3D Sub-nm Compositional Analysis of Radiation Damaged Materials with Atom Probe Tomography – Technology and Practical Considerations

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APT of Radiation Damaged Materials

- One Quick Example!
- An Introduction to Atom Probe Tomography
- APT Sample Preparation (LEAP/EIKOS)
- APT Applications – Nuclear Materials Applications
- Controlled Environment Sample Transfer in the Atom Probe
- Nuclearization of a LEAP System (CEA)
APT Example: Pressure Vessel Steel

Cu atom map – in this case clusters clearly visible

4% Cu isosurface

Provides easy visualization

65x65x90nm

Automated Cluster search algorithm – $D_{max} = 0.5\text{nm}; \ N_{min} = 10$

Provides Quantitative data

RPV embrittlement process
(a) primary radiation damage defects:
(b) formation of nanoscale solute and defect clusters
(c) pinning dislocations by nanofeatures;
(d) hardening enhanced cleavage fracture; at a stress concentration = BRITTLE

CAMECA Products Analytical Resolution

- CAMECA’s core technologies now span the entire achievable analytical capabilities

- SIMS/NanoSIMS
- EPMA/LEXES
- Mass Spec (Nu)
- APT
  - Subnanometer 3D
  - Isotopic/Elemental information
  - TOF – sees all
  - Equally sensitive to all

APT Advances
Description of Atom-Probe Operation

Atom Probe = projection imaging with time-of-flight mass spectrometer

~80nm tip → 80mm detector = 10^6 magnification

Evaporation initiated by:
- Field Pulsing (metals)
- or Thermal Pulsing (all materials)

High Voltage V~10 kV

Vacuum @ 10^-8 Pa (10^-10 mbar)

Time of Flight (TOF) identifies mass
TOF~500 ns for LEAP
ΔTOF < 1 ns

\[ (m/n)_2 > (m/n)_1 \]

\[ \text{neV} = \frac{1}{2}mv^2 \]

\[ v = \frac{L}{t} = \text{constant} \]

\[ \Rightarrow \frac{m}{n} = 2eV \frac{t^2}{L^2} \]

~80% Detection Efficiency

\( L \)
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Truly 3-Dimensional data enables visualizing features hidden by transmissive techniques
Specimen Preparation: General Liftout Method*

a) Protective strip (Pt) is deposited over the region of interest (ROI)

b) Material is removed around three sides of the region (arrows) as well as underneath to produce a long wedge of material containing the ROI

c) The wedge is removed by first attaching a micromanipulator to one end of the wedge (left arrow) and then cutting the wedge free from the substrate (right arrow)

d) The wedge is transferred to a carrier microtip (black dashed circle indicates location of flat 2 μm tip) and attached with FIB-deposited Pt.

e) Wedge is cut free of the carrier tip (dashed line) for transfer to additional tips.

f) The final mounted wedge-section is shown with FIB-deposited Pt at each wedge-tip interface.

g) Then the sharpening process with an annular mill pattern.

All scale bars are 5 μm.
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f) The final mounted wedge-section is shown with FIB-deposited Pt at each wedge-tip interface.
g) Then the sharpening process with an annular mill patter
h) **Also electropolishing for metals (cheaper and faster – not site specific)**
Thin Film Specimen Before and After APT

SEM Image before APT Analysis

Volume analyzed by LEAP

Post APT Analysis Image

C Concentration (at%)
The Growth of Atom Probe Tomography

Continued innovation in APT has lead to an explosion of sites and publications – especially in core applications (metallurgical)

Over 100 Systems worldwide
CAMECA Atom Probe Offerings

Introducing the LEAP 5000 platform

• Optimal performance
  • UV Laser
  • 80% detector efficiency
  • MHz pulse frequency
  • Microtip specimen handling
• Most diverse Applications Space
• Cryo/UHV Transfer Option

First working APT system demonstrated live at a tradeshow

• New hardware designs
  • Pre-aligned electrode
  • Simplified Specimen Stage
  • Simplified Cryo System
  • Simplified Green Laser
• Outstanding performance at lowest Cost of Ownership
APT – A Fast Growing Set of Applications

With the introduction of the Local Electrode Atom Probe (LEAP) in 2003, APT has been transformed from a useful but limited metallurgical technique to the standard material science method for the ultimate in 3D nanoscale compositional characterization.

- Advanced Alloys
- Thin Films
- Silicides
- Oxide growth
- Biominerals
- III/V – LED
- II-VI PVs
- Doping
- Transistors
- Geology-Zircon
Other APT applications for studying materials used in nuclear applications include:

- ODS steels
- Fusion vessel steels and heavy metals
- Aluminum Alloys
- Zr – Cladding (and oxidation)
- Welds of the above materials
- Irradiated Fuel
- SiC – Advanced Cladding
- Radiation damaging and healing
- SCCracking
- Pressure vessel steels

- And lots more.........
APT – Radiation Damage to Materials

Over the last 15 years - Atom Probe Tomography has been transformed from a useful but limited metallurgical technique to the standard material science method for the ultimate in 3D nanoscale compositional characterization.

Weld Damage
*Miller et al., JNM, 371 2007

ODS Steel
Miller, Mat. Sci. and Eng. 2003

Zircaloy-2 gb
Sundell JNM454 2014

Vessel Embrittlement
Miller et. Al. JOM (2001)
APT of Radiation Damaged Materials
-> Practical Considerations

- Collecting the Sample
- Reducing the volume (especially for HOT materials)
- Specimen Preparation – FIB LO – Hot/Shielded FIB
- Introduction of the Specimen into the Atom Probe
- Radiation Considerations of the Microscope

In typical FIB Liftout, the volume reduction (to less than 1 \( \mu \text{m}^3 \)) renders the specimen with unmeasurable radioactivity.
Specimen Introduction – Cryo/UHV Transfer

- Introduction of the Specimen into the Atom Probe
Specimen Introduction – Cryo/UHV Transfer

- Introduction of the Specimen into the Atom Probe – traditionally hand carried in an uncontrolled environment
- Classic 3 Chamber UHV System – All metal seals (except the Load Lock)
- Analysis Chamber ~ 1\(^{-11}\) torr
Specimen Transfer in a Controlled Environment

1. **Sample prep in Cryo**
   - FIB/glovebox/reaction chamber runs

2. **Suitcase attached to FIB/glovebox, sample transferred to cold stage.** (3-5 min)

3. **Suitcase travels to LEAP**

4. **Suitcase attached to LEAP loadlock chamber** (5 min)

5. **Carrier puck pre-cooled in LEAP analysis chamber at UHV (1 hour)**

6. **Carrier puck transferred to LEAP loadlock, specimen puck is attached and lowered to buffer chamber (30 seconds)**

7. **Specimen puck transferred to the analysis chamber (30 seconds)**

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**Images and Diagrams:**
- A figure showing an overview of a specimen transfer setup.
- Diagrams illustrating each step of the specimen transfer process.
NEW! UHV and Cryogenic Specimen Transfer

- LEAP 5000 UHV Cryo Transfer
  - Demonstrated by PNNL/ETH/UMich/Oxford
  - First commercial delivery to MPIE completed
  - New applications & potential increase in yield

- Variety of Applications Now Enabled
  - Rapid oxidizers (e.g. uranium, lithium)
  - Surface contamination (e.g. catalysts)
  - Characterization of hydrogen content in steels, semiconductors, etc.
  - Analysis of “soft” materials potentially encased in vitreous ice (e.g. biological)
  - Transport between various microscopic analysis/treatments (e.g. FIB-SEM, reaction chambers)
  - Radioactive sample transfer
  - Note - Operation and Interlocks integrated into the LEAP software
  - Second System to NTNU: Norwegian University of Science and Technology
Radiation Considerations – Microscope Design

- Remote Operation
- Detector Shielding

After sample loading, the system can be fully remotely operated.
Remote Operation
- Detector Shielding
  - Implemented at CEA in France

Nuclearization – Microscope Design

Electrostatic Reflectron

Specimen

MCP & DL Detector
Radiation Considerations – Microscope Design

- Thicker and more dense of a flight path shield
- Other minor modifications
- NOTE – Primarily Beta/Alpha protection – detection system would be swamped in a high gamma or neutron flux
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THANK YOU – Questions?
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TOF Mass Spectrum (Ni-based superalloy)

Light elements:
- B²⁺
- Al³⁺
- Si²⁺
- C²⁺
- C⁺

Elements with charge state 2⁺:
- Al²⁺
- Cr²⁺
- Ti²⁺
- Nb²⁺
- Ta⁴⁺
- W³⁺

Elements with charge state 3⁺:
- Fe²⁺
- Ni²⁺
- Mo³⁺
- W²⁺

(100x100x250 nm)