Atom Probe Tomography at the CCEM

Brian Langelier

Surface & Micro-Analysis Workshop

May 1 2019 – University of Western Ontario
I. Introduction to APT
   What is atom probe? How does it work?

II. Examples of APT Applications
    Highlights of APT research from the CCEM

III. Case Study: Internal Oxidation
     APT analysis of sub-surface internal oxidation in Alloy 600
Introduction to APT
Local Electrode Atom Probe (LEAP)
- Cameca Instruments LEAP 4000X HR
A sample is disassembled, atom-by-atom. From these data, a 3D model of the original sample is reconstructed, atom-by-atom.

Materials Characterization by APT

APT sample (unknown atoms)

Atoms are measured and identified

From these data, a 3D model of the original sample is reconstructed, atom-by-atom.
An Atom Probe Experiment

Acquisition

Reconstruction
Field Evaporation

Field depends on voltage ($V$) and sample radius ($R$)

$$F = \frac{V}{k_f R}$$

applied DC potential
Specimen Preparation

Electropolishing

Focused Ion Beam (FIB)
Data Acquisition

Voltage Pulse

applied DC potential

Laser Pulse

Time-of-Flight

T: 20-80 K
P: 10^{-9} \text{ Pa}

(x, y)

y

x

T: 20-80 K
P: 10^{-9} \text{ Pa}
Data Reconstruction

Detector x-y Hit Info

Evaporation Sequence

\((x, y, z, \frac{mass}{charge})\)

Reconstruction Parameters (spatial calibration)

Time-of-Flight

Fe

Mn

\(54\text{Fe}^{2+}\)

\(55\text{Mn}^{2+}\)

\(56\text{Fe}^{2+}\)

\(57\text{Fe}^{2+}\)

\(58\text{Fe}^{2+}\)

Counts

mass

charge [Da]

Time-of-Flight

Counts

mass

charge [Da]
Reconstructed Data

3D Atom Maps

C
Mo
Nb
Mn

Spectrum

Count (log)

Mass / Charge (Da)
Capabilities

- Sub-nanometer spatial resolution
- Mass resolving power \( \frac{M}{\Delta M} > 1000 \) at FWHM
- Detectability limit approaching ppm level
- Information provided in 3D
- Able to resolve individual isotopes
- Can analyze a wide variety of samples (laser-pulsing mode)

Limitations

- Detection efficiency <100% (but uniform across the spectrum)
- Peak overlaps in the mass spectrum
  - E.g. \(^{14}\text{N}^+\) (14Da) and \(^{28}\text{Si}^2+\) (14Da)
- Sample fracture can limit data yield

Sample/Material Dependant
Examples of APT Applications
<table>
<thead>
<tr>
<th>Metals &amp; Alloys</th>
<th>Semiconductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Steel transformation interfaces</td>
<td>- Si devices (finFETs)</td>
</tr>
<tr>
<td>- Carbide formation in pipeline steels</td>
<td>- GaN Nanorods</td>
</tr>
<tr>
<td>- Precipitation in Mg, Al alloys (6xxx, 7xxx)</td>
<td>- RE:SiN</td>
</tr>
<tr>
<td>- Nanoporous metals (Ag-Au)</td>
<td>- Si:YAG</td>
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<th>Oxidation &amp; Corrosion</th>
<th>Biological, Mineral, &amp; Ceramic</th>
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<tr>
<td>- Internal oxidation Ni Alloy 600</td>
<td>- Human bone, bone/Ti interface</td>
</tr>
<tr>
<td>- Surface corrosion Mn/Sn – bearing steel</td>
<td>- Lunar, Martian meteorites</td>
</tr>
<tr>
<td>- Oxidation of galvanized steel</td>
<td>- Zircon</td>
</tr>
<tr>
<td>- Stress corrosion cracking Alloy 800</td>
<td>- Cement</td>
</tr>
</tbody>
</table>
Liquid Metal Embrittlement

- Martensite
- Zn-Filled Crack

100 µm
2 µm
100 nm
50 nm
Surface Oxides in Nuclear Alloys

Surface Composition Profile: Fe-Cr-Al Alloy

- W Deposit
- Ni Cap
- Base Metal
- Oxide Layer
- Cr-rich Oxide
- Al-rich Oxide
- Base Metal
Surface Oxides in Nuclear Alloys

Sample Preparation

1 µm

500 nm

Reverse Orientation

Sub-Surface Metal

Surface Oxide

W Deposition

50 nm

Base Metal

Surface

APT Results

Fe Ni Oxide Cr Oxide

Ni Fe Cr O Pb
Damage in Irradiated Materials

Si Nearest-Neighbour Distribution

Collaboration: C. Judge, M. Mattucci, Canadian Nuclear Laboratories (manuscript in preparation)
Irradiated Damage in Irradiated Materials

Collaboration: C. Judge, M. Mattucci, Canadian Nuclear Laboratories (manuscript in preparation)
GaN Nanowires

Sample Preparation

S. Cheng, B. Langelier, Y.-H. Ra, R. Rashid, Z. Mi, G. A. Botton, Nanoscale (accepted manuscript)
GaN Nanowires

Composition Maps (5nm Section)

20 nm

Ga, N Concentration (at.%)

Al, In Concentration (at.%)

Ga, N Nanowires

S. Cheng, B. Langelier, Y.-H. Ra, R. Rashid, Z. Mi, G. A. Botton, Nanoscale (accepted manuscript)
GaN Nanowires

S. Cheng, B. Langelier, Y.-H. Ra, R. Rashid, Z. Mi, G. A. Botton, *Nanoscale* (accepted manuscript)
APT Analysis of Human Bone

Structure & Chemistry of Bone

Osseointegration with Implants


APT Analysis of Human Bone

Nanoporous Gold

- Structure and chemistry of nanoporous gold (NPG) requires nanoscale 3D analysis, for which APT is ideal
- APT analysis cannot tolerate open pores without fracture
- Method of back-filling nanoporous structure with Cu developed to facilitate APT
Nanoporous Gold

Composition Profiles

Concentration (at. %)

Distance (nm)

0.0 5.0 10.0 15.0

Case Study: Internal Oxidation
Internal Oxidation in Alloy 600

- Noble metal matrix: Ni
- Oxidation of reactive solutes: Cr and Fe

Steam exposure: 120h 480°C

Internal Oxidation in Alloy 600

Nodule + Oxides APT

Metallic Nodule

<table>
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<tr>
<th>Element</th>
<th>(at %)</th>
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<tbody>
<tr>
<td>Ni</td>
<td>95.3</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>1.33</td>
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%Ni Map

Internal Oxides


Composition Profile

-Internal oxide network composition of FeCr$_2$O$_4$
Internal Oxides

> 20 at% O  Ni  CrO

Internal Oxides

Composition Maps

Internal Oxides

Concentration Profile

- Cr-rich “cores” are found to be $\text{Cr}_2\text{O}_3$
- Transition to $\text{FeCr}_2\text{O}_4$ at greater sizes/distances

Thank you!

CCEM FACULTY & STAFF
- Gianluigi Botton
- Kathryn Grandfield
- Andreas Korinek
- Travis Casagrande

COLLABORATORS
- Roger Newman (Toronto)
- Suraj Persaud (Queens)
- Ayman El-Zoka (Toronto)
- Shahrzad Esmaeili (Waterloo)
- Hatem Zurob (McMaster)
- Colin Judge (Canadian Nuclear Labs.)
- Shaobo Cheng (McMaster)
- Xiaoyue Wang (McMaster)