Thermoelectric Materials Characterization at the High Temperature Materials Laboratory

Arvid Pasto

Director,

High Temperature Materials Laboratory

Oak Ridge National Laboratory

The HTML is a DOE-Designated User Facility at Oak Ridge National Lab

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www.html.ornl.gov

Six HTML user centers focused on materials characterization

Materials Analysis
Thermophysical Properties
Diffraction
Residual Stress
Machining, Inspection,and Tribology Research
Mechanical Characterization and Analysis

The HTML Programs are funded by DOE's Office of FreedomCAR and Vehicle Technologies
Dr. James Eberhardt, Program Manager

There are Numerous Ways to Work with the HTML

- **HTML User Program**
  - **short-term materials characterization**
    - **= non-proprietary or proprietary**
- **CRADA with individual staff members**
- **Work for Others (WFO)**
- **Personnel exchanges**
- **Collaborative research**

HTML Capabilities are Available to Users for Hands-On Materials Characterization Research

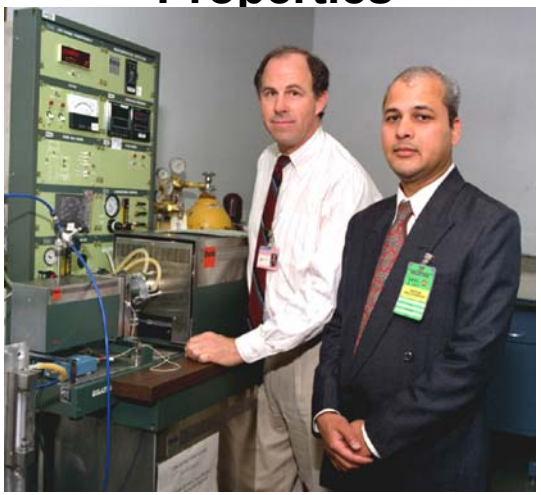
Materials Analysis

Characterize structure and composition

Mechanical Characterization and Analysis

Characterize mechanical properties and performance

Thermography and Thermophysical Properties



Measure physical properties as a function of temperature

HTML Capabilities are Available to Users for Hands-On Materials Characterization Research

Diffraction

In-situ characterization of crystalline materials (x-ray, synch., neutron diff.)

Residual Stress

Characterize and map residual stress and texture

Machining, Inspection and Tribology

Investigate grinding processes and characterize surfaces, friction, and wear

HTML Programs and Staff Have Benefited Industry and Universities

- **Many institutions have signed User Agreements:**

  402 industries
  265 universities (thru FY2003)
  25 government agencies
  692 total institutions

- **These have resulted in over 1250 projects**

- **Industries range from small (7 people) to large (GM, Ford, GE, Honeywell,.....)**

- **Many repeat visits from user institutions indicates success of projects**

HTML Is Especially Well-Suited for Characterization of Thermoelectrics

- **Thermography and Thermophysical Properties User Center can measure thermal conductivity, diffusivity, specific heat, electrical conductivity, Seebeck coefficient as functions of temperature**

- **Materials Analysis User Center specializes in microstructural and micro-compositional measurement**

- **Diffraction User Center examines structures by x-ray, synchrotron, and neutron diffraction as function of temperature, atmosphere**

- **Mechanical properties, friction and wear behavior, as well as stress state can also be measured in three other centers**

The Thermophysical Properties User Center Features Several Types of Instrumentation

- **Thermal Transport**
  - **Several fast IR cameras**
  - **Laser Flash Thermal Diffusivity Apparatus**
  - **Xenon Flash Thermal Diffusivity Apparatus**

- **Thermal Analysis**
  - **High Temperature Dual Pushrod Dilatometer**
  - **Bi-layer Dilatometer (for thin films, coatings)**
  - **STA w/ attached Mass Spectrometer**
  - **1600°C Differential Scanning Calorimeter**
  - **High Mass TGA/DTA**

Thermal Conductivity Measurements and Expertise at HTML

- HTML was the host of two International Thermal Conductivity Conference (ITCC)
  - ITCC23 in Nashville, 1995
  - ITCC27 in Knoxville, 2003
- 3 HTML staff are current members of ITCC Board of Governors
- Thermal conductivity measurements capability:
  - Laser flash thermal diffusivity (77K – 2700K)
  - Room temperature xenon flash thermal diffusivity (30-40 samples per day)
  - Hot Disk Thermal Constants Analyzer (77K-1000K)
  - 3-Omega (thin films)

The Laser Flash Thermal Diffusivity System Has Wide Ranging Capability

- **Four furnaces suitable for temperatures from -150°C to 2500°C**
- **Insert, reducing, or oxidizing conditions**
- **Multiple sample carousels for speed in data collection**
- **Quenching capability**
- **Molten metal handling**

Thermography Facility at HTML

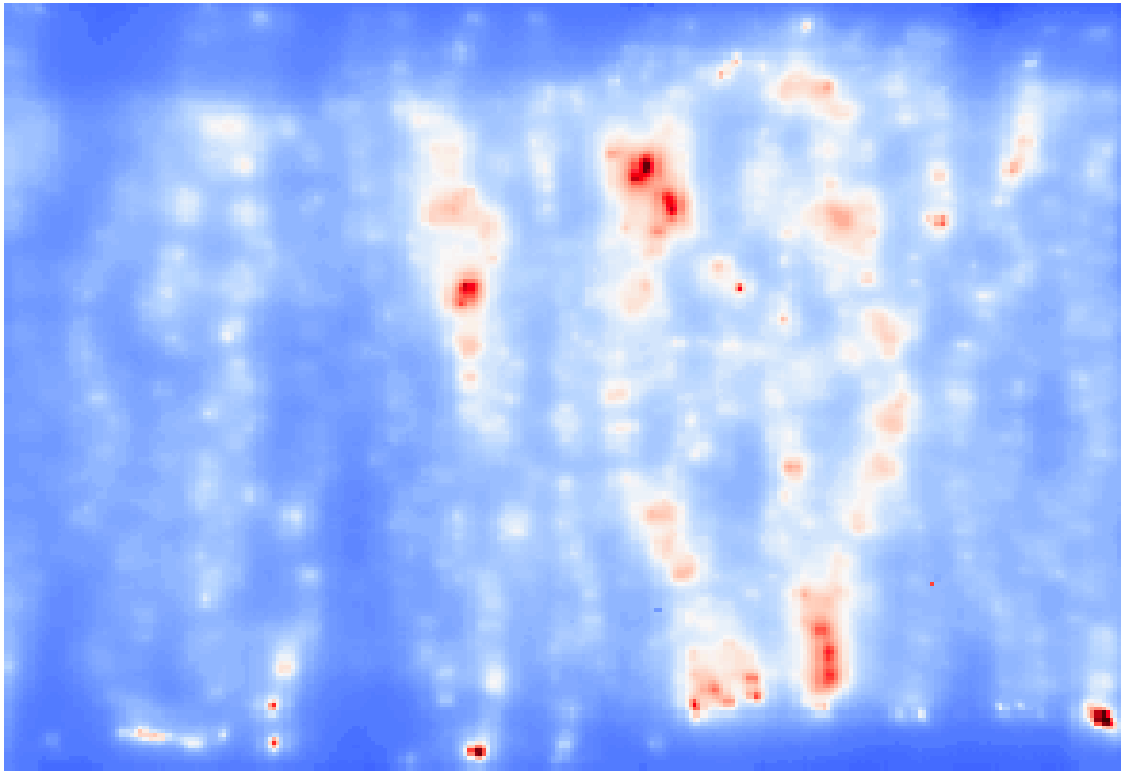
- Five infrared cameras:
  - Indigo Phoenix Near-IR: InGaAs, 320 x 256 pixels
  - Indigo Phoenix Mid-IR: InSb, 320 x 256 pixels
  - Raytheon, Radiance HS: InSb, 256 x 256 pixels
  - Indigo Alpha: Micro-bolometer 160 x 128 pixels
  - Indigo Omega: Micro-bolometer 160 x 128 pixels
- Hyper spectral imaging (3-5 microns)
- Spectrometers: UV-IR
- Single-point IR detectors: one color and two-color detectors
- Features: High-speed: 346Hz to 38kHz; high-sensitivity: 0.015 K; spatial resolution from 5 mm/pixel

Example Projects: Thermophysical

- **Thermal conductivity/diffusivity of:**
  - **ultra-low dielectric constant thin films(Dow-Corning)**
  - **SiC/SiC composites (UTK)**
  - **single-wall nanotubes in coatings (Rice Univ.)**
  - **ceramic shell materials for metal air foils (PCC)**
  - **thermal barrier coatings (PSU)**
  - **linear cellular materials(GT)**

- **High speed IR camera studies of:**
  - **battery pack spot weld (Motorola)**
  - **aircraft brakes (SIU)**
  - **fatigue behavior of steels (UTK)**
  - **thermionic microcoolers (ORNL)**
  - **GaN heterostructure FET temperature distrib. (USC)**

Local Heating at GB



NDE Technique to Monitor Current Distribution

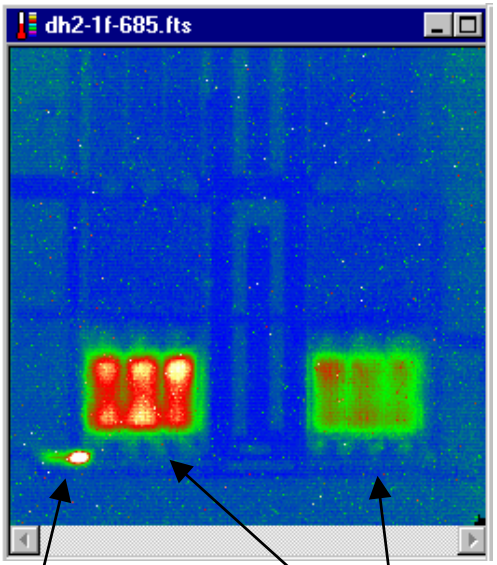
A Microscope Lens Allows the Study of Integrated Circuit Power Transistors During Operation and Failure

TPUC User Project with Motorola

Movie During Failure

QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

2 mm



2 mm

Power Transistors Bank 1

Power Transistors Bank 2

Unexpected design flaw

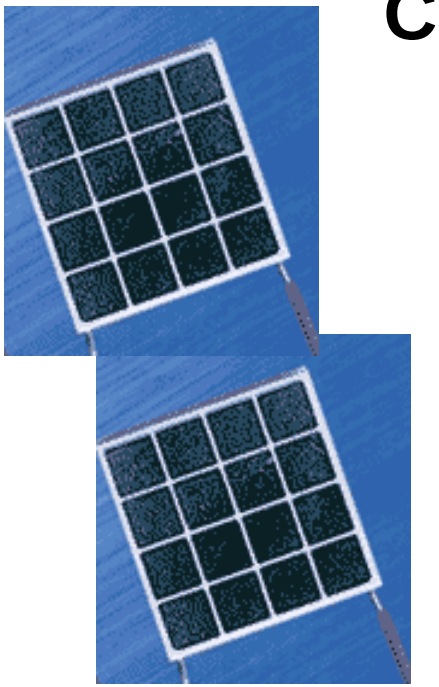
Non-uniform temperature distribution

Thermoelectric Characterization at HTML

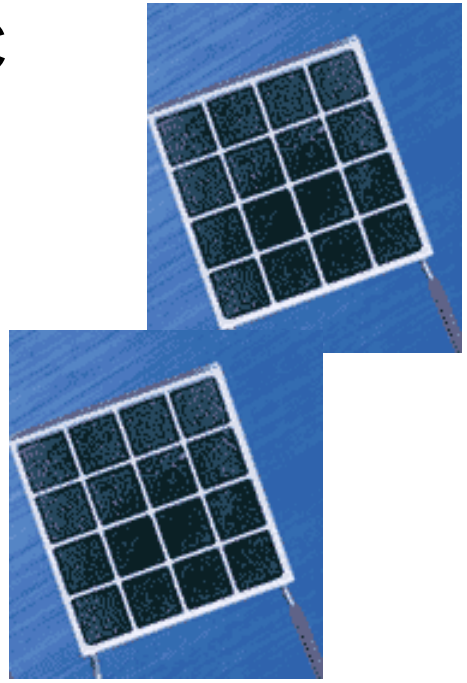
- University of Virginia: Thermoelectric alloys of Bi_2Te_3-Sb_2Te_3-Sb_2Se_3
- General Motors: Thermal conductivity of skutterudites
- ORNL Condensed Matter Sciences Division: Filled skutterudites thermal conductivity
- UC Santa Barbara/Santa Cruz: Infrared imaging of SiGe thermionic cooling devices
- ORNL Solid State Division: Thermionic device characterization

Thermoelectric Characterization

Seebeck Coefficient and Electrical Conductivity: up to 1600°C

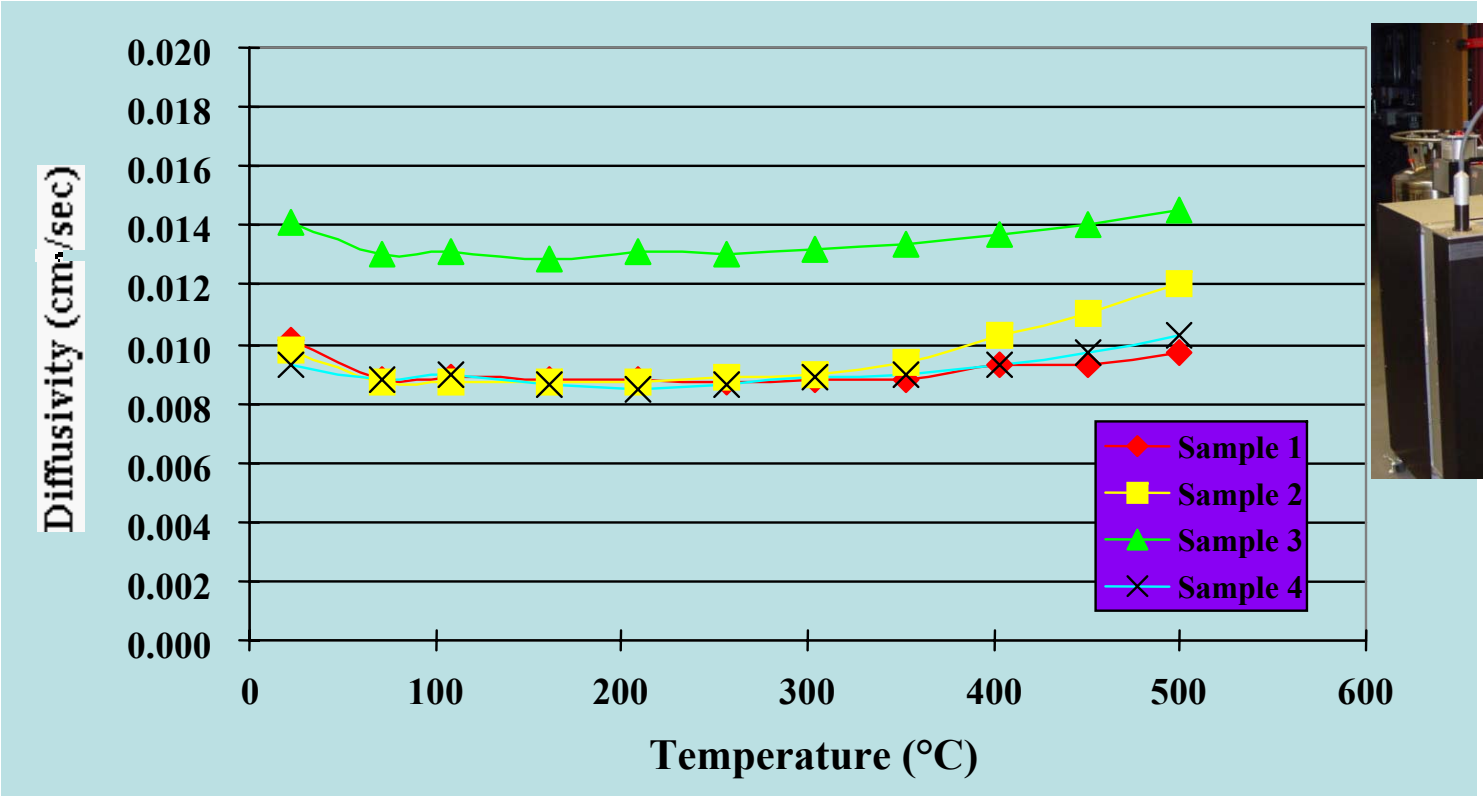


$$ZT = \frac{S^2 \sigma T}{k}$$



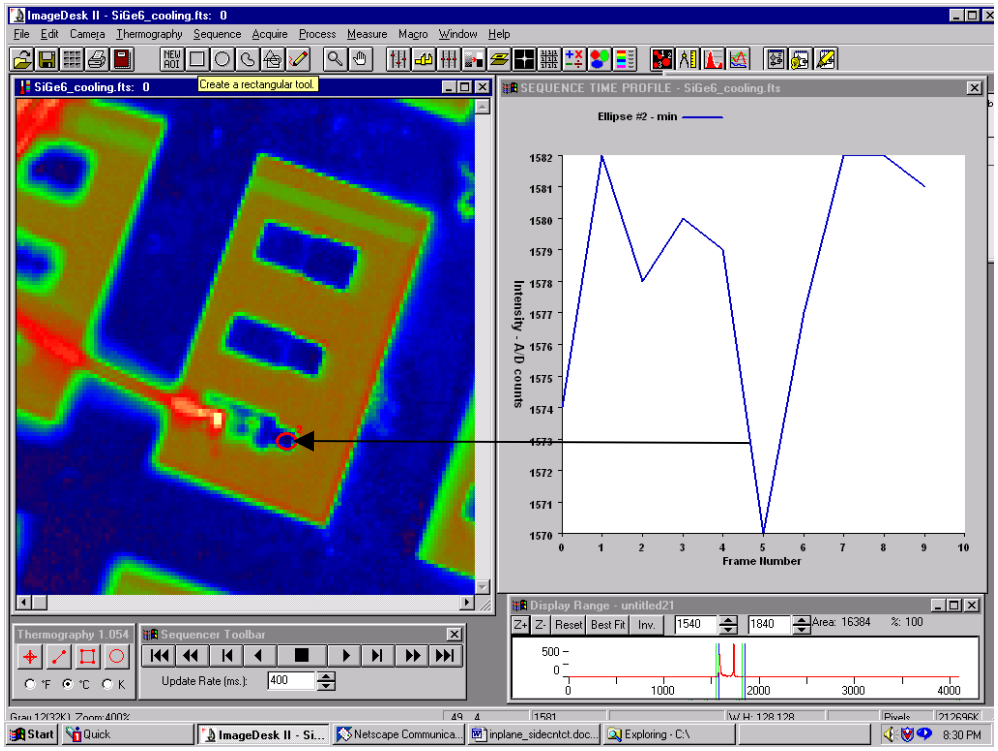
Thermal Conductivity: up to 2400°C

Thermal Diffusivity of Filled Skutterudites



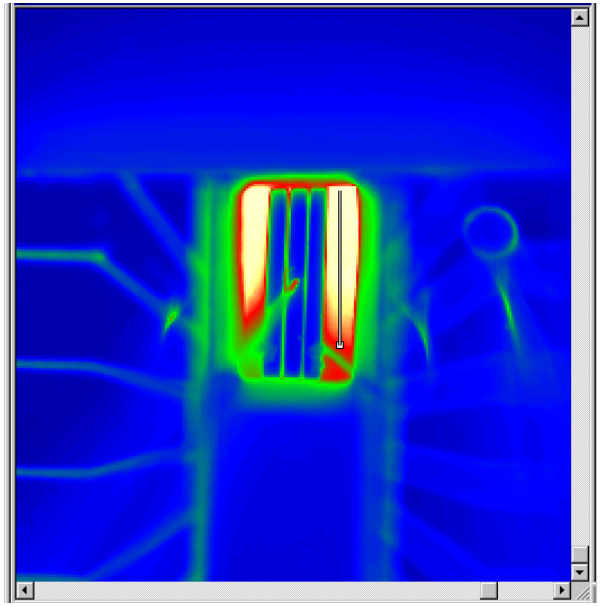
Laser Flash System Can Measure 6 Samples in One Run

IR Imaging of Thermionic Cooling Observed During Current Pulses



Cooling during a current pulse

IR Microscopy
2 mm x 2 mm
5.4 mm/pixel resolution

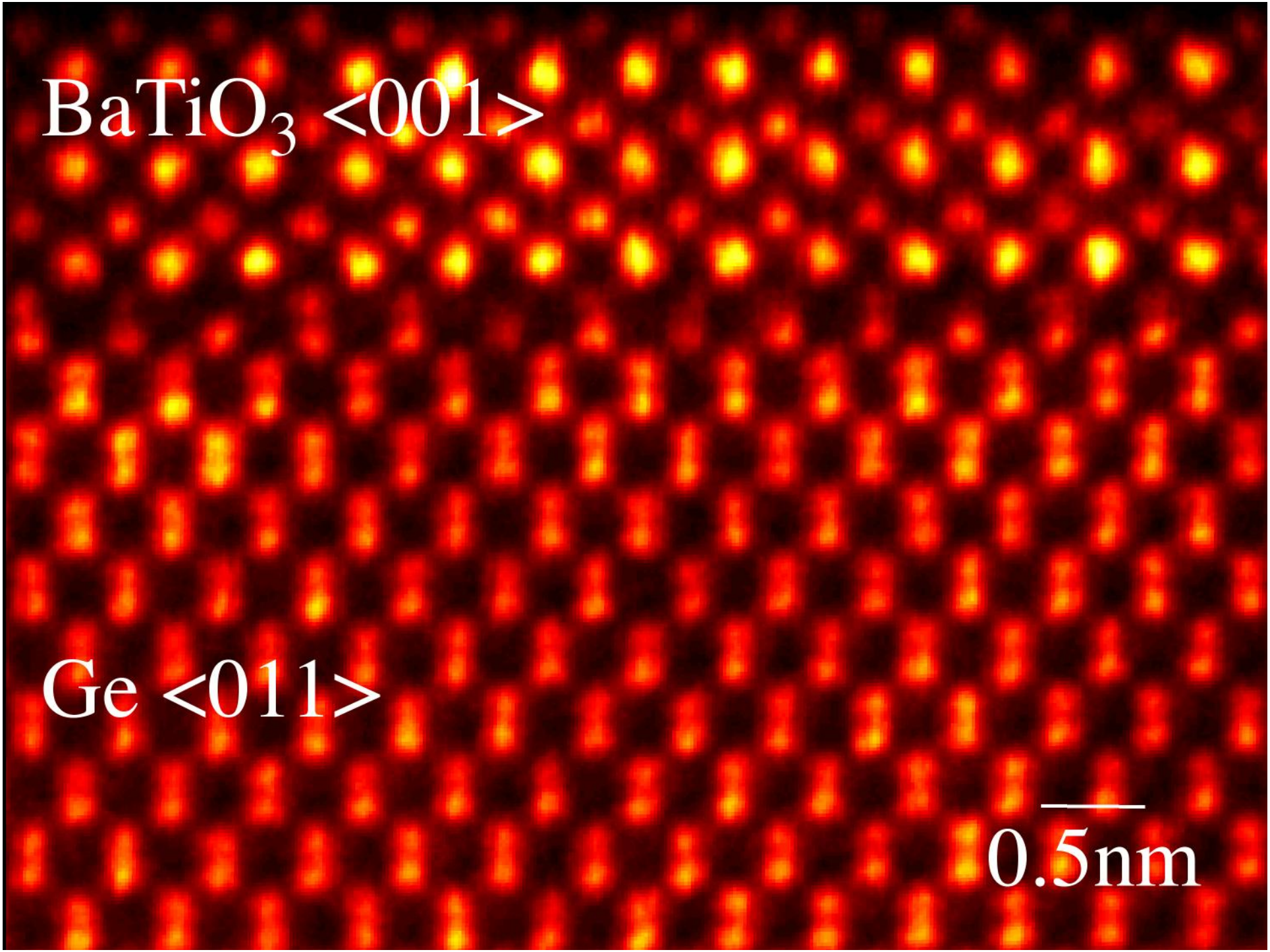


[With UCal-Santa Cruz/Santa Barbara]

HTML Well Equipped for Microstructural and Microcompositional Characterization

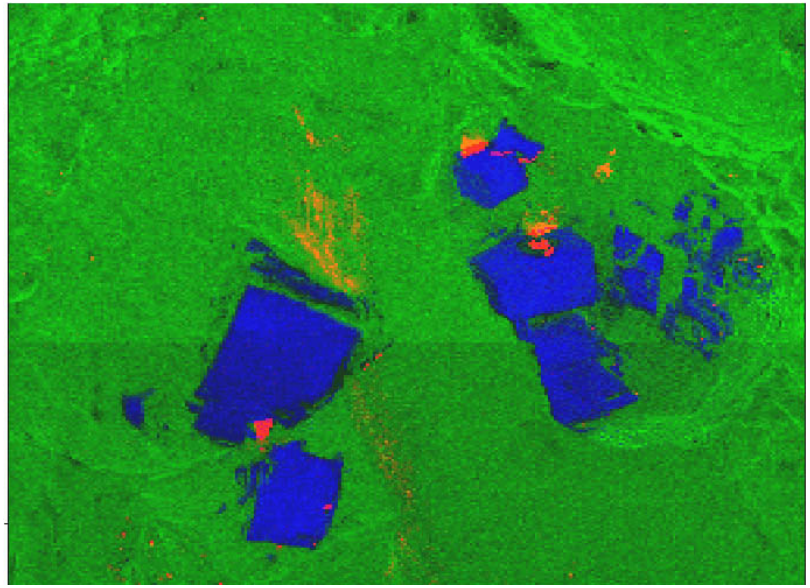
- **Hitachi HF-2000 FEG-AEM w/EDS**
- **Hitachi S-4700 FEG-SEM w/EDS, Kikuchi backscatter detector**
- **Hitachi FB-2000 FIB Micro-mill**
- **Hitachi HD-2000 Dedicated STEM**
- **JEOL 8200 Electron Microprobe**
- **JEOL 2010F TEM**
- **PHI 680 Scanning Auger Nanoprobe**

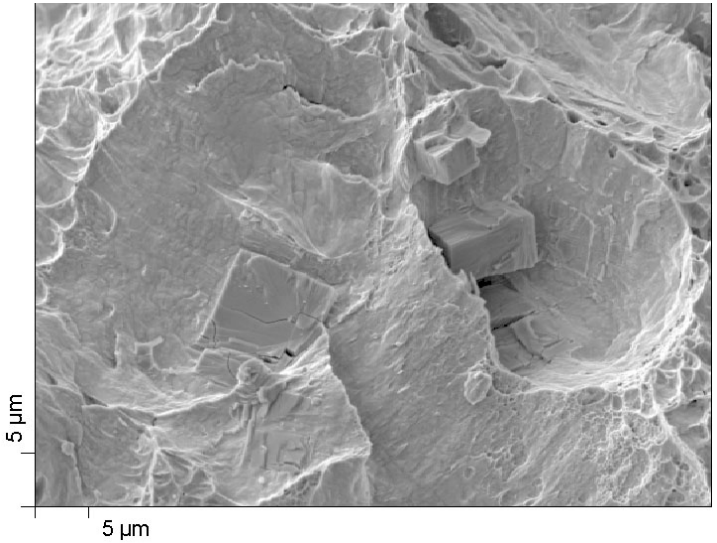
- **Sub-angstrom resolution TEM/STEM coming in spring of 2004 (JEOL 2200FS-AC)**


$BaTiO_3$ <001>
Ge <011>
0.5nm

Caterpillar and HTML Staff
Studied Element Distribution on Fractures

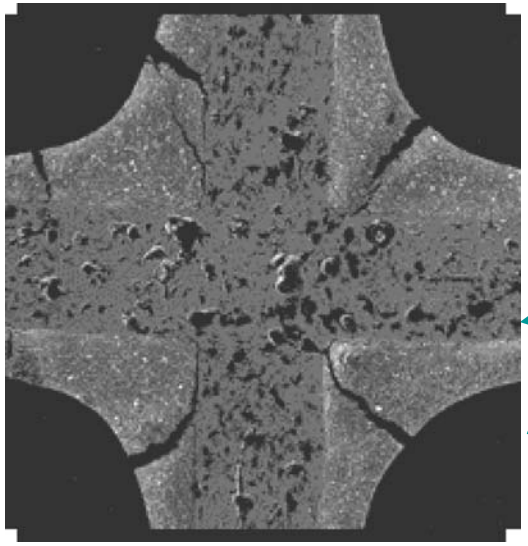
The secondary electron image shows the fracture surface of high-strength steel sample. Note the presence of “cuboid” structures at the center of the fracture pits. The cuboids are TiN as determined by Auger analysis.





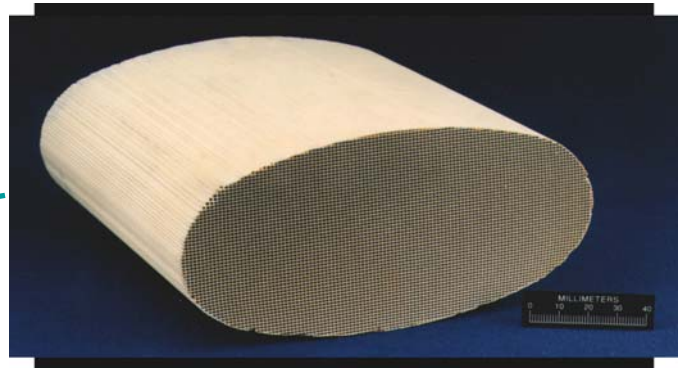
Elemental maps of **iron**, **titanium**, and **sulfur** reveal the presence of sulfur at the interface between the steel matrix and the cuboids.

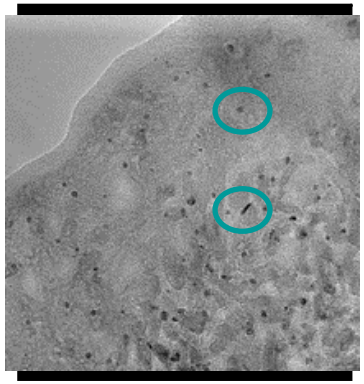
The HTML is a National Leader in Characterizing Catalyst Materials

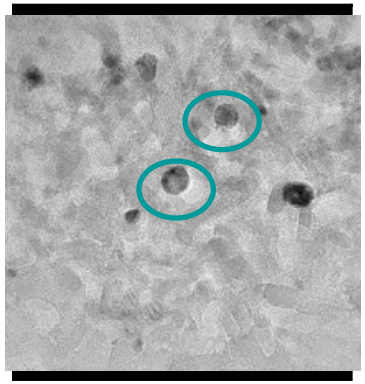


SEM shows corderite substrate with washcoat in corners

Automotive catalyst brick







High-resolution TEM of catalyst particles shows changes

HTML has/had catalyst activities with

- AC Delphi
- U. Delaware
- U. New Mexico
- Ford Research Laboratory
- Cummins Engine Co.
- W.R. Grace
- General Motors
- United Emission Catalyst
- AlliedSignal
- U. Michigan

HTML Placed ACEM Contract 9/22/00;
Instrument due at ORNL April 2004

ACEM will:

- be first probe corrected STEM/TEM in US
- have sub-Å resolution for structure
- have sub-Å resolution for chemical analysis
- resolve single Pt atoms on alumina
- be totally automated and remote ready
- very user friendly
- be delivered April 2004
- require a special facility- low EM fields, etc.

JEOL has provided us an interim 2010F STEM/TEM

- with 1.4 Å structural and chemical resolution
- worth about $1.4 M

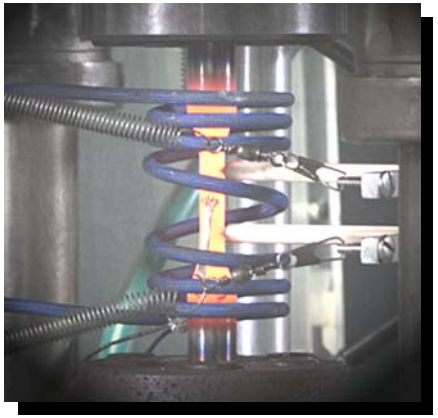
New Building Will Be Styled to Mesh With HTML

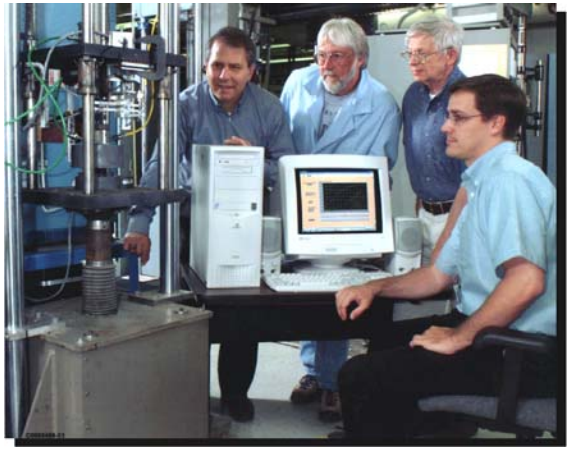
Currently called the Advanced Materials Characterization Laboratory (AMCL)

Mechanical Characterization and Analysis User Center has Complete Facilities

- **28 Electromechanical universal testing machines**
- **23 servohydraulic universal testing machines, at rates up to 1000 Hz**
- **14 test frames with pneumatic actuators**
- **166 dead-weight frames**
- **3 Biaxial (axial/torsional) test frames**
- **Test facility for internal pressurization of tubular components**
- **30 Environmental & High Vacuum chambers**
- **2 Nanoindenters**
- **1 Micromechanical test unit**
- **1 Thermal shock facility**
- **1 Infrared camera**

Development of Low-Cost Austenitic Stainless Steel for Gas-Turbine and Diesel Engine Components





- **Diesel portion funded by OTT HVPM program**
- **CN12 (Fe-25Cr-13NiNbCN alloy) for exhaust manifolds and turbocharger housings.**
- **Comparison with SiMo ductile cast iron and the baseline CN12**
  - **strength, isothermal fatigue, and creep.**
- **Alloy development and screening at ORNL**
  - **"super" CN12 with 10 times the creep resistance at 850°C**
  - **"super" CF8C (Fe-20Cr-12NiNbC alloy)**
- **Alloys can be used at 850°C, are comparable to standard CN12 but cheaper!**
- **Invention disclosure on the modified CN12 and modified CF8C stainless steels**

Diffraction User Center Has X-Ray, Synchrotron, and Neutron Capability

Several laboratory systems up to 18KV with furnaces, atmosphere control, position-sensitive detectors

NSLS at Brookhaven National Laboratory, beamline X-14A, with furnace, atmosphere control

Beamline HB-2 at the High Flux Isotope Reactor at ORNL, with furnace and Atmosphere control

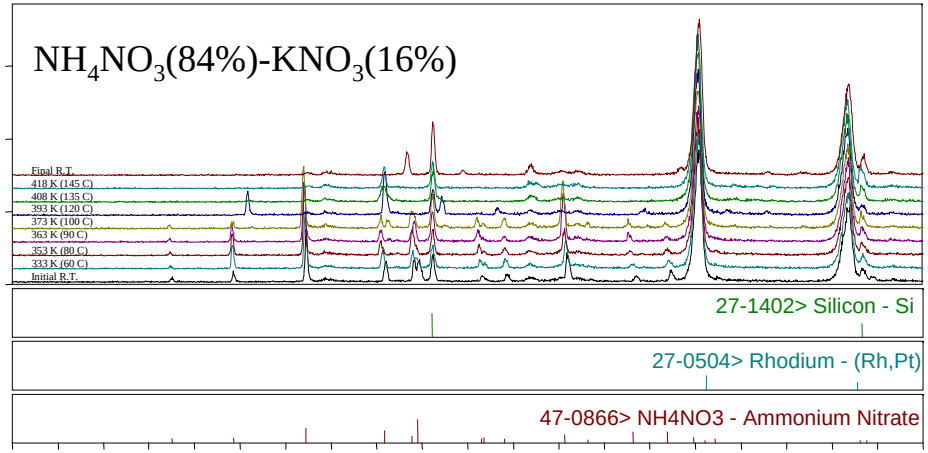
Example Projects: Diffraction

- **Phase transitions in NH_4NO_3-KNO_3 solid solution - U. of Nevada, Reno and TRW, Inc.**
- **Structure of substituted hexagonal barium aluminum silicate by neutron diffraction - Corning**
- **Negative thermal expansion materials - Georgia Tech**
- **In-situ studies of Zr_2Fe hydrides - U. of Nevada, Reno**
- **Nitridation of two-phase Cr-Pt alloys - University of Tennessee**
- **Development of nanocrystalline ceramic particles and thin films - ORNL-BES**
- **Thermal expansion anisotropy in ternary molybdenum silicide intermetallics - ORNL-BES)**
- **In-situ HTXRD study on formation of ceramic superconductors**

In Situ X-Ray Diffraction Helps Researchers Understand Automotive Components at Temperature

Ammonium nitrates are oxidizers in new generation automobile air-bag propellant and need be phase stable between -50 ˚C to 150 ˚C

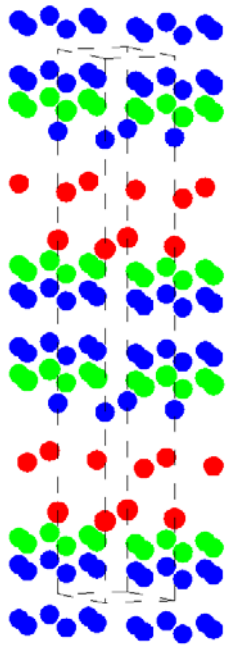
TRW Vehicle Safety Systems



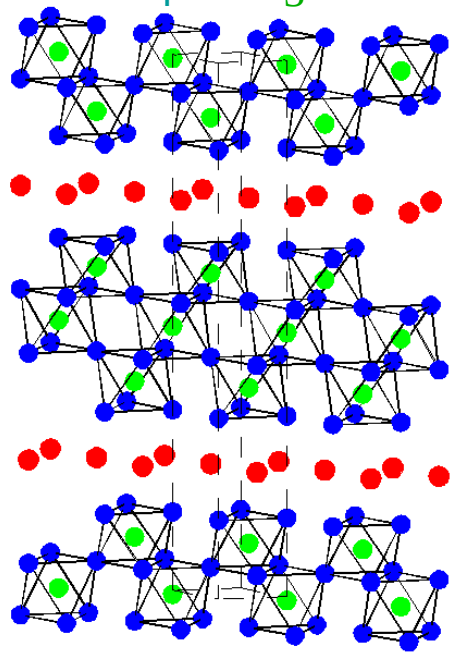
High Temperature Neutron Diffraction Resolved Correct Structure for Ti_4AlN_3

$Ti_3Al_2N_2$

Structure originally proposed by Schuster and Bauer

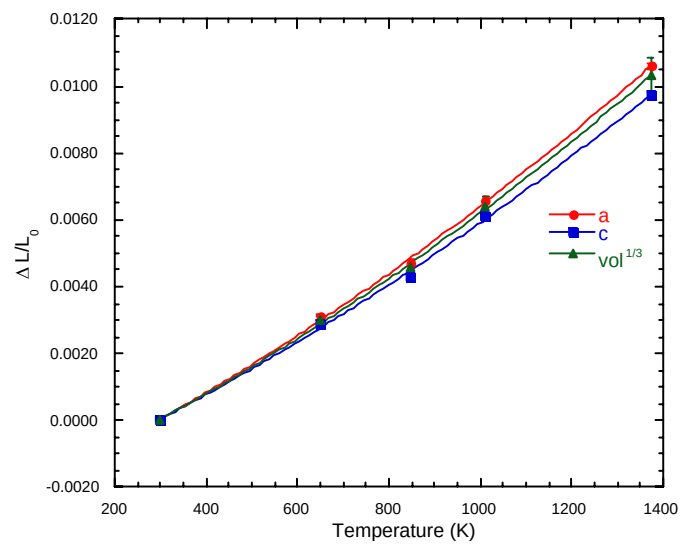


Ti_4AlN_3



a = 2.9875,
c = 23.350 Å
P31c

a = 2.9888(3)
c = 23.382(1) Å
P6$_3$*/mmc*



Michel Barsoum
Tamer El-Raghy
Dept. of Materials Engineering
Drexel University

Example Projects: Residual Stress

- **Cummins Engine - Residual stress depth profiling**
- **Cummins Engine - Induction hardened steels**
- **Lehigh - Residual stresses in ferite to austenite steel welds**
- **Texas A&M - Texture in ECAE processed Cu**
- **Ohio State/Honda - Residual stresses in aluminum engine blocks**
- **EWI - Friction stir welds in aluminum**
- **U. of S. Carolina - Friction stir weld in 2024-T3 Al; Tank car welds**
- **Georgia Tech - Residual stresses about Al fastener holes**
- **U. of Tennessee - NiTi reinforced aluminum; Co superalloys**
- **Honeywell - Residual stresses in direct photo shaped Si_3N_4**
- **Northwestern U. - Stresses in directionally solidified eutectic oxides**
- **UAB- Hydroxyapatite on Ti; Stress distribution in bone**
- **LANL - PIGMA welded Be rings**
- **Alfred U. - Electrostrictive PMN**

Residual Stresses Measured in Al Engine Blocks

Machining releases constraints allowing pre-existing residual stresses to cause distortions

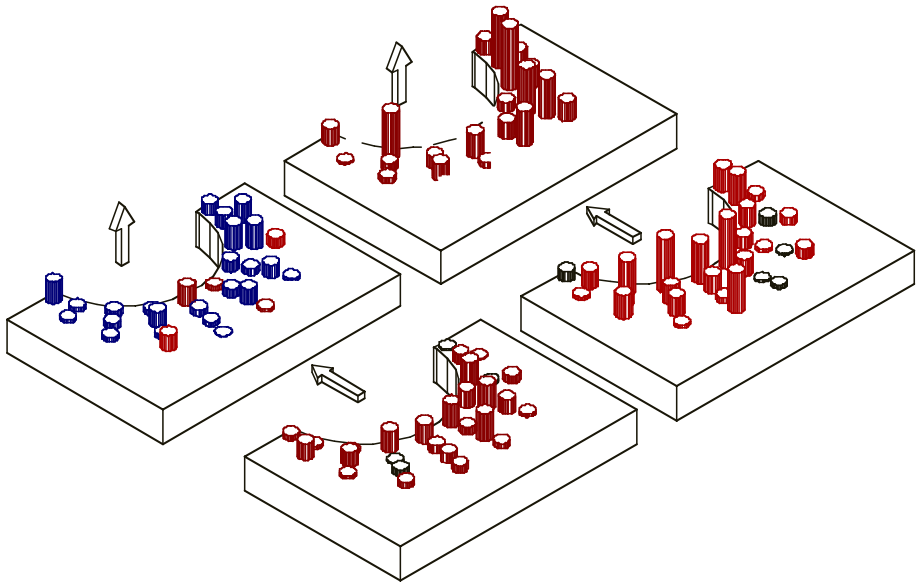
Requires additional heat treatments prior to machining

Thus, a major production-volume limiting step!

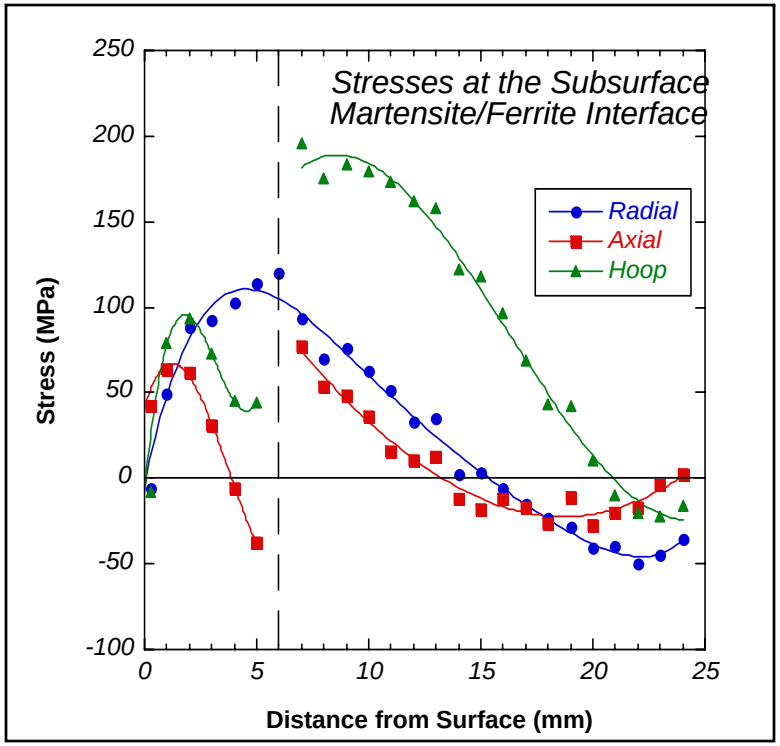
Collaboration amongst:

HTML – Ohio State University - Honda Engine (Marysville, OH)

Residual stress: Neutron and x-ray diffraction techniques employed



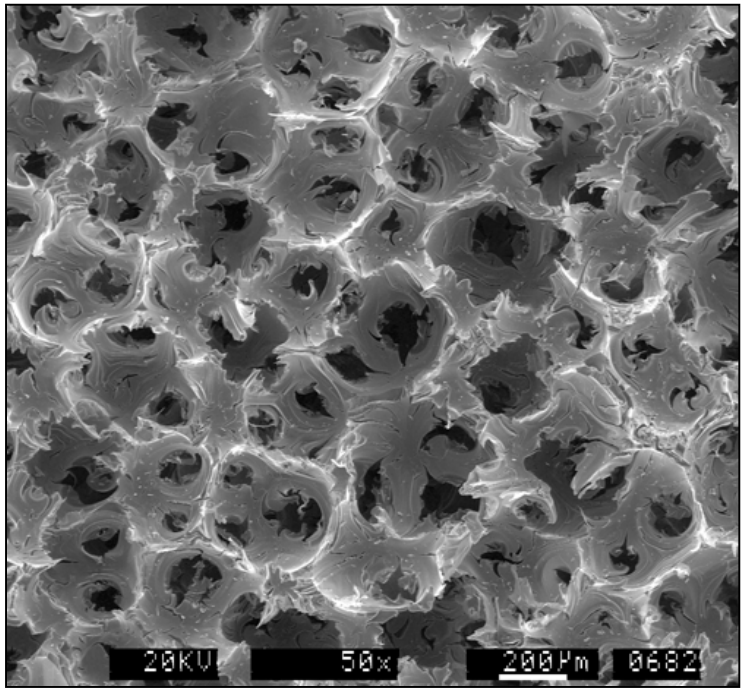
Induction hardened steels - a cost saving process



- Induction hardened crankshafts
  - More reliable
  - Lower cost via energy savings
- Renewed interest in process
- Residual stress: Neutron and x-ray diffraction techniques used
- EERE State Partnership Program:
  - HTML@ ORNL – Cummins Engine
  - Indiana State Energy Office

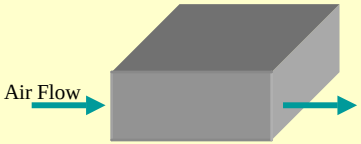
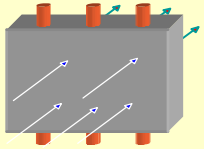
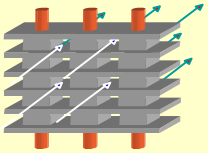
New ORNL Graphite Foam Allows Novel Methods for Heat Management

- Very high specific thermal conductivity
- Lightweight, dimensionally stable, low CTE
- Open cell, high porosity & surface area
- Can improve heat transfer in radiators & cooling fins by more than 10 to 100 X
- Can provide lighter, more compact cooling systems for vehicles, electronics, & personnel



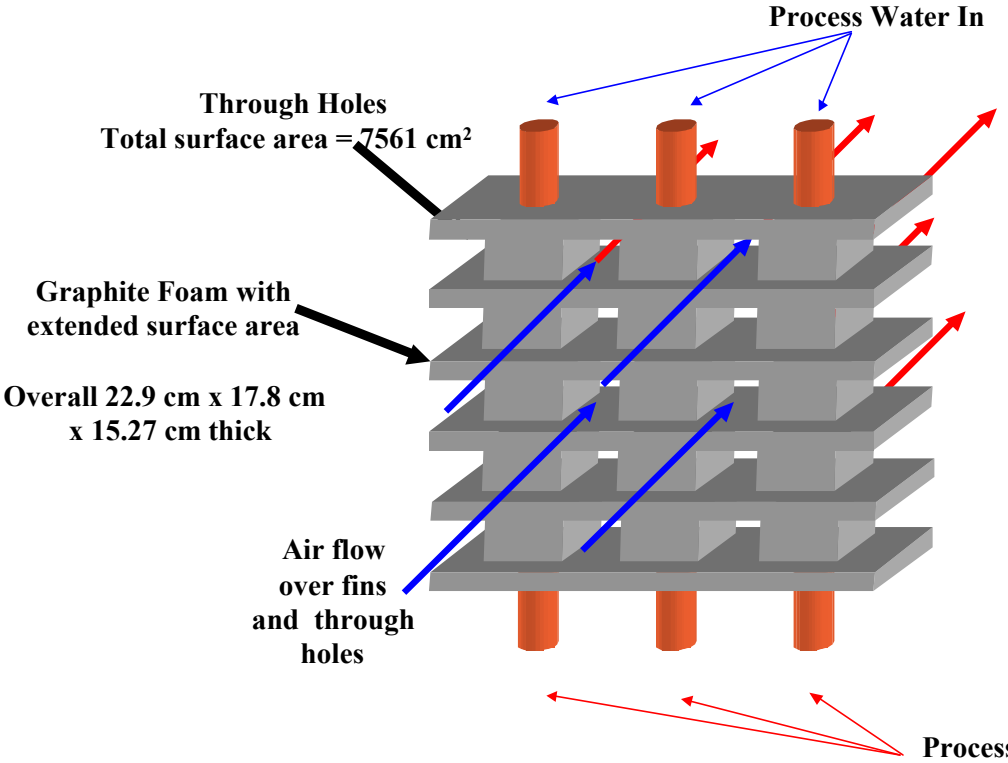
	Graphite Foam	Al	Cu	
Density	0.56-0.58	2.88	8.9	g/cm^3
Specific Conductivity	218-313	63	45	(W/m-K) (g/cm^3)

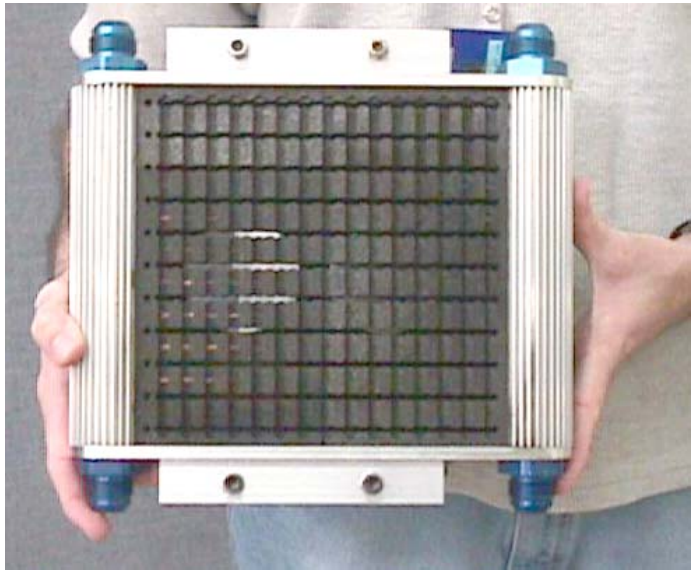
Graphite Foam-Based Heat Exchangers Provide Significantly Improved Performance

		Heat Transfer Coefficient ($W/m^2 \cdot K$)	$\Delta P/L$ (psi/in)
Heat Sinks	Solid Foam 	3,000	2
	Finned Foam	1,000	<0.05
	Aluminum Finned	70-350	<0.05
Radiators	Solid Foam 	10,000*	2
	Finned Foam 	1,000*	0.05

*Current radiators ≈ 30 -100

Prototype Radiator Demonstrated



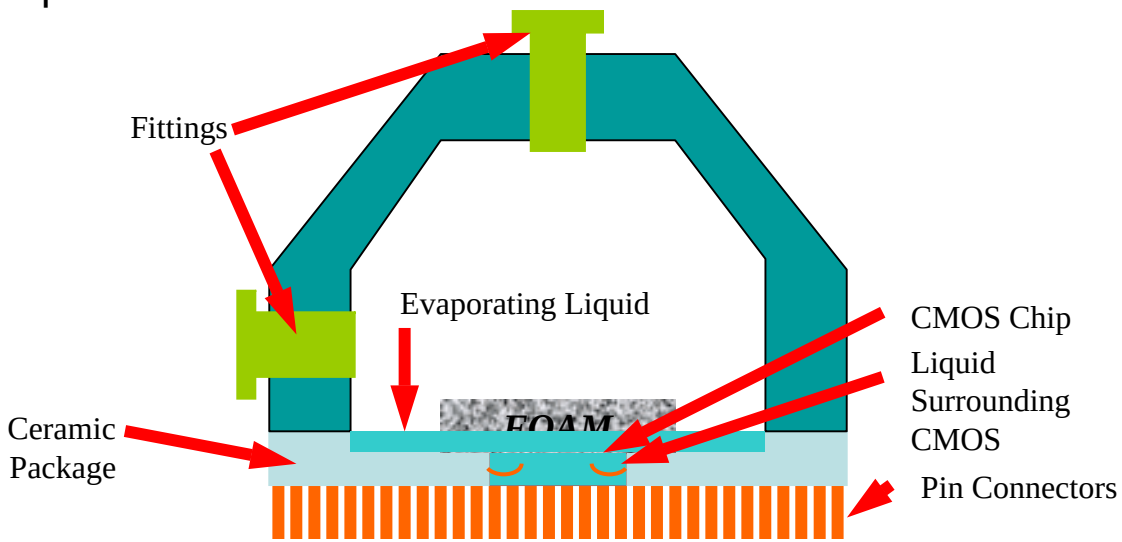


Measured U_o **= 1000 W/m² ·K depending on air humidity**

Similar design tested successfully for 800 hp Winston Cup racing engine

NSA is Working with ORNL to Develop Ultrahigh Performance Cooling of Electronics

- Foams will replace copper and diamond evaporators and condensers in thermosyphon for ultrahigh performance electronics
- Typical diamond evaporators yield ~ 28W/cm^2 maximum cooling power
- First test using foam bonded to silicon die yielded 43W/cm^2
  - 53% improvement in power density over current optimized design
- Redesigned system expected to dissipate 100 W/cm^2
  - 357 % improvement



User Program Requirements

(1) User agreement between your institution and ORNL (legal, IP items)
(2) Technical proposal describing your project
(3) Clearance into the laboratory
(4) Funds into ORNL (if required)
(5) You come do the work here <u>with</u> us

(1) thru (3) can be accomplished simultaneously; schedule is typically dependent on your lawyers or our clearance process (foreign nationals from sensitive countries take ten weeks minimum). Work cannot begin without (4).