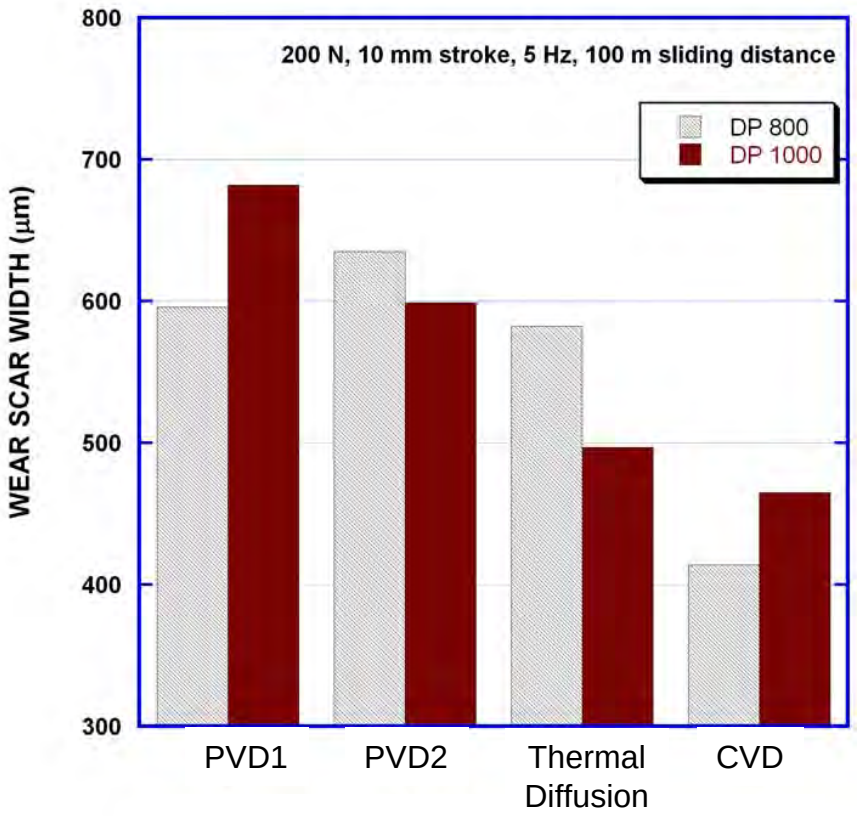
Research problem	To determine the relative wear resistance of coated and surface-treated die materials for use in forming high strength, automotive steel sheet materials.
Technical approach	Utilized equipment for tribological measurements and microscopy to characterize worn surfaces.
Implications	Reduced material cost and increased die surface durability in metal stamping processes for high strength, dual-phase steels for lightweight automotive components.
Barriers	Cost, Manufacturing
Collaborators	**VCU Users**: Professor Muammer Coç and Dr. Omer Cora, Virginia Commonwealth University **HTML Staff**: Peter Blau, Kevin Cooley

Dr. Omer Cora (VCU) preparing a test using a reciprocating cylinder-on-flat configuration .

User Project with Virginia Commonwealth University "Surface treatment of dies for high strength steel forming"



- Cylinder-on-flat configuration under high contact forces.
- Two sheet steels, (DP 800 and DP 1000) were used as sliding partners against surface treated cylinders of die material.
- Die material: Type DC53, 8%Cr, 2%Mo, 1%C, 1%Si, 0.4%Mn, 0.3% V.



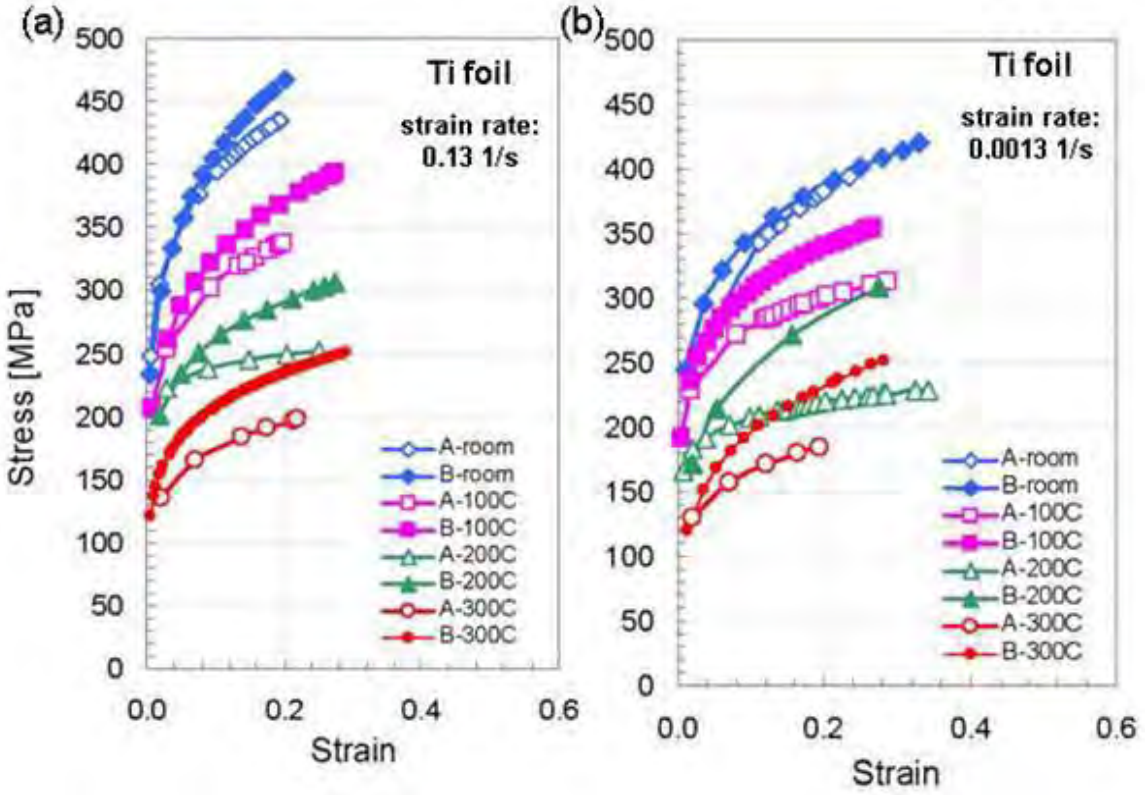
Surface Treatment

User Project with Virginia Commonwealth University "Characterization of ultrasonically consolidated Ti-Al laminates"

Research problem	To evaluate the mechanical properties of thin sheet lightweight metals, and to understand the stresses induced within lightweight composite alloys before and after warm hydroforming.
Technical approach	Utilized X-ray diffraction to quantify residual stresses and an electromechanical testing machine to determine the tensile behavior of laminates as a function of rolling direction, temperature and strain rate.
Implications	Understanding the behavior of lightweight materials under certain forming conditions that will lead to determining their optimal forming limits as well as their requirements for mass production conditions.
Barriers	Cost, Manufacturing
Collaborators	**VCU Users**: İrfan Kaya and Muammer Coç, Virginia Commonwealth University **HTML Staff**: Rosa Trejo, Tom Watkins, Chris Stevens

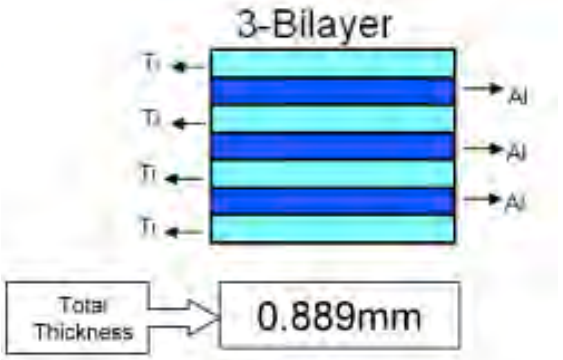
User Project with Virginia Commonwealth University "Characterization of ultrasonically consolidated Ti-Al laminates"

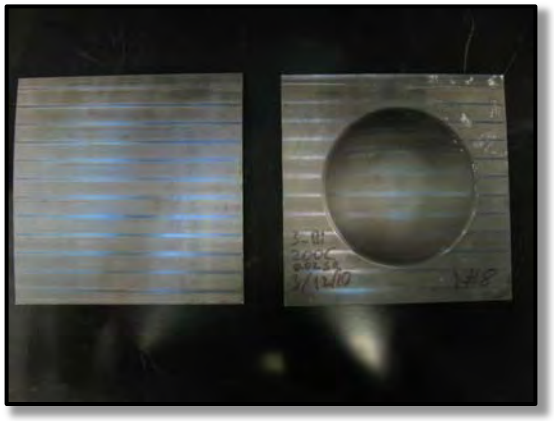
VCU's İrfan Kaya mounting a sample for high temperature tensile testing



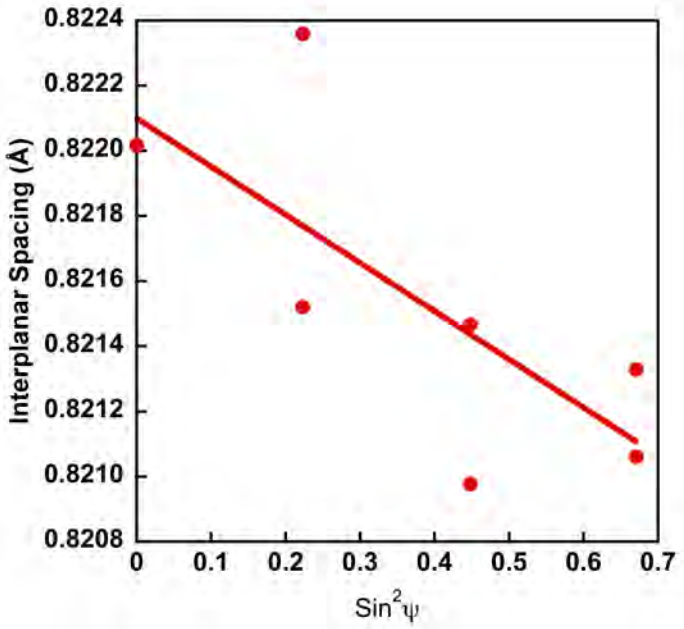
Stress-Strain curves of thin Ti foil tested at (a) 0.13 1/s and (b) 0.0013 1/s. Samples were obtained (Type A) and normal (Type B) to the rolling direction.

User Project with Virginia Commonwealth University "Characterization of ultrasonically consolidated Ti-Al laminates"





Warm-hydroformed (200°C at a strain rate of 0.02/s), ultrasonically welded Ti-Al LMC (by Solidica Inc.)



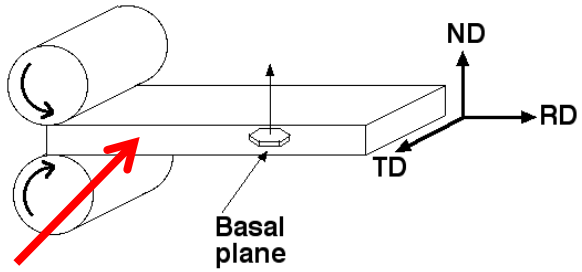
The interplanar spacing as a function of $\sin^2\psi$, where ψ is the tilt angle at the center of the warm hydroformed portion of the sample. The spacing between the planes decreases with increasing square of the sine of the tilt angle, which indicates compression.

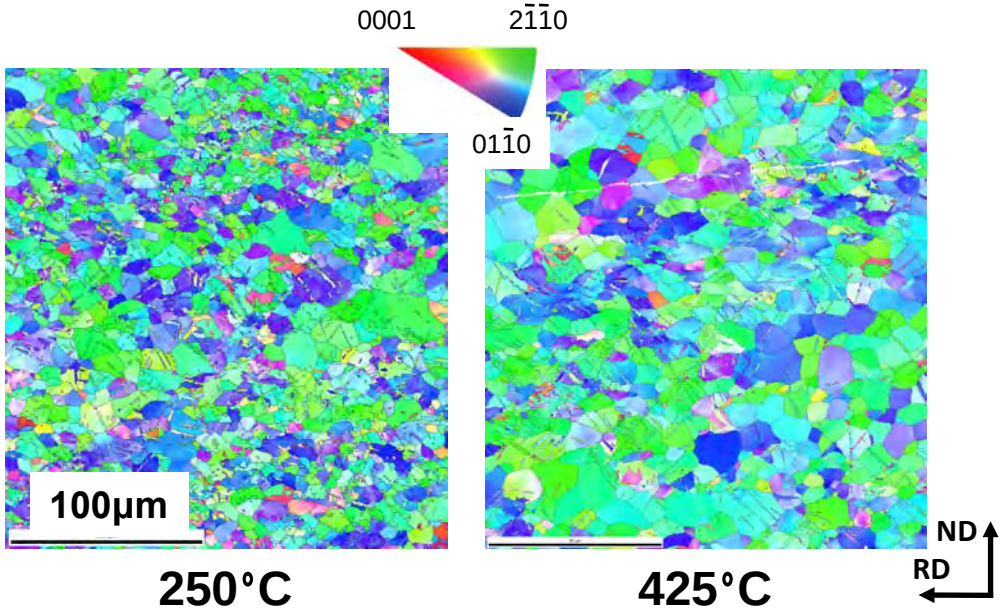
User Project with Magnesium Elektron NA **"Texture in asymmetrically rolled magnesium alloys"**

Research problem	To assess the influence of asymmetric shear rolling on the texture and microstructure of Mg sheet alloys (AZ31B and ZEK100) and in turn on their their formability.
Technical approach	Utilized X-ray diffraction and electron backscattered diffraction techniques to characterize microstructure and texture.
Implications	The development of methods for the cost-competitive production of automotive structures using magnesium alloys.
Barriers	Cost, manufacturability, lack of knowledge of advanced material properties and performance characteristics
Collaborators	**Magnesium Elektron User**:David Randman, **HTML Staff**:Tom Watkins, Ed Kenik, Don Erdman, Burl Cavin, Edgar Lara-Curzio

David Randman from Magnesium Elektron setting up a test in the X-ray Diffractometer

User Project with Magnesium Elektron NA "**Texture in asymmetrically rolled magnesium alloys"**





- Alloys AZ31B and ZEK100 processed by shear rolling under different preheat temperatures and reduction ratios
- Asymmetric rolling resulted in a weaker basal texture under all temperature conditions and rolling schedules
- Basal={0002} poles were observed to be tilted along the RD but toward the trailing edge.
- Rolling at lower temperatures resulted in cracking.
- Rolling at low temperatures results in shear band and recrystallization; at higher temperatures, grain growth.

Magnesium Elektron continues using the wide array of materials characterization capabilities available to industry users through the HTML User Program to develop methods for the cost-competitive production of automotive structures using magnesium alloys

HTML User Project with Fiberforge:
"Crashworthiness of glass fiber reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process"

FIBERFORGE
Lightweighting Your World

Research problem	To assess the feasibility of adhesively bonding hat-section profiles to produce composite tubular structures with high energy absorption
Technical approach	Utilized the Test Machine for Automotive Crashworthiness and infrared imaging to determine the energy absorption of glass fiber-reinforced thermoplastic tubular structures. Tests were performed at different strain rates on specimens having different matrices and fiber architectures
Implications	The availability of structural materials for body and chassis applications that can significantly reduce the weight of passenger vehicles without compromising lifecycle cost, performance, safety or recyclability.
Barriers	Cost, Manufacturability, Performance, Joining
Collaborators	**Fiberforge Users**: Benjamin Hangs and Andrew Burkhart **HTML Staff**: Don Erdman, Mike Starbuck, Ralph Dinwiddie

Benjamin Hangs and Andrew Burkhart of Fiberforge reviewing the results from a TMAC test

HTML User Project with Fiberforge:

"Crashworthiness of glass fiber reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process"

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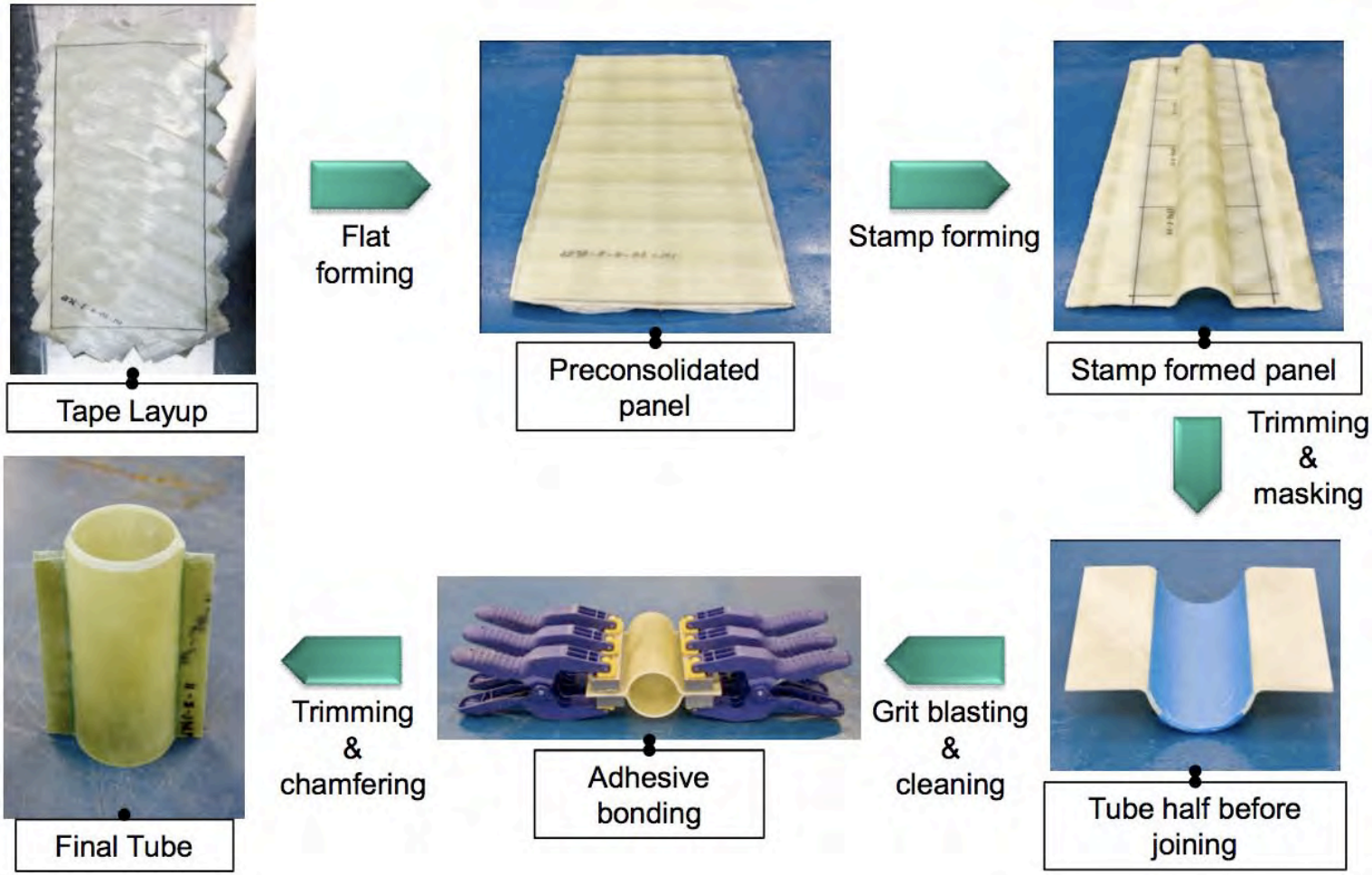
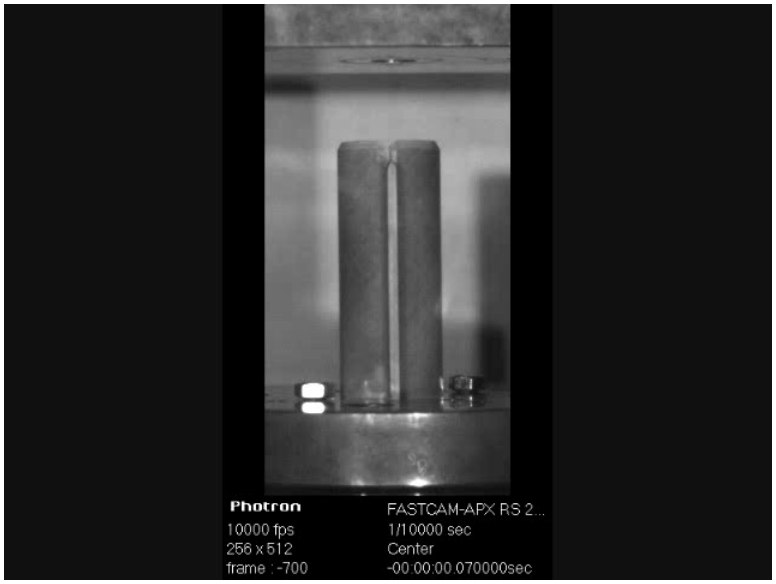
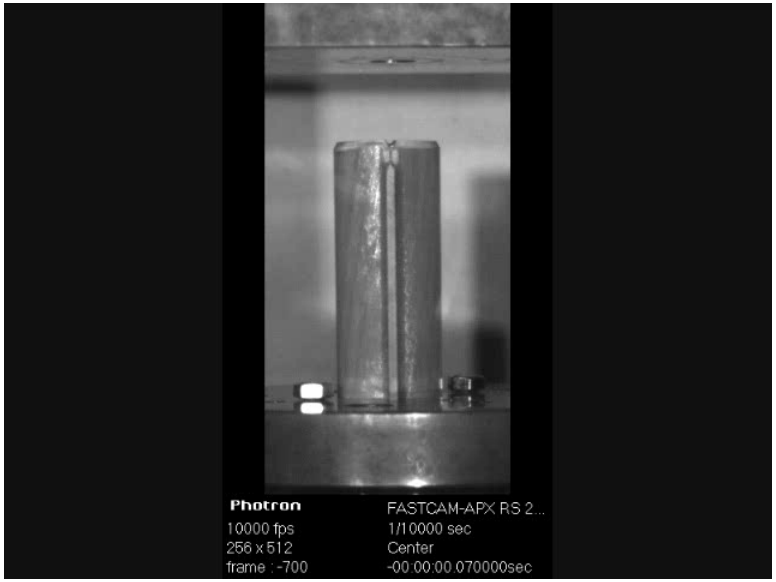
Lightweighting Your World







Tests were carried out at ambient conditions using ORNL's Test Machine for Automotive Crashworthiness (TMAC) at a crosshead speed of 4m/s.

HTML User Project with Fiberforge:

"Crashworthiness of glass fiber-reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process"

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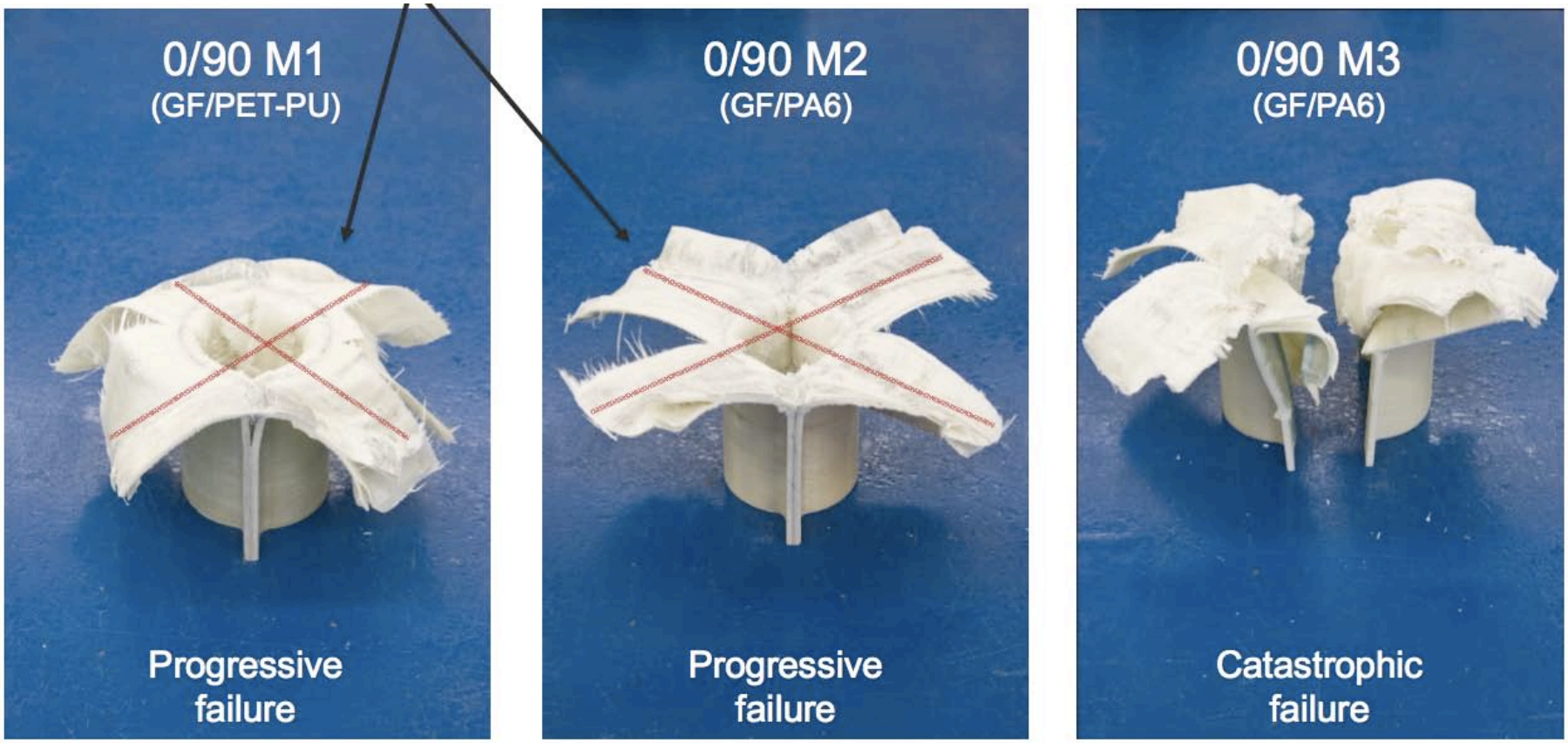

Tests were carried out at ambient conditions using ORNL's Test Machine for Automotive Crashworthiness (TMAC) at a crosshead speed of 4m/s.

HTML User Project with Fiberforge:

"Crashworthiness of glass fiber reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process"

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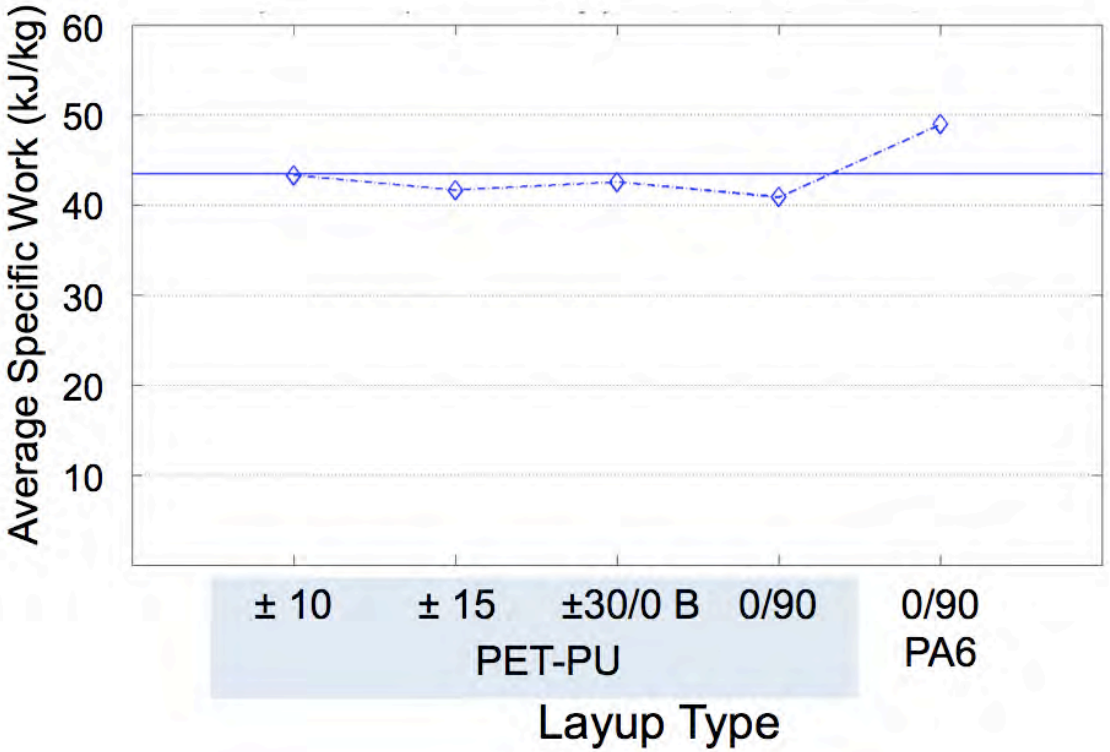
- Specific energies up to 43 kJ/kg were obtained for PET-PU matrix composite tubes
- Specific energies of up to 50kJ/kg were obtained for GF/PA6 matrix composite tubular structures
- These results demonstrate the potential of Fiberforge composite structures for energy management in automotive applications that could result in reduced vehicle weight, increased fuel economy, and better safety during crashes



Metalsa
Quality as a way of life

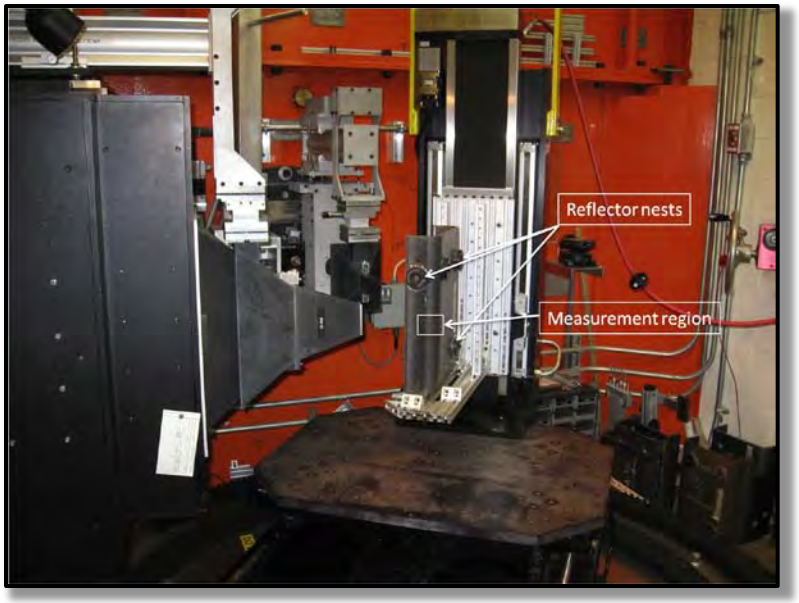
HTML User Project with Metalsa

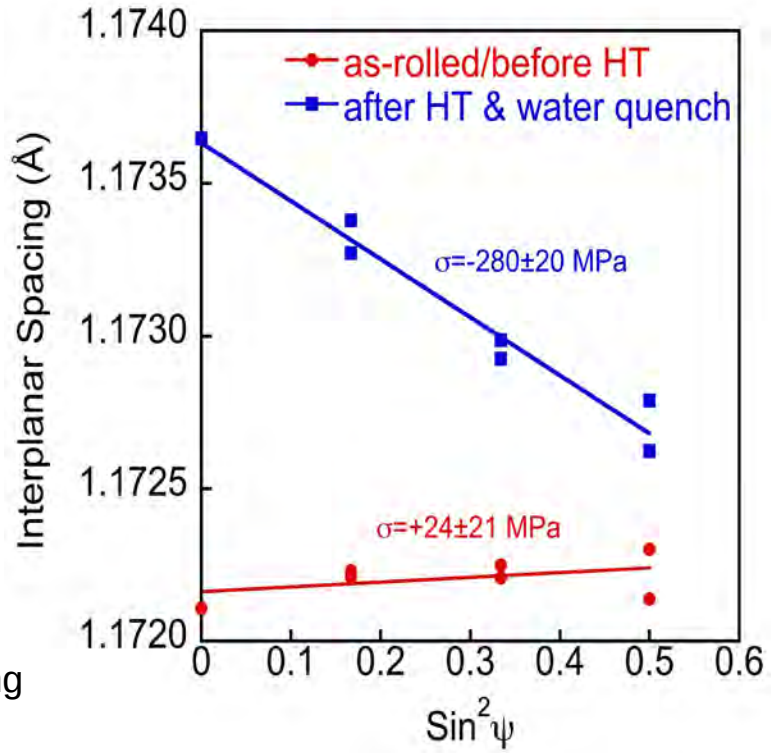
"Quenching Stresses and Distortions in Vehicular Structures"

Research problem	To assess and understand the thermal and transformation stresses induced in vehicle side-rails before and after quenching as a function of both plate thickness and steel supplier.
Technical approach	Collect X-ray and neutron diffraction data at the HTML User Program's neutron residual stress facility (NRSF2) as a function of heat treatment and steel supplier. Determined texture using X-ray diffraction.
Implications	Improved understanding of the origins of shape distortion will guide adjustments to the metals specifications and manufacturing processing to minimize distortion, reduce re-work, and improve process efficiency, helping to meet DOE's goal of reduced energy consumption during manufacture and improved reliability of vehicular components.
Barriers	Cost, manufacturability, durability.
Collaborators	**Metalsa User**: Joaquin del Prado Villasana **HTML Staff**: Camden Hubbard, Josh Schmidlin and Thomas Watkins

Metalsa's Joaquin del Prado Villasana prepares for an X-ray diffraction measurement

HTML User Project with Metalsa
"Quenching Stresses and Distortions in Vehicular Structures"





- Twelve C-shaped channels 14" long, representing three thicknesses, two suppliers, and two stages of processing were examined.
- The through-thickness stresses for the as-rolled samples show little variation with depth, while the heat-treated and quenched C-channels exhibit considerable residual stress.
- Metalsa has begun analyzing the measured data and will use these results to determine the process adjustments needed to reduce distortion, leading to efficiencies in both production and energy use.

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User Project with NRC Canada

"Determination of residual stresses in V6 engine block"

National Research Council Canada

Research problem	To understand residual stresses in aluminum web and iron liners of a V6 engine block and their impact on distortion.
Technical approach	Utilize neutron and X-ray diffraction techniques to obtain a distribution of residual stresses around and between cylinders.
Implications	By measuring residual stresses as a function of heat treatment and processing conditions, it will be possible to understand the origins of undesirable distortions in engine blocks and develop strategies to prevent them.
Barriers	Manufacturability
Collaborators	**Users**: Dimitry Sediako, NRC-Canada **HTML Staff**: Camden Hubbard

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GM

OAK RIDGE National Laboratory

User Project with NRC Canada

"Determination of residual stresses in V6 engine block"

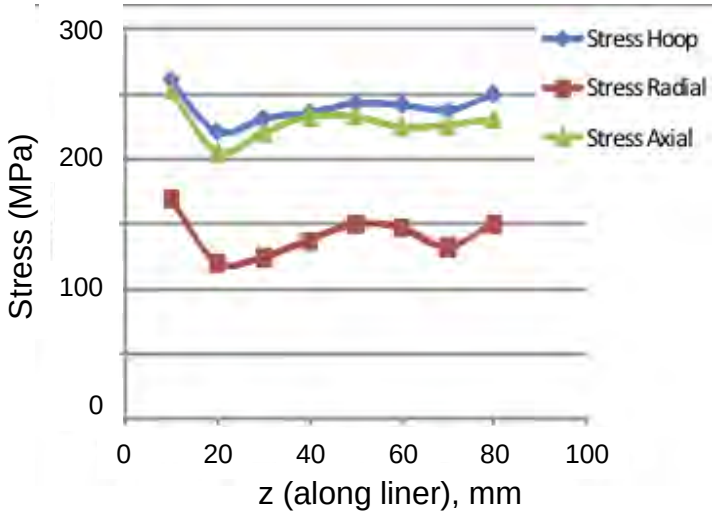
National Research Council Canada

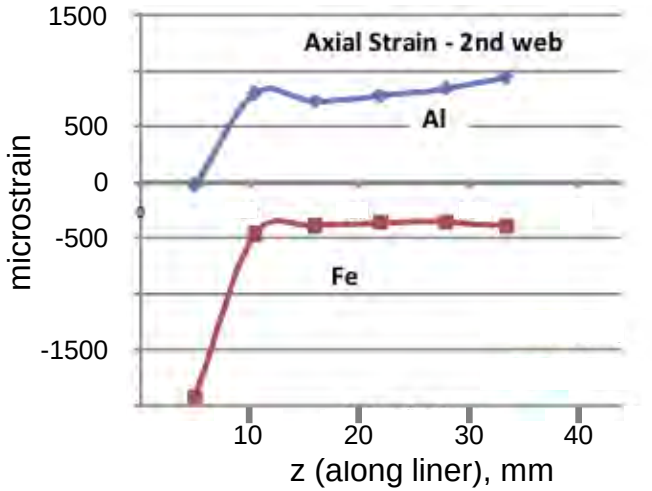
- GM 3.6L V6 gasoline engine block.
- Al 319 (Al-Si-Cu alloy) sand casting around Fe-liner cylinder inserts. The engine block is subsequently given a T7 heat treatment.
- Residual stresses along and between the Fe liners induce undesirable distortions and are a critical factor in determining the quality of the final product.

User Project with NRC Canada

"Determination of residual stresses in V6 engine block"

National Research Council Canada





- Values of stress in the Al were found to exceed the alloy's tensile yield stress. This suggests that while the Fe liners prevent fracture of the Al at the interbore regions, a high build-up of stress in the Fe liners and Al occurs, which results in dimensional distortions.
- The impact of variations in casting practices (e.g. cooling/solidification rate) on grain size and residual stress level is being considered for future studies

User Project with Cummins

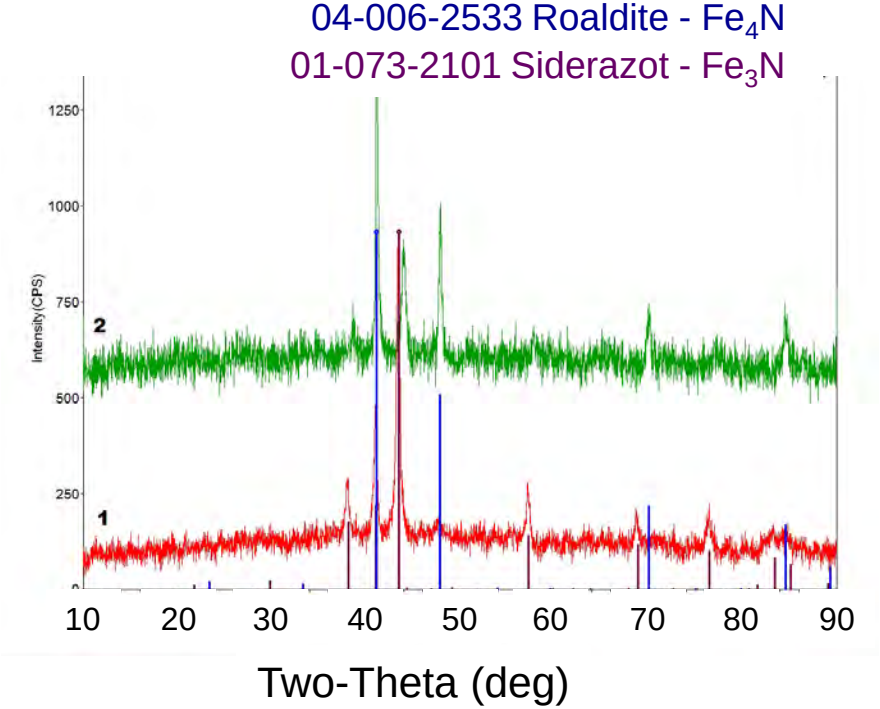
"Structure Property Relations for Different Nitriding Processes"

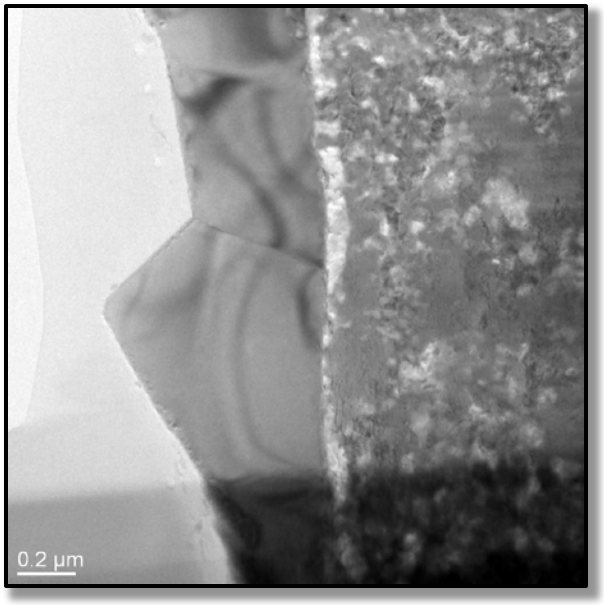
Research problem	Determine the differences between white layers from two different nitriding processes.
Technical approach	Utilized X-ray diffraction, transmission electron microscopy, and nanoindentation to characterize the nitrided layers.
Implications	Nitriding is an important industrial process that needs to be better understood.
Barriers	Lack of knowledge of advanced materials properties and performance characteristics. Changing internal combustion engine combustion regimes
Collaborators	**Users**: Madeleine Smith and Lisa Behrens **HTML Staff**: Tom Watkins, Larry Allard, Rosa Trejo

Madeleine Smith and Lisa Behrens of Cummins mounting a test specimen for X-ray diffraction measurements

User Project with Cummins

"Structure Property Relations for Different Nitriding Processes"





- X-ray diffraction and transmission electron microscopy are being used to identify the crystallographic phases in the while layer and their morphology. Nanoindentation is being used to determine their hardness and elastic modulus.
- By establishing structure-property relationships it will be possible to identify the optimum nitriding process for engine components.

User Project with Atriax

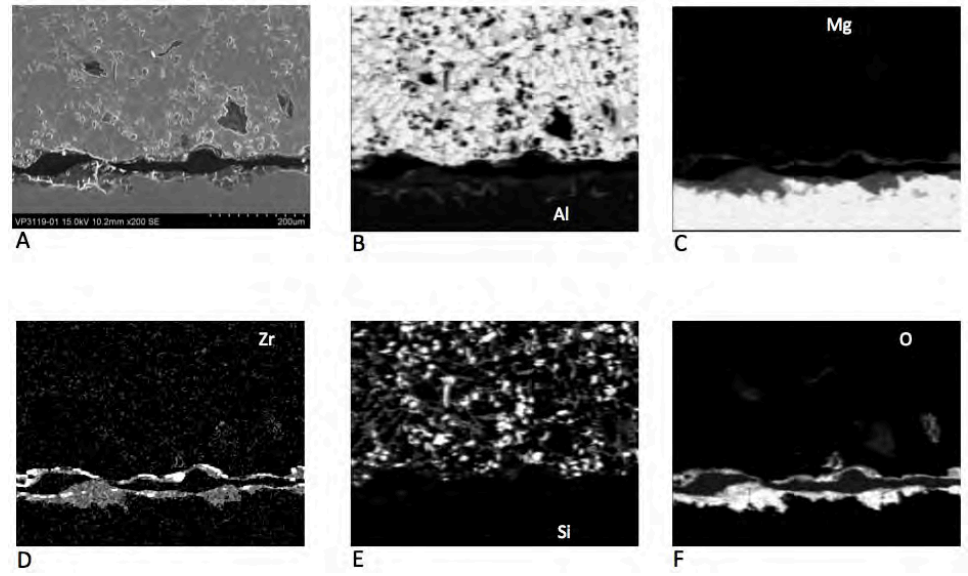
"Corrosion in magnesium compressor housings"

Research problem	To assess and understand the nature and cause of apparent corrosion and casting defects between the cast Mg housing and the aluminum (A359) metal matrix composite (MMC) cylinder liner.
Technical approach	Utilized X-ray diffraction and electron microprobe analyses for chemical and phase identification.
Implications	Understanding the interactions between magnesium castings and dissimilar materials.
Barriers	Cost, Manufacturing, Durability
Collaborators	**Atriax Users**: Mike Black and David Weiss, Atriax **HTML Staff**: Thomas Watkins and Larry Walker

Davis Weiss of Atriax placing a test specimen in an X-ray diffractometer.

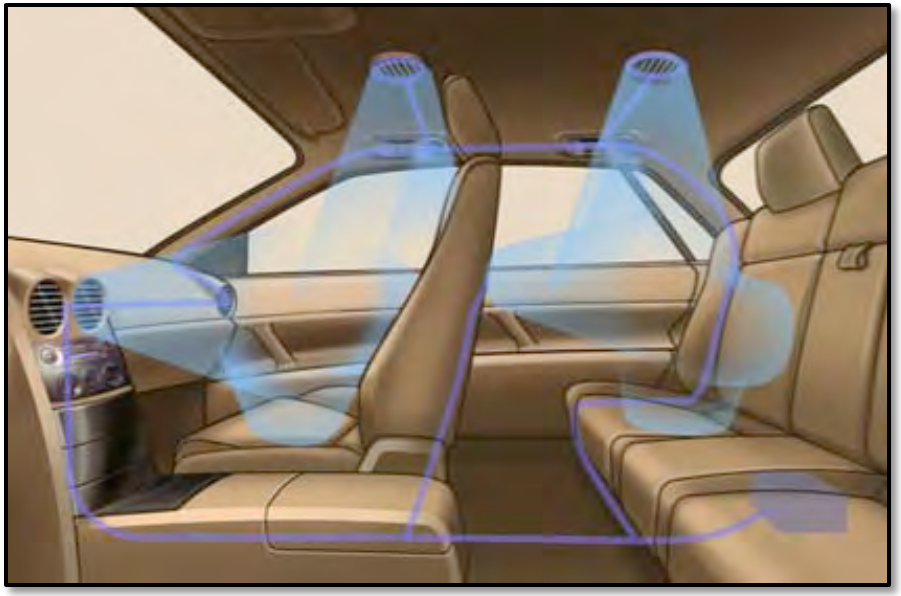
User Project with Atriax

"Corrosion in magnesium compressor housings"



- Analysis of the interface between the AZ91 block and the Al MMC liner (SiC particulate + Ni-coated graphite particulate) using XRD identified the presence of silicon, aluminum, Mg_2Al, SiC and $NiAl_3$.
- Elemental maps using electron microprobe revealed the presence of Zr and O at that interface, possibly from a liquid dye penetrant, which might have facilitated corrosion.
- Cast A356 aluminum blocks with the same liner had no corrosion or interfacial issues.
- Lessons learned regarding the use of dye penetrants for inspection.

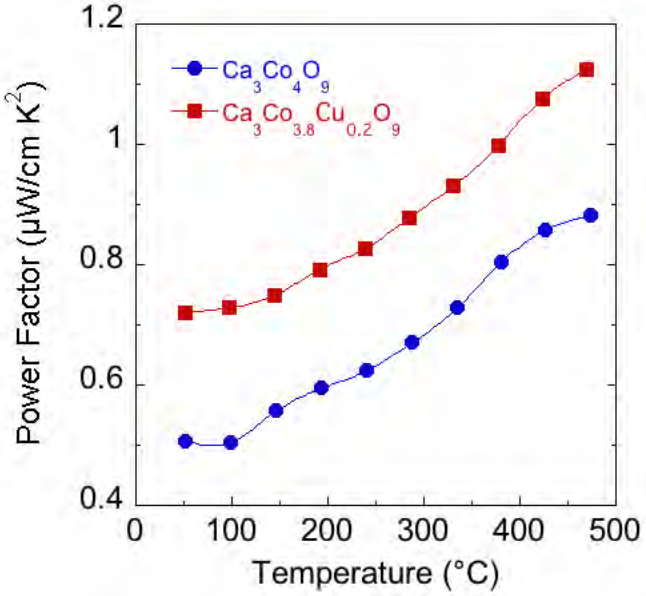
HTML User Program projects on characterization and evaluation of materials for solid-state energy conversion

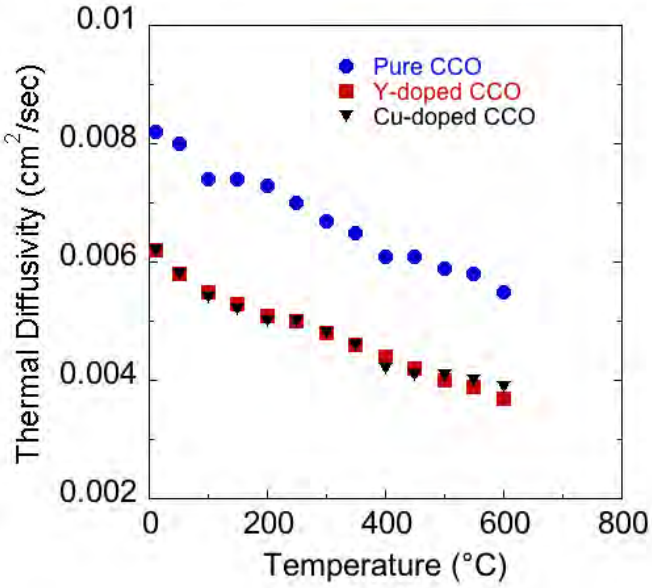


http://www.sae.org/mags/aei/6384

Effective use of waste heat from combustion engines would significantly increase overall engine efficiency and reduce emissions. The use of thermoelectrics for HVAC systems could result in additional fuel savings and reductions in GHG emissions.

HTML User Program Projects on Thermoelectrics

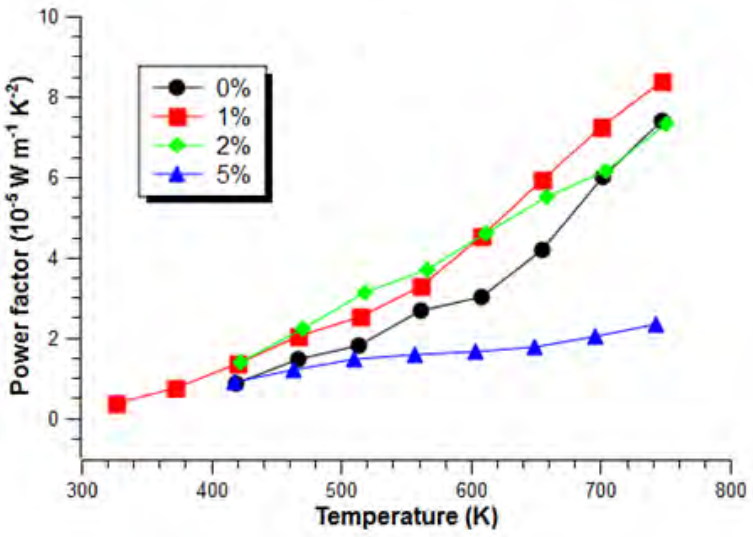


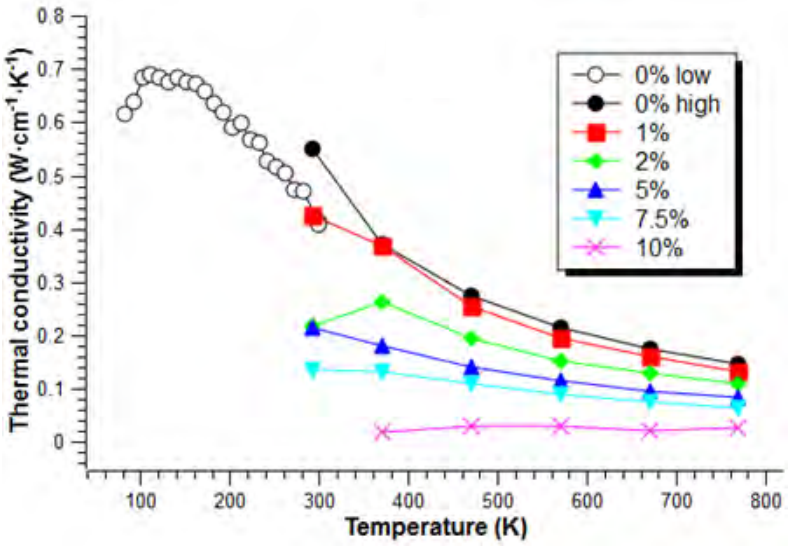


- The effect of Cu and Y doping on the thermoelectric properties of $Ca_3Co_4O_9$.
- Cu additions result in a significant increase in power factor caused by a reduction in electrical resistivity.
- Cu- and Y-doped doped $Ca_3Co_4O_9$ exhibited lower thermal diffusivity than $Ca_3Co_4O_9$.
- Doped $Ca_3Co_4O_9$ compounds exhibit greater ZT factor

Collaborators	**NJIT Users**: Dr. Trevor Tyson and graduate student Tao Wu **HTML Staff**: Hsin Wang

HTML User Program Projects on Thermoelectrics

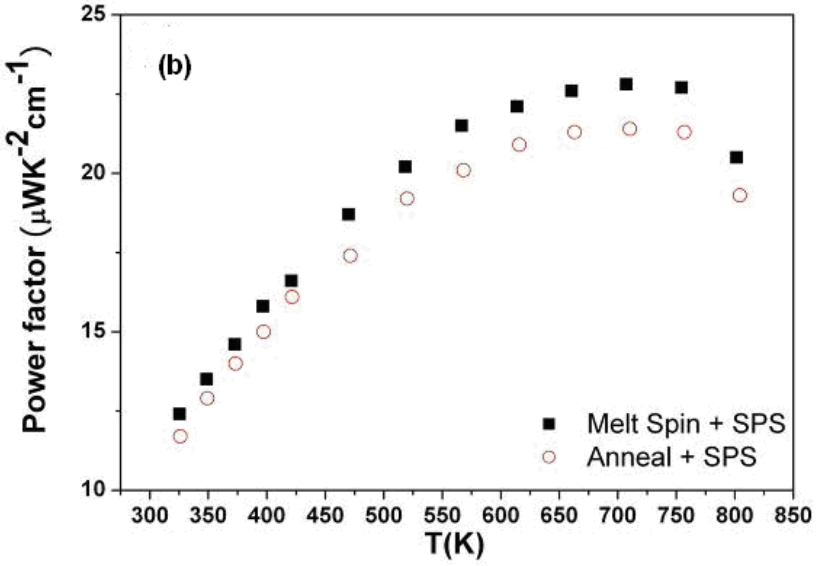


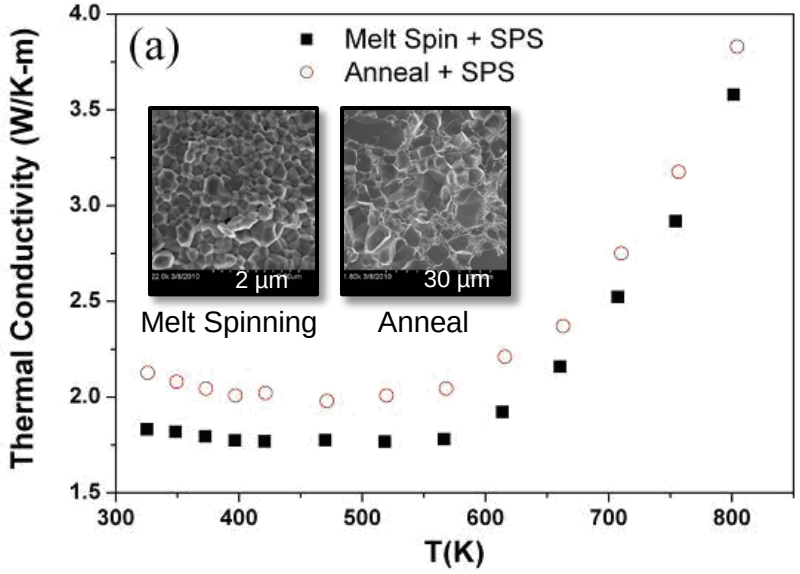


- The effect of Mg doping (1-10%) on the thermoelectric properties of hot-pressed **$CuAlO_2$** with delafossite structure.
- Samples with 1% and 2% Mg exhibit greater power factor. For higher Mg concentrations the power factor decreased and for concentrations above 7.5% the material exhibited very high electrical resistivity.
- Good consistency was found for thermal conductivity data for $CuAl_{1-x}Mg_xO_2$ obtained under cryogenic conditions.

Collaborators	**MSU Users**: Professor Don Morelli and graduate student Liu Chang **HTML Staff**: Hsin Wang

HTML User Program Projects on Thermoelectrics

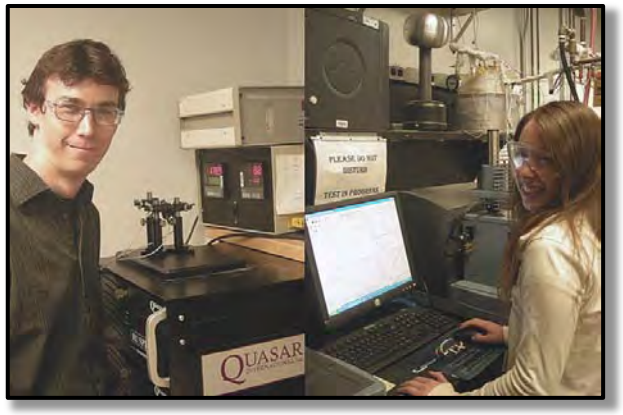


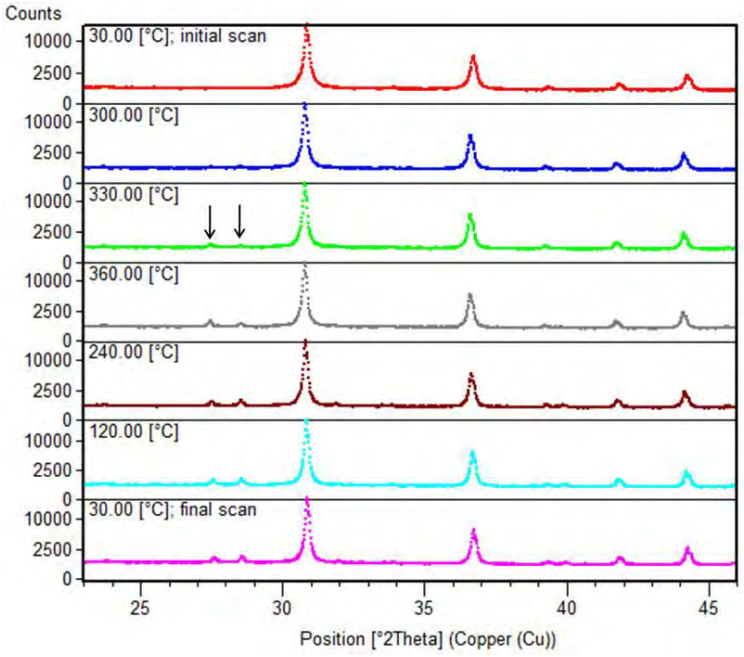


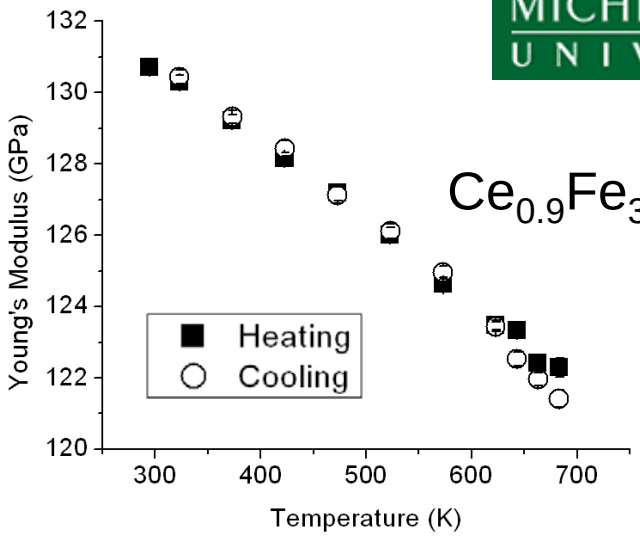
- p-type Ce-filled skutterudite $Ce_{0.9}Fe_3CoSb_{12}$
- BNL-developed melt-spinning methods to reduce the processing time to obtain skutterudite materials (a few minutes vs. traditional processing routes, which involve long-term annealing periods (5-7 days)).
- The p-type skutterudite was formed by melt spinning, followed by grinding and sintering by SPS at 620˚C under 50 MPa for 2 minutes.
- Another part of the quenched ingot was placed in a furnace and annealed at 700˚C for 30h, followed by grinding and SPS sintering at the same conditions.
- The melt-spun material has lower thermal conductivity and higher power factor. **The ZT value was improved** and a 15% peak enhancement was achieved.
- This project has demonstrated that non-equilibrium melt-spinning processing methods has the potential of producing materials with improved ZT**.**

Collaborators	**BNL Users**: Dr. Qiang Li and Dr. Jie Qing **HTML Staff**: Hsin Wang

HTML User Program Projects on Thermoelectrics



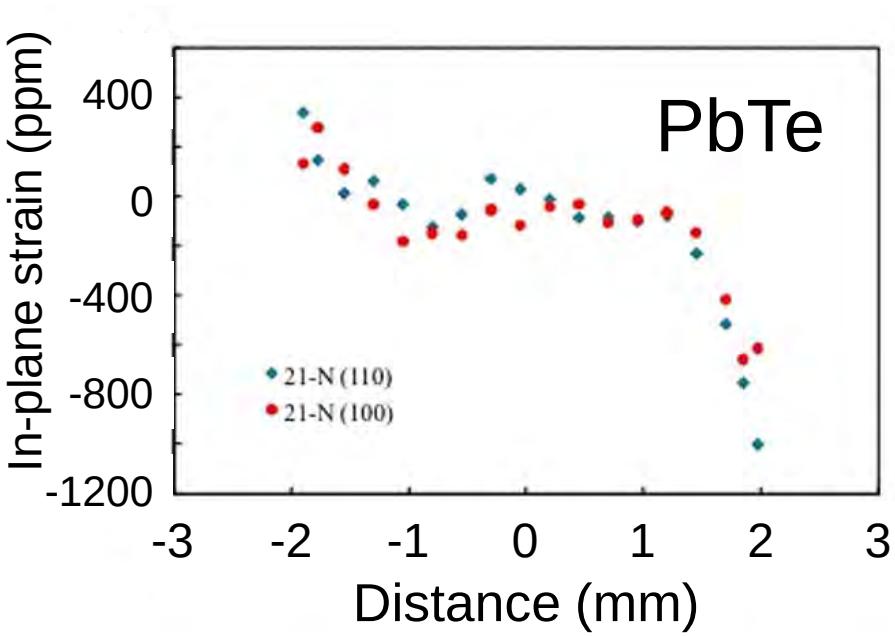


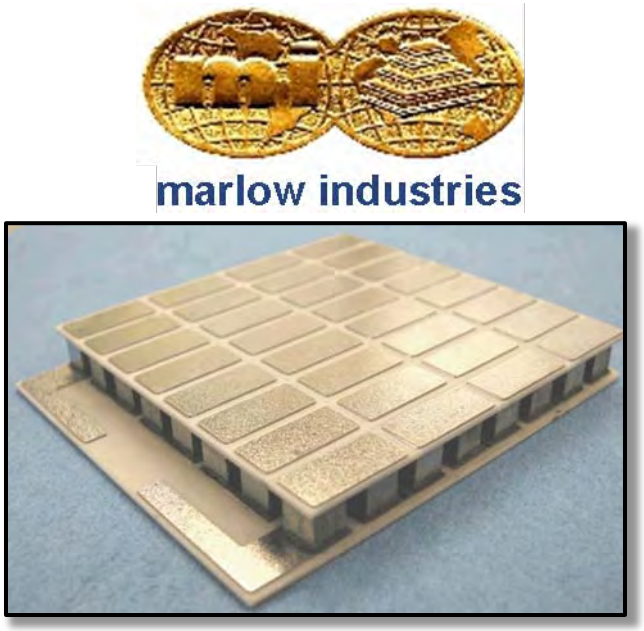


- Thermal expansion and elastic moduli of antimony-based skutterudites and lead-telluride—lead-sulfide thermoelectric materials were determined as a function of temperature.
- Phase stability is being investigated as a function of time and temperature using X-ray diffraction

Collaborators	**MSU Users**: Professor Eldon Case and graduate students Jennifer Ni and Robert Schmidt **HTML Staff**: Rosa Trejo, Andrew Payzant, Melanie Kirkham and Edgar Lara-Curzio

HTML User Program Projects on Thermoelectrics





- Temperature gradients in thermoelectric modules induce stresses that can lead to fracture of the legs or interface debonding.
- Used neutron diffraction techniques to map the distribution of strains in both n-type and p-type PbTe legs at one corner of a module.
- The analysis revealed a stress/strain distribution similar to the finite element simulation performed at Marlow. The successful strain mapping technique for thermoelectric modules will be applied by Marlow on the next-generation thermoelectric modules the company is developing for vehicle applications.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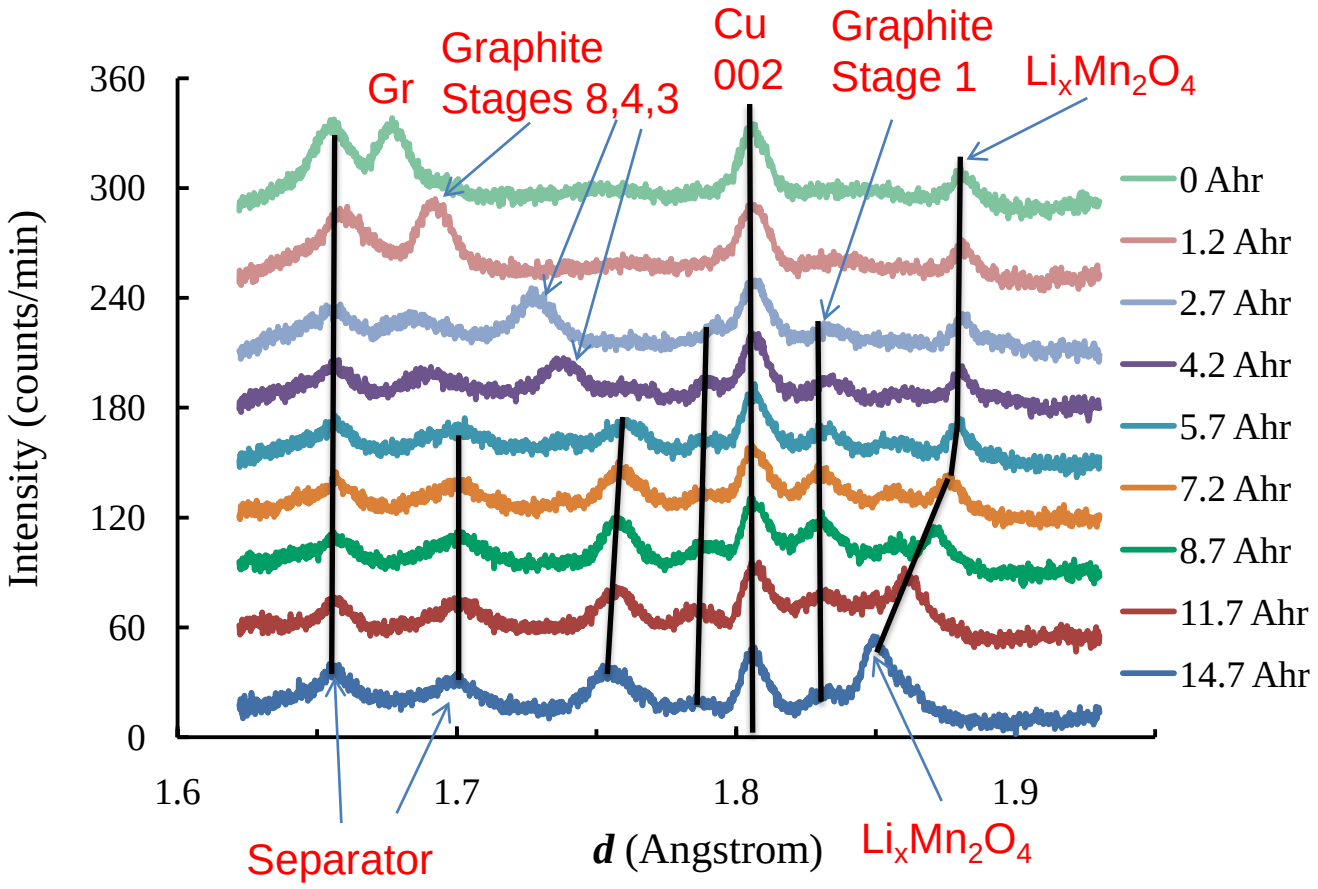
User Project with General Motors

"Characterization of Li-ion batteries Using Neutron Diffraction and Infrared Imaging Techniques"

Research problem	To determine the local temperature variation during charging and discharging and to explore phase changes in electrodes using in situ neutron mapping; information needed for GM to estimate life and reliability of full-scale battery system.
Technical approach	Utilized the unique capabilities of the HTML User Program for *in situ* studies. A high-speed infrared camera was used for temperature mapping, and the neutron strain mapping facility was used for *in situ* phase monitoring during charging and discharging.
Implications	Batteries with higher energy density that can meet the requirement of 5,000 deep discharge cycles over the life of the battery.
Barriers	Performance, Life
Collaborators	**Users**: Jihui Yang, Robert S. Conell, GM R&D Center **HTML Staff**: Hsin Wang, Cam Hubbard and Wei Cai

General Motors R&D Center User Project: Accomplishments – *In situ* Neutron Diffraction

Neutron diffraction peaks in Region #3 between 1.62 – 1.93 Å as a function of cell capacity. Data were collected in 9 steps during discharging.



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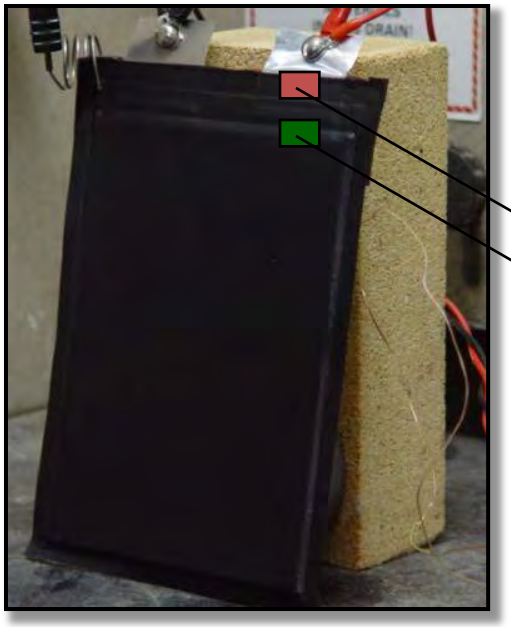
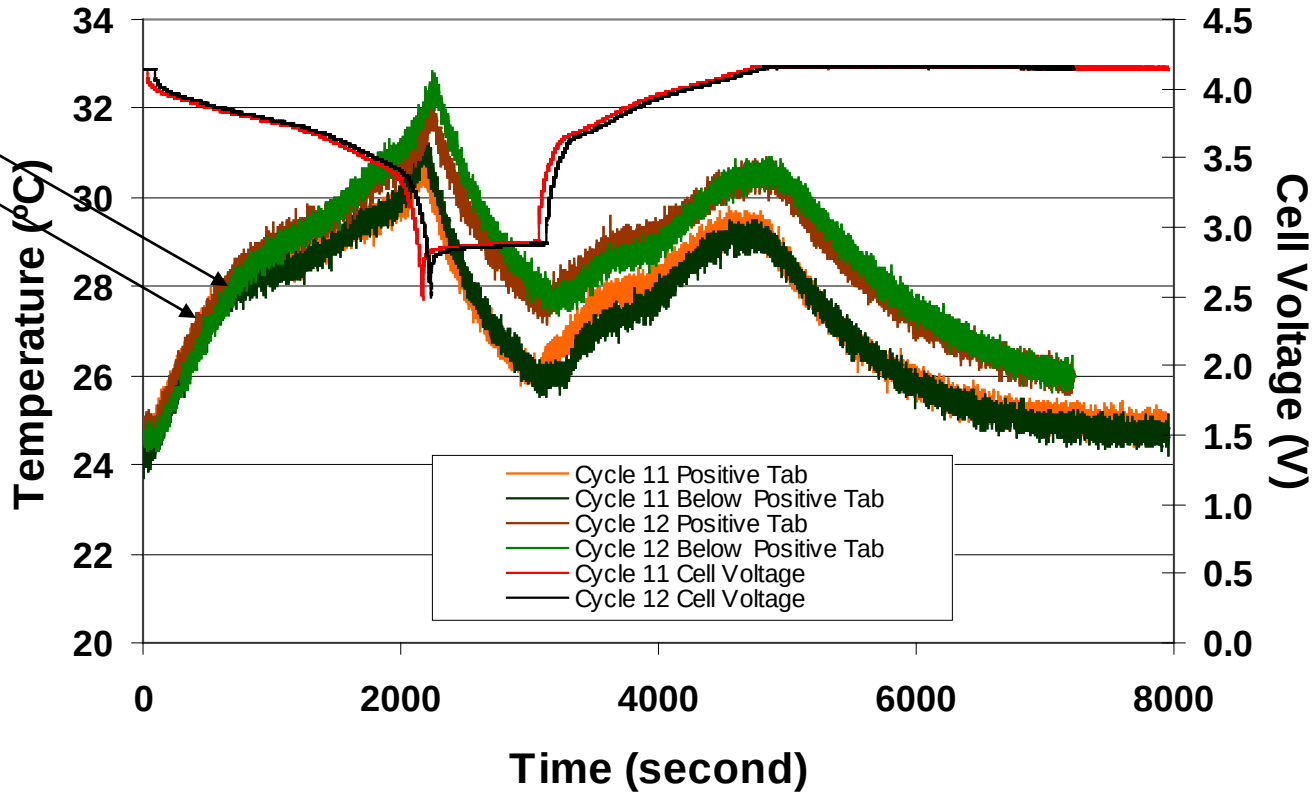
User Project with General Motors

"Characterization of Li-ion batteries Using Neutron Diffraction and Infrared Imaging Techniques"



15 A-hr enclosed in pouch used for this study

Temperature vs. time plots for two cycles



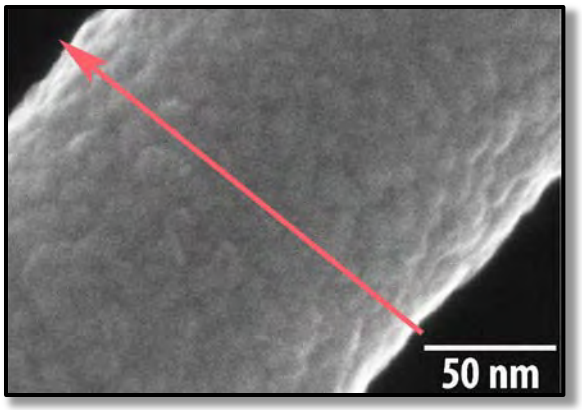
The results obtained from this HTML User Program project have enabled GM to develop a better understanding of cell performance, which will result in cells with improved performance and durability

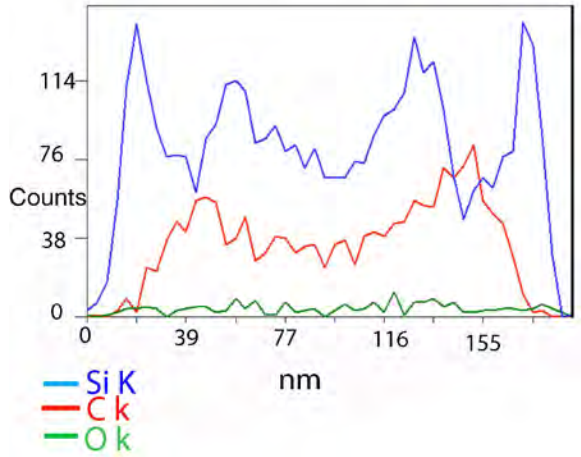
HTML User Project with Applied Sciences Inc/GM Team "Characterization of novel Li-ion battery anode"

Research problem	To understand the effect of microstructure of Si/C composite anodes on the performance of Li-ion batteries.
Technical approach	Utilized scanning-transmission electron microscopy and X-ray photoelectron spectroscopy to characterize the microstructure of Si/C composite anodes before and after cycling.
Implications	Si/C composite anodes could enable the development of Li-ion batteries with high capacity and durability, which are critical for the commercialization of electric vehicles.
Barriers	Battery Performance and Life
Collaborators	**ASI User**: Max Lake **HTML Staff**: Jane Howe and Harry M. Meyer III

HTML User Project with Applied Sciences Inc/GM Team "Characterization of novel Li-ion battery anode"

- ASI has produced anodes for Li-ion batteries consisting of low-cost hollow carbon nanofibers (CNF) coated with nanosized silicon (uniform coating about 12-nm thick, or an array of sub-20nm nodules that partially cover the surfaces).
- By depositing silicon on both inner and outer surface of a hollow carbon nanofiber it is possible to maximize the efficiency of the Si/CNF composite during cycling.
- Capacities in excess of 1000 mAh/g after 20 cycles and 500 mAh/g after 50 cycles in half-cell configuration and near 1000 mAh/g (full cell configuration) were achieved.
- Battery cyclability varied from batch to batch.
- Work is in progress to correlate the effect of processing conditions with the microstructural features of the coatings and the electrochemical performance of the composite anodes.



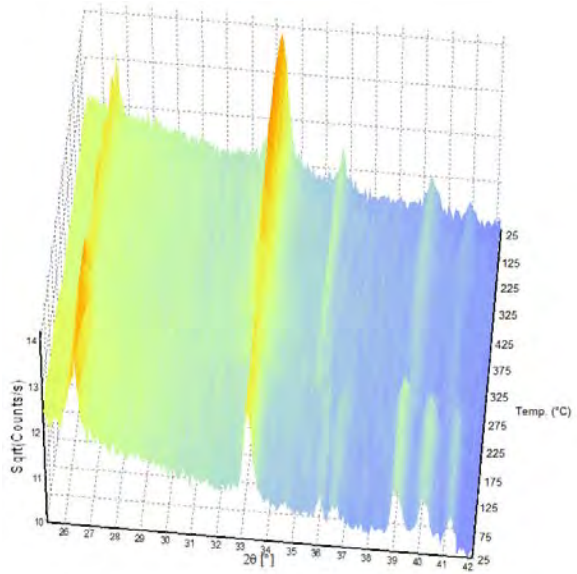


User Project with National Renewable Energy Laboratory **"Annealing of composite electrodes for Li-ion batteries"**

Research problem	To better understand the interaction between active materials (metal oxide) and single-wall carbon nanotubes (SWNTs) in binderless composite electrodes for Li-ion batteries and to determine the optimum annealing temperature to obtain stable structures.
Technical approach	Utilize X-ray diffraction technique to monitor, i*n situ*, phase stability during annealing at different temperatures.
Implications	Optimized electrode materials will enable high-performance, durable, and affordable Li-ion batteries for power-assisted HEVs and PHEVs that meet the DOE's Vehicle Technologies targets.
Barriers	Performance, Life
Collaborators	**NREL User**: Dr. Chunmei Ban **HTML Staff**: Melanie Kirkham and Andrew Payzant

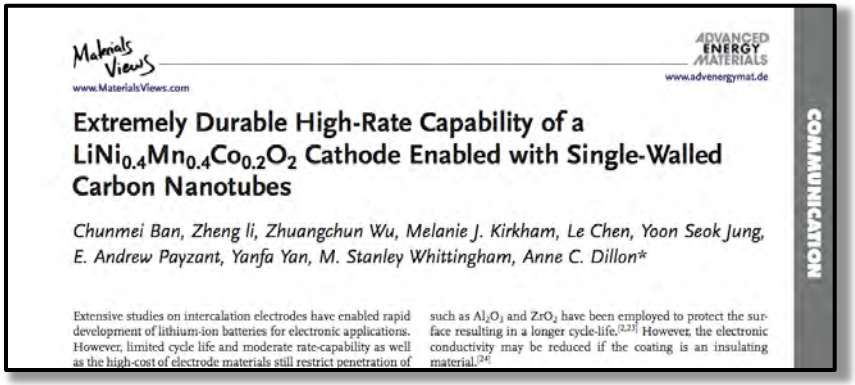
NREL's Dr. Chunmei Ban preparing a test in the HTML's X-ray diffractometer

User Project with National Renewable Energy Laboratory **"Annealing of composite electrodes for Li-ion batteries"**



- A phase transition was observed in the iron oxide samples as the FeOOH precursor converts to Fe_2O_3 at around 250°C, whereas the carbon peak showed little change up to the maximum temperature of 550°C.
- No phase transition was observed in the LCO phase, although a change in lattice parameters upon cooling suggests that structural modifications might have occurred during annealing. Additionally, changes in the carbon peak suggest structural changes may also occur in the SWNTs.
- Work continues to understand the mechanisms responsible for these changes.

- Iron oxide/SWNT composite electrodes in a coin-cell configuration greatly improve performance, with the highest reversible capacity obtained using 5wt% SWNT, reaching 1000 mAh/g at C rate and 800 mAh/g at 5C.
- The performance of these iron oxide/SWNT composite electrodes has been observed to improve even further after annealing.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COMMUNICATION

Extremely Durable High-Rate Capability of a $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ Cathode Enabled with Single-Walled Carbon Nanotubes

*Chunmei Ban, Zheng li, Zhuangchun Wu, Melanie J. Kirkham, Le Chen, Yoon Seok Jung, E. Andrew Payzant, Yanfa Yan, M. Stanley Whittingham, Anne C. Dillon**

Extensive studies on intercalation electrodes have enabled rapid development of lithium-ion batteries for electronic applications. However, limited cycle life and moderate rate-capability as well as the high-cost of electrode materials still restrict penetration of

such as Al_2O_3 and ZrO_2 have been employed to protect the surface resulting in a longer cycle-life.[2,23] However, the electronic conductivity may be reduced if the coating is an insulating material.[24]

HTML User Project with University of Minnesota **"Characterization of Iron Nitride Magnetic Materials"**

Research problem	To characterize the microstructure and chemical composition of $Fe_{16}N_2$ thin films at the atomic level.
Technical approach	Utilized X-ray photoelectron spectroscopy and transmission electron microscopy along with magnetic property measurements at the University of Minnesota.
Implications	The development of magnetic materials that do not contain rare earth elements.
Barriers	Rare Earth Minerals
Collaborators	**University of MN Users**: Professor Jian-Ping Wang and Dr. Nian Ji **HTML Staff**: Larry Allard and Edgar Lara-Curzio

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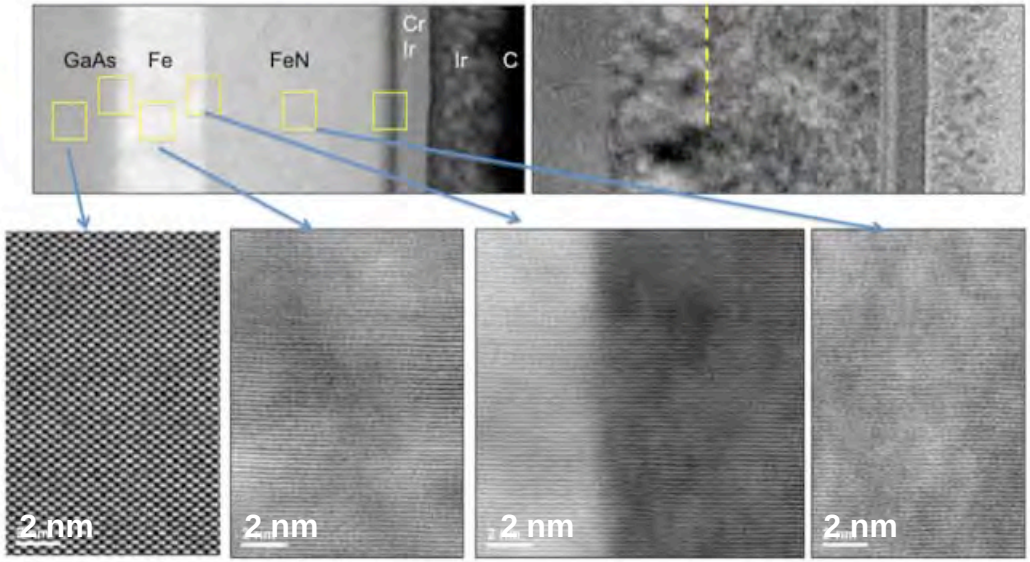
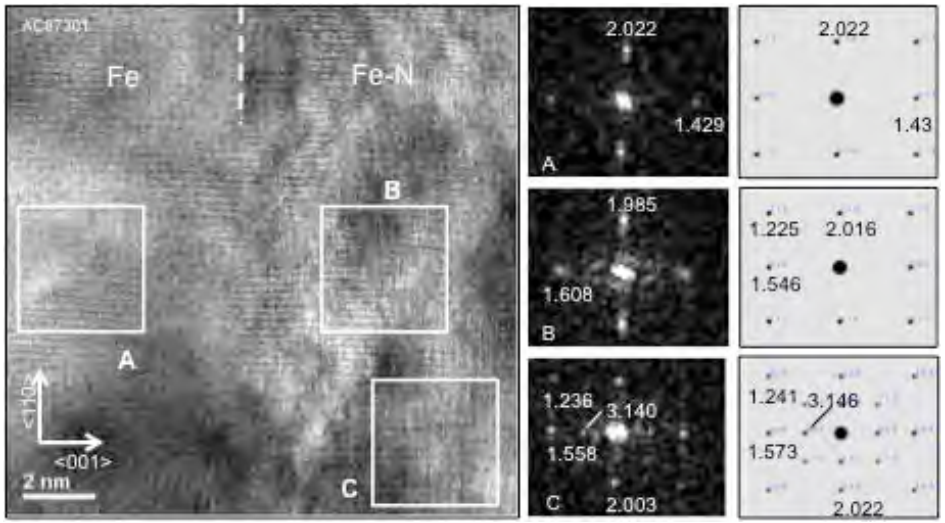
HTML User Project with University of Minnesota
"Characterization of Iron Nitride Magnetic Materials"





- The combination of XPS and STEM results allowed verification of the presence of domains of $Fe_{16}N_2$, which has the highest saturation magnetization value ever reported.
- These results will enable the development of processing strategies for producing iron nitride materials with a high concentration of the metastable phase $Fe_{16}N_2$. The development of iron nitride magnets addresses an important barrier associated with the use of rare earth minerals in magnetic materials for multiple automotive components (e.g., electric motors, actuators).

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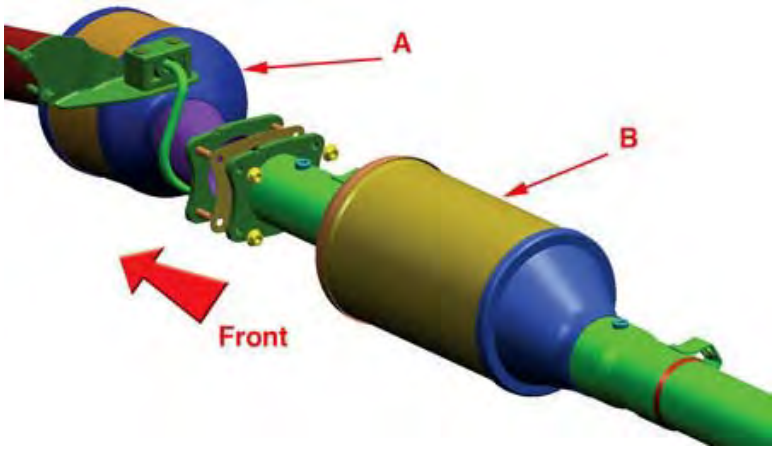
User Project with ORNL's Fuels Engines & Emissions Research Center

"Platinum catalyst particle growth in field-aged diesel oxidation catalysts and lean NOx traps"

OAK RIDGE NATIONAL LABORATORY
Fuels, Engines and Emissions Research Center

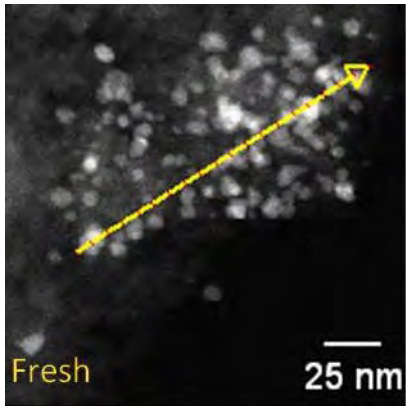
Research problem	To analyze the deactivation of diesel oxidation catalysts and lean NOx traps due to platinum group metal sintering.
Technical approach	Utilize transmission electron microscopy and X-ray diffraction to characterize the structure and composition of fresh and aged catalysts.
Implications	Improvements in diesel oxidation catalysts will enhance the durability of emissions control devices for biodiesel vehicles.
Barriers	Lack of cost-effective emission controls; Durability
Collaborators	**Users**: Dr. Todd Toops (ORNL) and graduate student Will Brookshear (University of Tennessee) **HTML Staff**: Jane Howe and Andrew Payzant

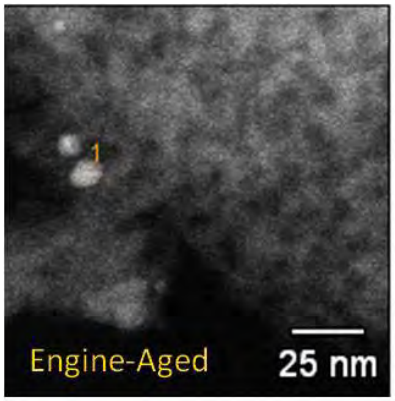


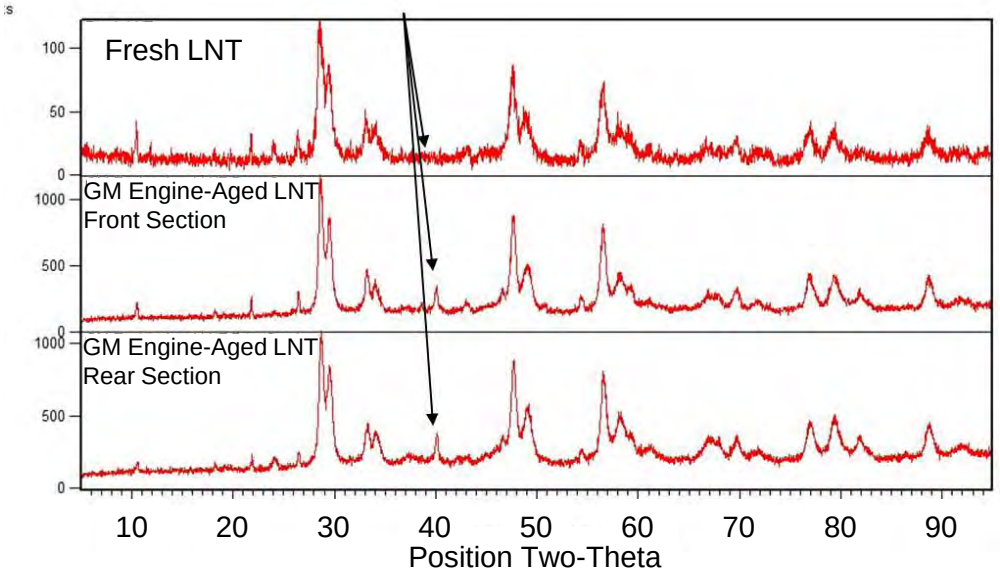
GM Tech Link

User Project with ORNL's Fuels Engines & Emissions Research Center

"Platinum catalyst particle growth in field-aged diesel oxidation catalysts and lean NOx traps"







- The periodic high temperatures that can be achieved in exhaust gases can cause platinum group metal (PGM) sintering, resulting in decreased PGM surface area. This leads to a drop in the maximum conversion of NOx to N_2 attained in LNTs.
- The sharper platinum peaks apparent in the engine-aged samples indicate PMG, which corresponds to a reduction of precious metal surface area for the oxidation of NO to NO_2. This is consistent with images obtained with scanning transmission electron microscopy.
- Analysis of the XRD data and STEM images have provided further understanding of the deactivation mechanisms associated with biodiesel fuels and can be used to improve the thermal durability of diesel after-treatment devices.

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User Project with General Motors and Sandia National Laboratories

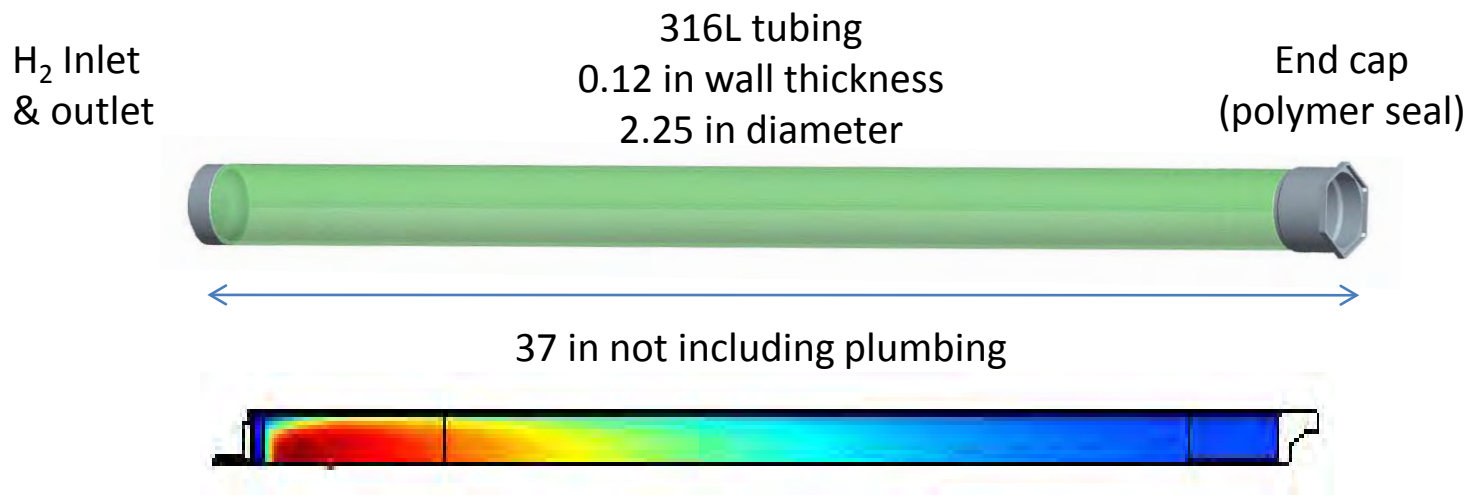
"Distribution of Hydrogen in Storage Media"

Research problem	Quantify axial and radial hydrogen concentration gradients as a function of time during hydrogenation using sodium alanates.
Technical approach	Utilize neutron scattering techniques at ORNL's High Flux Isotope Reactor and Vulcan diffractometer to map hydrogen distribution.
Implications	Development of models to explain hydrogen transport mechanisms.
Barriers	Availability of alternative fuels
Collaborators	**Users**: Scott Jorgensen (GM), Terry Johnson (Sandia) **HTML Staff**: Andrew E. Payzant

Scott Jorgensen (GM), Terry Johnson (SNL) and Andrew Payzant (ORNL) at the Vulcan diffractometer

User Project with General Motors and Sandia National Laboratories

"Distribution of Hydrogen in Storage Media"



(10 – 150 atm) and (120 – 180 °C)

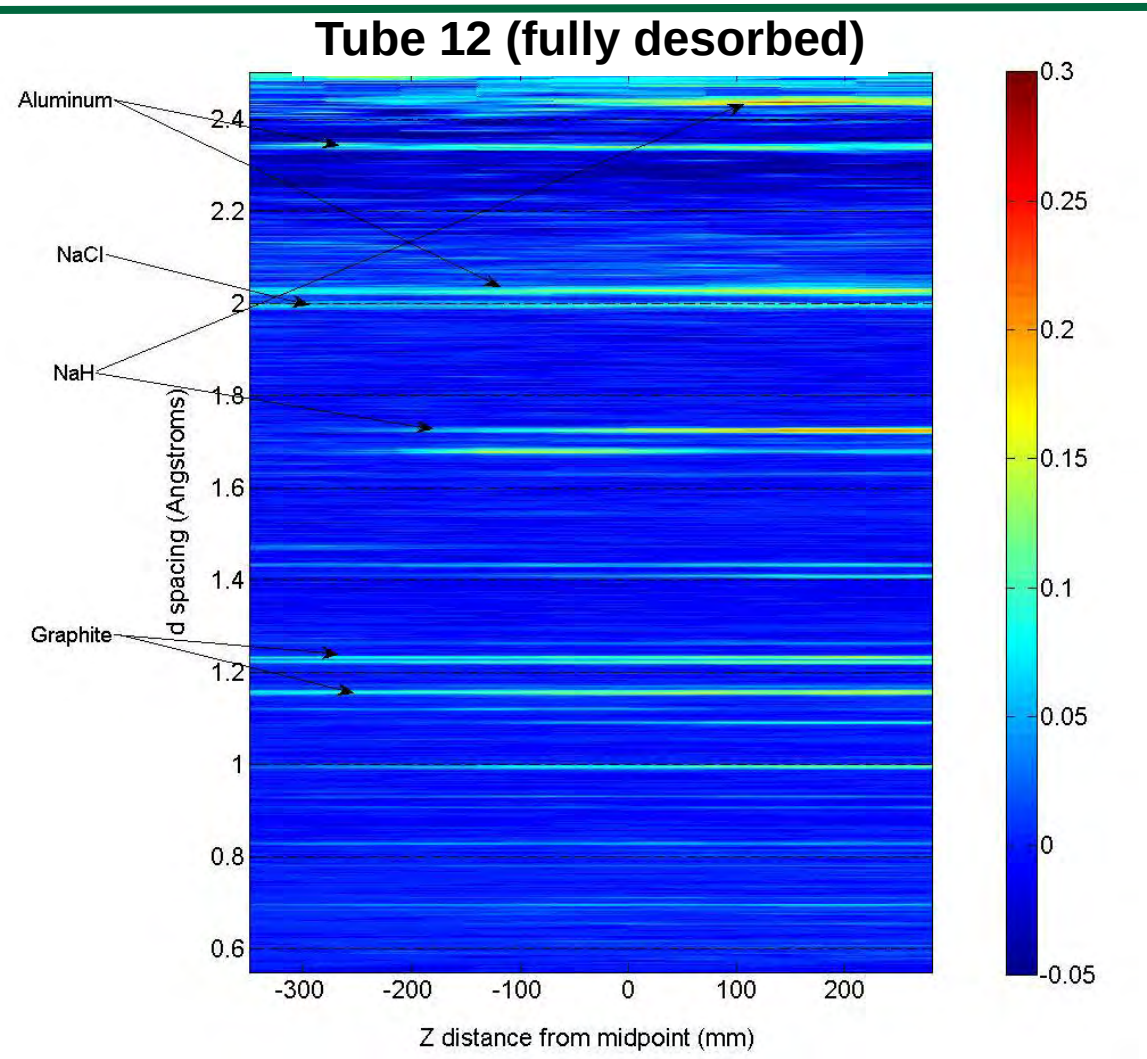
- **H_2 depleted state: NaH + Al + 3/2H_2**
- **First step: 1/3 Na_3AlH_6 + 2/3 Al + H_2**
- **Second step: $NaAlH_4$**

Hydrogen depleted state

Component	mol %	mass %
Al	45.1%	49.9%
NaH	32.6%	32.0%
Carbon (graphite)	18.4%	9.1%
NaCl	2.9%	7.0%
Ti	1.0%	1.9%

User Project with General Motors and Sandia National Laboratories

"Distribution of Hydrogen in Storage Media"



Nominally NaH

- Hydride more crystalline near gas inlet/outlet but more amorphous at end.
- Graphite and NaCl phases evenly distributed.

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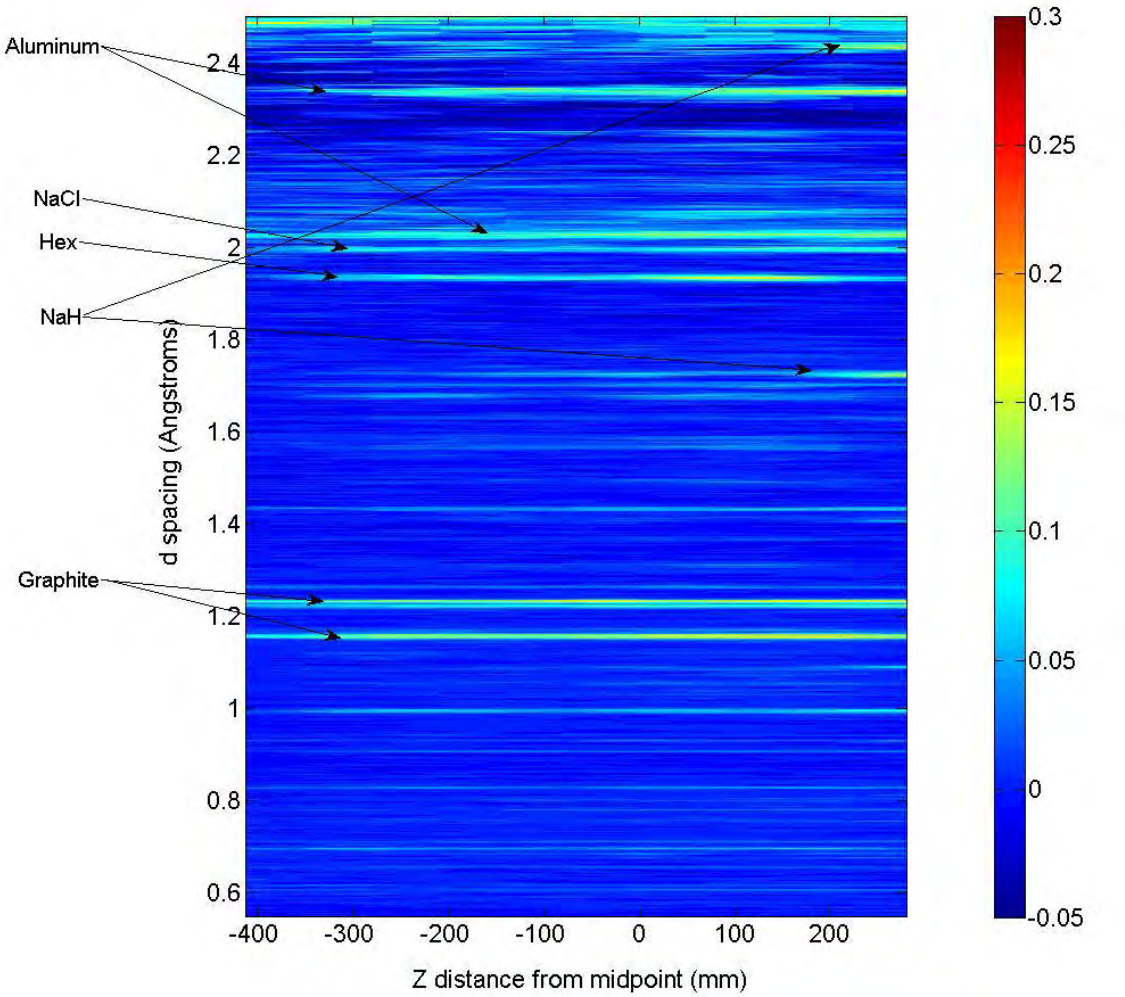
User Project with General Motors and Sandia National Laboratories

"Distribution of Hydrogen in Storage Media"

Tube 1 (partially absorbed)

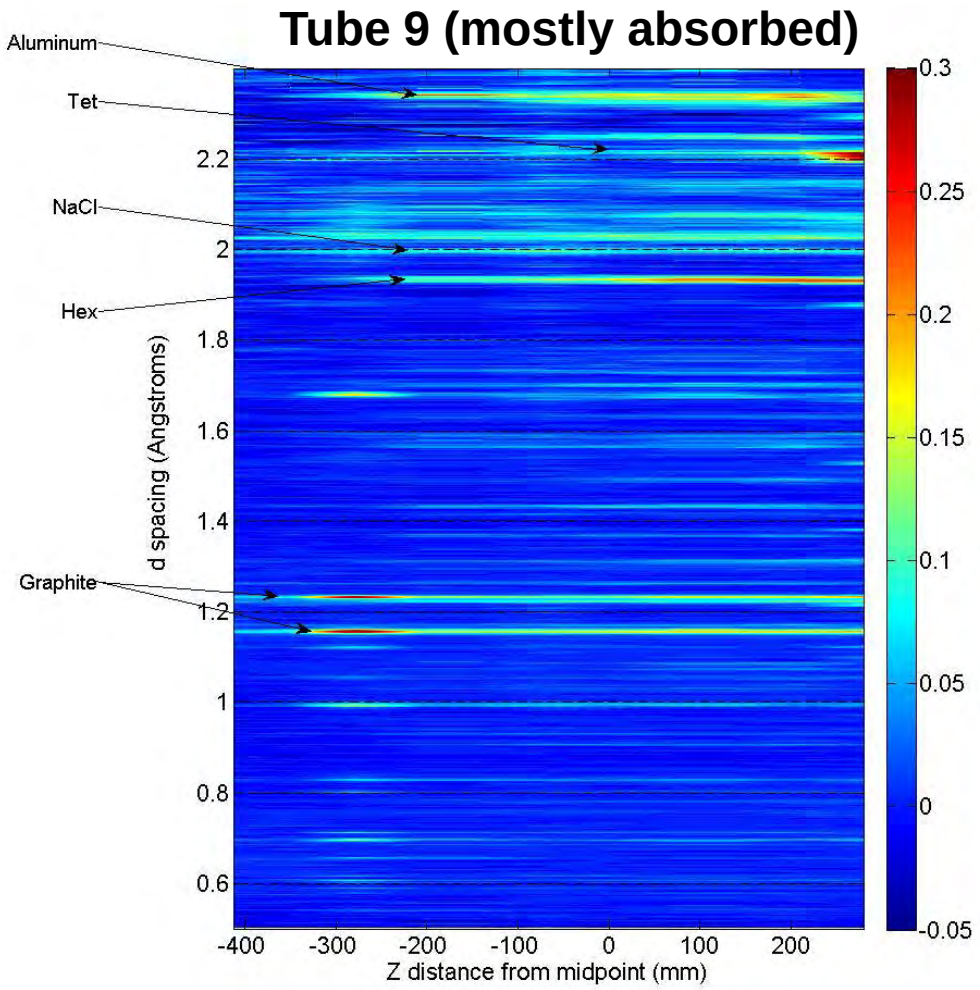


Data revealed unexpected complexity of hydride phase distribution

- More crystalline hydride near gas inlet/outlet but more amorphous at end.
- Graphite and NaCl evenly distributed.
- Unexpected NaH phase near inlet.
- Hexagonal Na_3AlH_6 phase distributed throughout tube.

User Project with General Motors and Sandia National Laboratories

"Distribution of Hydrogen in Storage Media"



Data revealed unexpected complexity of hydride phase distribution

- More crystalline hydride near gas inlet/outlet but more amorphous at end.
- Graphite and NaCl evenly distributed.
- Tetragonal $NaAlH_4$ phase found mainly near inlet/outlet.
- Significant amount of hexagonal Na_3AlH_6 phase observed distributed throughout tube.

User Project with General Motors

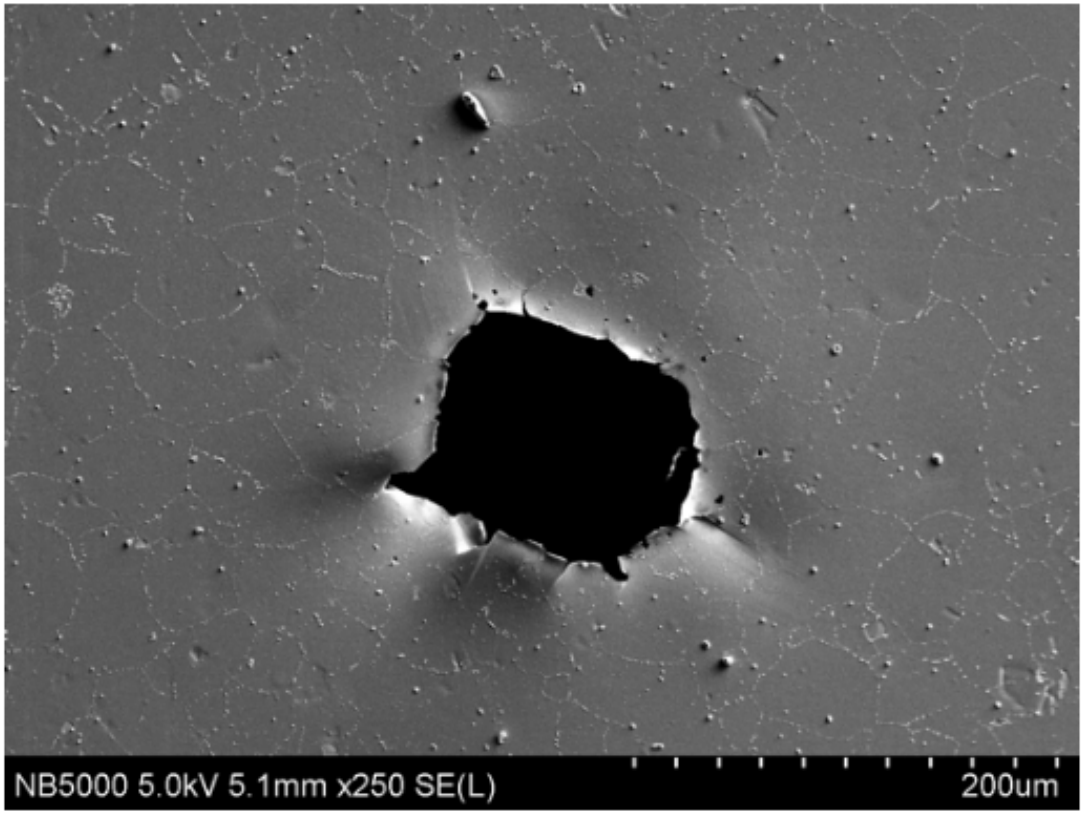
"Forming Technologies for Al Intensive Automotive Body Panels"

Research problem	To characterize the kinetics of precipitation and aging in Aluminum alloy 6111 and evaluate the effect of loading rate and temperature on its mechanical behavior.
Technical approach	Utilized *in situ* scanning electron microscopy and electron backscattered diffraction to study the kinetics of precipitation and aging. Used high-rate tensile testing to determine tensile properties
Implications	The development of production methods
Barriers	Manufacturability Lack of knowledge of advanced materials properties and performance characteristics
Collaborators	**Users**: Raj Mishra **HTML Staff**: Larry Allard, Chad Parish, Chris Stevens, Edgar Lara-Curzio

GM's Raj Mishra and the HTML's Larry Allard examining a test specimen in the scanning transmission electron microscope

User Project with General Motors

"Forming Technologies for Al Intensive Automotive Body Panels"



Summary

- The HTML is a National User Facility that supports the missions of the Vehicle Technologies Program, in particular by working with industry, universities and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum and reduce greenhouse gas emissions.
- The HTML User Program capabilities are also being utilized to support Vehicle Technologies Program projects at ORNL in the program's technology areas of Lightweight Materials, Propulsion Materials, Energy Storage and Thermoelectric Conversion.
- During FY2010 the HTML User Program collaborated with 49 different organizations (industry, universities, national laboratories) in the execution of 68 user projects. These projects addressed a wide range of materials technologies including lightweight materials, propulsion materials, materials for lithium-ion batteries, thermoelectric materials, catalysis, magnetic materials and materials for the manufacture of vehicular structures.

Future Work

- Marketing efforts will continue to be focused on developing collaborations with Vehicle Technologies Program stakeholders and other sponsors to address the proposed budget reduction in FY12.
- The HTML User Program will continue its collaborations with industry, universities, and national laboratories to address critical barriers to achieving the goals of DOE and EERE.
- The development of special tools to enable the *in situ* characterization of materials and processes will continue. These include high-speed extensometry to measure deformation of materials and structures at high-strain rates, and hot stages and environmental cells to monitor the evolution of microstructures in physical processes, in real time, with atomic resolution, at elevated temperatures and controlled environments, using electrons, X-rays and neutrons for imaging and diffraction.