MICROANALYSIS IN A FIB/SEM:
EDX IN 3D
WHAT CAN WE EXPECT, WHERE ARE THE LIMITS...?

Marco Cantoni, Pierre Burdet

Centre Interdisciplinaire de Microscopie Electronique
(EPFL-CIME)

Since August 2008: NVision 40

- e-beam: ZEISS Gemini
  - 1-30kV, 1nm @ 30kV, 2.5nm @1 kV
- Ion-beam: 1-30kV, 4nm @ 30kV
- EDS X-MAX (SDD) 80mm² detector
- Kleindiek micromanipulator (TEM prep)
- 2-3 Ga Sources / year

FIB Applications @ CIME

- **Materials Science:**
  - TEM Lamellae preparation
  - cross-sectioning, SE/BSE imaging, EDX
  - 3D reconstruction
  - 3D EDX (collaboration with ZEISS)
  - 3D reconstruction of biocompatible materials
- **Life Science:**
  - Serial sectioning of Brain tissue:
    - SUPER-STACKS
The 4 Challenges for 3D EDX

1) Acquisition of a stack speed, overhead, drift control
   Technique

2) Acquisition of EDX maps Detector solid angle, speed
   Technology

3) Interaction with specimen HT -> interaction volume
   Artifact x-rays
   Physics

4) Post processing Quantification “deconvolution”, poor statistics
   Computing

3D Microanalysis by FIB/SEM volume reconstruction
3D FIB/SEM: volume reconstruction

- **Isotropic resolution**
  - Slice thickness (z) = image pixel size (x,y)
  - Z dimension ~ X or Y, typical: 10nm, possible 5nm (3nm)
  - Z-Resolution: low kV !!!

- **High Throughput**
  - Acquisition time “Image” ~1min / slice (~60 slices / hour)
  - high S/N ratio, beam current (1-1.5nA), detector efficiency
  - Dwell times/pixel 5-15µsec.
  - minimise overhead, no tilting, rotating, (drift correction)

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3D Microanalysis by FIB/SEM volume reconstruction

What is the spatial resolution of BSE electrons?

Scatter range in Nb₃Sn:

<table>
<thead>
<tr>
<th>Energy range (keV)</th>
<th>HT (nm)</th>
<th>BSE esc. depth (nm)</th>
<th>Penetration (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10keV - 0keV</td>
<td>100</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>1.6keV - 0keV</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>1.6keV - 1.4keV</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(low loss, EsB grid at 1.4kV)

Energy selective BS
### Typical voxel sizes

- Cement: $(10\text{nm})^3$ voxel
- Solar cell: ZnO: $(10\text{nm})^3$ voxel
- Rat brain: $(5\text{nm})^3$ voxel
- SOFC: $(10\text{nm})^3$ voxel
- Malaria parasite: $(8\text{nm})^3$ voxel
- Clay: $(10\text{nm})^3$ voxel

### 3D EDX with Si(Li) detectors, first steps

**Signals**

@ 20 keV: 100 electrons generate

- $\approx 50-75$ SE
- $\approx 30-50$ BSE
- $\approx 0.7$ X-rays

<table>
<thead>
<tr>
<th>Method</th>
<th>Signal required</th>
<th>Detection solid angle</th>
<th>Bottleneck</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D FIB/SEM</td>
<td>256 grey levels of SE/BSE</td>
<td>small</td>
<td>current in small probe</td>
</tr>
<tr>
<td>EBSD</td>
<td>320x240 pixel image</td>
<td>big</td>
<td>camera speed</td>
</tr>
<tr>
<td>EDX</td>
<td>spectrum $&gt; 10000$ counts</td>
<td>small (getting bigger)</td>
<td>detection speed</td>
</tr>
</tbody>
</table>
The “Si(Li) age”

Quantitative Chemical Analysis 3D EDX-microanalysis

- Separate volume of interest from the bulk
- Cut the sample slice by slice with the I-beam
- Map each cross-section with the e-beam and EDXS
- Reconstruct 3D-model from 2D maps


The preparation technique

- U-pattern
- ion beam current / voltage 3.0 nA / 30 kV
- number of slices 30
- nominal slice thickness 360 nm
- electron beam current / voltage 6.2 nA / 15 kV
- EDXS map size 256 x 200 pixels
- EDXS map pixel size 70 x 89 nm²
- mapping technique EDXS spectrum images
- pixel dwell time (EDXS) 25 ms
- total time per slice ~60 min
- reconstructed volume 12.32 x 17.26 x 9.0 µm³

**Fully automated 3D-FIB EDXS experiment**

3D Ca distribution

3D Mg distribution

3D Ti distribution

3D Si distribution

3D void distribution (reconstr. from BSE images)


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**F. A. Lasagni: EMAS 2009, Gdansk, Poland**

3D NANO-CHARACTERISATION OF MATERIALS BY FIB-SEI/EDS TOMOGRAPHY

Figure 3. (a, b) 3D-reconstruction from EDS maps of the investigated AlSi12 alloy (Si: green, Al: transparent). Note the aliasing effect due to the large distance between serial slices (310 nm) in the turned volume (b).

30min.- 40 min. per slice/map
310 nm voxel dimension (z)
The “SDD age”

New detectors speed up the acquisition! Faster processing and larger surface areas dreaming of 1M counts/sec. 50-100k counts/sec. are more realistic at the moment.

2008 (“SDD age”) installation of Nvision 40 @ CIME use the full potential of the machine

3D-EDX

Pierre Burdet: Ph.D. Thesis in collaboration with ZEISS

Goal: FIB Nano-Tomography based on EDX-elemental maps new generation of EDX detectors (80mm², SDD)

Develop algorithms do "deconvolute" the interaction volume of characteristic X-ray

Ion beam

Sample: Al/Zn, Jonathan Friedli, STI-LSMX

Stack of 269 EDX maps
- High tension: 5kV
- Voxel size: 20 x 20 x 40 nm
- Pixel per map: 256 x 192 (x 269)
- Time per slice: 4+1 minutes
- Time of acquisition: 24 hours
3D EDX is not like FIB/SEM Tomography

“The detector doesn’t see everything”

- Not all X-rays reach the detector

EDX geometrical limitations

“...The detector sees everything....”

- Parasitic X-rays generated by:
  - BSE hitting the trench walls
  - X-rays hitting the trench walls (Fluorescence)
EDX limitations

Parasitic X-ray signals

$\text{Nb}_3\text{Sn}$ (no Cu) in Cu matrix

- Parasitic signal of Cu
  
  Up to 7% at (@ HT = 7 kV)
  
  Up to 20% at (@ HT = 20 kV)
  
  Depends on position on the face

EDX limitations

- Parasitic X-ray signal depends on:
  
  - Geometry and composition of surrounding
  
  - Detector position

- Solutions
  
  - Remove VOI out of surrounding: Block lift-out
  
  - Move the wall facing detector further away

Bigger trenches

Edge geometry (similar to 3D-EBSD)

Complete lift-out
EDX resolution

Resolution limit: Interaction volume

- Lower the high tension as much as possible
- Big voxels (voxel > interaction volume)
- Small voxels: “convolution” problem
  - Delocalisation (metrology !)
  - Quantification (inhomogeneity, interfaces, multiple phases)

EDX resolution

evaluation of delocalisation: model system

- Simulated linescan across the interface normal to y
  - Signal is shifted towards Al because of the incident angle
  - Positions of threshold (10 %, 50 % and 90 %) are used to compare with other geometries
EDX resolution

model system: AlZn

- Stack of 269 EDX maps
  - Acquisition parameters
    - High tension: 5kV
    - Voxel size: 20 x 20 x 40 nm
    - Pixel per map: 256 x 192 (x 269)
    - Times per map: 4+1 minutes
    - Time of acquisition: 24 hours
  - Al Kα elemental map, x/y aligned, smoothing filter (median 3D), surface reconstruction with a single threshold
- Study of the delocalisation of interface (normal to main axes)

EDX resolution

Delocalisation of interfaces

- Implication of delocalization
  - Cubic Al precipitates in Zn matrix (edge 400nm)
  - Errors in volume and surface v.s. edge length of the precipitates
Improving 3D quantification: Idea

- When interaction volume is bigger than voxel size
  - Each spectrum contains a contribution of neighboring voxels
  - Standard quantification inappropriate for voxels close to GB
  - Possibility of quantification enhancement

Algorithm to enhance 3D EDX quantification

Recursive relation
Composition of a voxel depends also on the subsequent voxels (along z)
Sample considered as stratified

\( f \) function: Thin film \( \phi(\rho z) \) quantification*

Recursive relation
\[ C_A^i = f(k\text{-ratios}^i, C_{A-1}^i, C_{A-2}^i, \ldots) \]

Element index

* Pouchou, J. Analytica Chimica Acta 283(1), pp. 81-97 November 1993

PhD thesis of Pierre Burdet
Application: enhanced quantification

- Geometry of acquisition: tilt of 36°
  - Interaction volume delocalized in y
- $C^{i-2}$ = weighted mean of neighbors in y
  - Mean electron y-distribution per z-layer
  - Simulated from pure material

NiTi - steel welding

Jonas Vannod, EPFL-CIME / LSMX

- Wire welding by laser
  - NiTi wire
  - Stainless steel wire
  - 300 mm of diameter
- Molten region
  - Liquid diffusion (fast)
  - Phase formation during solidification
- Characterization
  - Microstructure and composition of the different phases

N. L. Abramycheva, V. Mosko, Univ. Ser. 2: Khimiya 40 (1999) 139-143
Application Example

Experimental: $E_0$ and voxel size

- EDX spectrum image
  - C $\kappa\alpha$, Ti $\kappa\alpha$, Cr $\kappa\alpha$, Fe $\kappa\alpha$, Ni $L\alpha$
  - Fe $\kappa\alpha$ (6.4 kV) $\rightarrow$ 10kV
  - Max X-ray range: 500 nm
  - Voxel size for z: 100 nm
  - For x, y: 100 nm (isotropic)

- SEM image
  - SE image $\rightarrow$ 12.5 nm for z
  - For x, y: 12.5 nm (isotropic)

SE escape depth

EDX Spectrum at 10kV

X-ray depth distribution at 10kV

Application Example: NiTi-Steel

Experimental: Analyzed volume

- On NiTi side
  - Phases of main interest

- Analyzed volume
  - Surface: 12.8 x 4.4 $\mu$m
  - Depth: 9.6 $\mu$m

- 44 EDX maps
  - 6 min per map

SEM image of analyzed volume

SEM image of welding region

FIB slicing direction

SS 100 $\mu$m NiTi

Eu-F-N 2017 Graz Tutorial
Results: SEM image contrast

- SEM image
  - SE (Secondary e-) contrast: no direct interpretation
  - Mean z roughly similar (excluding TiC) → low contrast for BSE (Backscatter e-)

10kV SE image

Application Example: NiTi-Steel

Results: EDX map

- Intensity Maps
  (X-ray line intensity)

- Quant Maps
  Standard EDX procedure

- Noise treatment
  - 3D Median filter (3x3x3)
Phases identification: Ternary histogram

- Ternary EDX map histogram
  - From three main EDX quantified maps (noise treated)
  - Compared to ternary phase diagram
- Phase identification
  - \( \min_A \leq C_A < \max_A \) (\( A=\text{Ti,Fe,Ni} \))
  - \( \min_A \) and \( \max_A \) refined with SE image contrast

Application Example

Phase identification: Fe-poor phases

- Red: NiTi
- Blue: Between (Fe,Ni)Ti and Ni\(_3\)Ti
- Green: Ni\(_3\)Ti
Phase identification: Fe-rich phases

- Green: Between Ni$_3$Ti and Fe$_2$Ti
- Red: Fe$_2$Ti
- Blue: γ-(FeNi)

Applications: NiTi - steel welding

- Small microstructure
  - EDX phases used as mask
  - Threshold on SE contrast
Applications: NiTi - steel welding

- Visualization

Ternary diagram

Reverse Solid Oxide Fuel Cell

2 data sets

SE(InLens) & BSE imaging
@1.8 kV 2.5nA
10x10x10nm voxel
1100 images

EDX mapping
@10kV, 4.5nA
40x40nm every 10 slices (100nm)
110 elemental maps

37x10x11 \( \mu \text{m}^3 \).
MICROANALYSIS IN A FIB/SEM:
EDX IN 3D
WHAT CAN WE EXPECT, WHERE ARE THE LIMITS...?

- FIB/SEM Nano-Tomography: powerful tool for micro(structure)analysis at the nano-scale
- 3D-EDX: Experimental challenges: choice of parameters, geometrical constraints
- 3D EDX: careful interpretation of results

Deconvolution procedures (at least locally)
Statistical treatment of data (PCA, ICA etc.)

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Zeiss (PhD Thesis P. Burdet)

Thank you for your attention!