Recent Atom Probe Tomography Evolution
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Outline

- Description of the technical principle
- Introduction to atom probe data
- Sample preparation
- Cutting Edge Applications
  - Correlative microscopy for grain boundary analysis
  - TBC
  - TEBSD & APT Tomography
  - Shear Bands in BMG
- Summary and questions

Available in 2017
APT Relative to other Techniques

- APT combines high spatial resolution (in 3D) and excellent detection sensitivity.

- Ion detection efficiency pushes APT up against the information limit for a given volume.

- 1 nm$^3$ of Si: 50 atoms 2% detection limit.
**Description of Atom-Probe Operation**

\[ neV = \frac{1}{2}mv^2 \]
\[ v = \frac{L}{t} = \text{constant} \]
\[ \Rightarrow \frac{m}{n} = \frac{2eV t^2}{L^2} \]

\(~80\text{nm tip} \rightarrow 80\text{mm detector} = 10^6 \text{ magnification}\)

Needle-Shaped Specimen \(~80\text{nm radius at apex}\)

Evaporation initiated by:
- Field Pulsing \((\Delta E \sim 1\%)\)
- or Thermal Pulsing \((\Delta E \sim 0\%)\)

Laser Beam

3-Dimensional Reconstructed Model of Specimen

\( z \) is determined from sequence of evaporation events

2D Detector

Determines \(x,y\) coordinates of atom

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

High Voltage \(V \sim 10 \text{kV}\)

At UHV Vacuum levels
NiCr ML before and after APT

SEM Image before APT Analysis

Volume analyzed by LEAP

Ni

Cr

NIST SRM2135c

Cr

Ni

56nm

57nm

Post APT Analysis Image (acquired at same conditions)
All peaks identified, mainly Ga and N with In, Al and Mg
Introduction to APT Data: Atom Distribution

- Backlight for LCD Displays
- Solid State Lighting (Replace the Light Bulb)

Structure
- Multi-Layer Quantum Well Films
- GaN/InGaN (~nm scale thicknesses)

Characterizations Challenges
- Film Interface Abruptness
- Film Composition Uniformity
- Defects

http://www.medicaldesignbriefs.com/component/content/article/1059-gdm/tech-briefs/9163-gdm0009

'V Defect' disruption to a QW structure

GaN
In
Mg

~150 nm
APT Sample Preparation:

LEAP® 5000

EIKOS™

www.cameca.com
Requirements for Atom Probe Specimens

- Specimens must be sharp as the electric field is inversely proportional to specimen radius.
- Radius of curvature at specimen apex ~100nm or less is required.
- Feature of interest within ~100nm of specimen apex is desired ("site specific" preparation).

Focused Ion Beam: 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
Correlative Microscopy for Grain Boundary Analysis:

Transmission Electron Backscatter Diffraction
Transmission Kikuchi Diffraction
Electron Forward Scatter Diffraction
Transmission EBSD/Transmission Kikuchi Diffraction

- Good for large areas
- Requires a highly polished surface
- Resolution ~100s of nm
- Sample tilted at 70 deg towards the camera
- Diffraction patterns come from top surface

- Good for small sample volumes
- Up to 10x resolution improvement
- Sample positioned flat or slightly tilted away from the camera
- Diffraction patterns generated near the bottom surface
Transmission EBSD can be used to target a specific grain boundary by taking maps during the milling process.

The misorientation between each grain can be measured from the t-EBSD maps and correlated to the chemical segregation at the grain boundary as measured by APT.

In this example, a grain boundary in a Ni alloy was targeted during FIB milling and subsequent APT analysis shows Boron and Si segregation at the grain boundary.
Thermal Barrier Coatings

- TBC protects the hottest component in jet engines and gas turbines, which requires:
  - Low thermal diffusivity
  - High resistivity to oxidation and corrosion
  - Good adhesion on metal substrate
  - Failure usually occurs at oxide/metal interface
- Reactive elements (REs such as Y, Zr, Hf...) can promote the life-time of TBC
- The substrate composition also strongly affects the life-time of TBC

This work focuses on understanding the interface chemistry and the role of REs in TGO
Example Application: Diffusion in Thermal Barrier Coatings

- Structure from top to bottom
  1) Yttrium stabilized zirconia (YSZ)
  2) Thermally grown oxide (TGO)
  3) Pt modified Ni and Al-based bond coat
  4) Ni superalloy (not shown)

- The TGO consists of two layers
  - Mixed oxide
  - Coarse grained alumina

- Reactive elements (REs such as Y, Zr, Hf...) promote the lifetime of TBC by decreasing the growth rate of TGO
- Chemical variations for Zr along the grain boundaries in TGO have been observed by EDS

HAADF STEM

STEM/EDX map for Hf, Y and Ta

GB segregation in TGO

- Mapped with 30 keV electrons
- Mixed oxide region on top
- Image quality (IQ) is higher in grains than grain boundaries
- Spinel and cubic zirconia are not distinguishable based on EBSD patterns
  - Both are cubic
  - Although lattice parameters are different but produce very similar patterns in EBSD
tEBSD/APT Correlative Analysis

Mixed oxide
ZrO₂ & spinel

Alumina
Zr decorated GBs

Alumina
Hf decorated GBs & dislocations

ZrO₂
Ni₃Al₂O₄
20 nm

Atom map

Coarse-grained alumina

200 nm

50 nm

100 nm

Coarse-grained alumina

Dislocation lines
T-EBSD & AP Tomography Analysis for Nanosized Features
Transmission EBSD tomography

- Transmission EBSD only probes the exit surface, so multiple grains in the beam direction can be missed.
- Rotating the sample and taking successive maps can provide a more complete picture of the specimen.

![Diagram of EBSD setup with ions and electrons](image-url)
Transmission EBSD and APT

- tEBSD was carried out to investigate the misorientations of the grains
- Multiple surfaces are mapped and combined into one tEBSD dataset
- Grain boundaries with bright contrast in SEM image
- The bright phase is NdO
- APT reveals Cu and Nd segregation to GBs

NdFeB sample provided by W. Li at Delaware U
tEBSD Tomography and Atom Probe Tomography

- tEBSD maps acquired at 52° tilt
- Combining EBSD datasets and APT dataset into the .pos format
- Cu map highlights grain boundaries
- The non-indexed points in tEBSD are shown in gray
- Better tEBSD pattern quality and indexing when grains are parallel to the e-beam
- Overlapping grains make the indexing more challenging
Structure of Shear Bands in Bulk Metallic Glass
Shear Bands in ZrAlCu

- In collaboration with Prof. Rob Mass’ group at U of Illinois
- Super elasticity, but bad ductility
- APT specimens were prepared to be normal to the shear bands
- The remaining crack clearly indicate the location of shear bands

Exposed Crack  Deformed zone

Shear band
Sliding direction
normal to screen

Pt

Si post
Atom Distribution in Shear Bands

HADDF STEM

Zr  Cu  Al  AlCu/Zr iso-surface  Density iso-surface  Density contour

R5079_170696
Better Throughput and Better Yield

48 hours run acquired in 2008

15x15x60 nm³

X1000 times larger dataset

150x150x600 nm³

36 hours run acquired in 2017
LEAP® and EIKOS™ are the two APT product lines manufactured by CAMECA

The application team at CAMECA Madison is fully devoted to developing new methodology on sample preparation and data analysis.

Correlative analysis with tEBSD facilitates improved crystallographic analysis and site-specific sample preparation.

Precise targeting of grain boundaries

High sensitivity compositional analysis with crystallographic information

Evolution of structural analysis on shear bands in bulk metallic glass

APT provides unique information that reveals a deformation mechanism in metallic glass systems.
Welcome to the CAMECA APT User’s Group Meeting

June 12-15, 2017

Madison, Wisconsin

Registration Date Deadline: June 5, 2017
Be sure to register by this date!

Hello Atom Probe Enthusiasts!

We invite you to take part in our biennial atom probe tomography user’s meeting this June in Madison, Wisconsin. The event will be held next to the beautiful Wisconsin State Capital building at the Park Hotel. Madison is beautiful in June and the opportunity to improve your skills in the art and science of APT will be worth the trip.

This meeting will be workshop oriented and is intended to provide a forum for discussing and proposing action on a wide range of atom probe tomography topics. There will be opportunities for all skill levels to learn from each other at this workshop including a pre-meeting APT tutorial session for those new to APT and a post meeting discussion. An APT Standards Committee meeting is scheduled for Thursday, June 15th. Please pass this message on to your group members and collaborators.

Pre-registration is required. There is no charge for registration, lunches, dinners, or group activities. Travel arrangements and accommodations are the responsibility of the participants.

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Thank you for your attention!

Moving to new building in July 2017!