FUNDAMENTALS ON MICROSTRUCTURAL TECHNIQUES

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Irradiation produces different kinds of nano-features.

Need of quantitative data (size distribution, number density, chemical composition, distribution in material...) to predict structural evolution and correlate with properties.

Any technique is able characterize all kinds of features.

Needs of complementary techniques to identify and quantify these nano-features (PAS, SANS, APT – FIM, TEM, SEM...).
Which technique to observe what?

- **Positron annihilation spectroscopy (PAS)**
  - **Principle**: annihilation characteristics of positons into a sample (depend of electronic density and electron momentum distribution)
  - **Raw data**: Positon lifetime spectrum (PALS) and energy of the photons resulting from annihilation (CDB)
  - **Microstructural information**:
    - Size and density of vacancy-type defects (from mono vacancies to nano-voids)
    - Chemical environment of annihilation sites

- **Small Angle neutron Scattering (SANS)**
  - **Principle**: Scattering of mono-energetic neutron beam by a sample (submitted to magnetic field)
  - **Raw data**: Scattered intensity as a function of scattering angle (∥ and ⊥ to applied magnetic field)
  - **Microstructural information**: Size distribution, volume fraction, range of chemical composition of scattering features (solute clusters...)

16/09/2018  SOTERIA Training School - September 2018 - Polytechnic University of Valencia
Atom Probe Tomography (APT) – Field Ion Microscopy (FIM)

- **Principle**: field evaporation of a small sample
- **Raw data**: position and chemical nature (APT) of atoms in the analysed volume (3D reconstruction)
- **Microstructural information**: shape, size distribution, number density, chemical composition of solute clusters, precipitates, segregation on crystalline defects (APT)
  - Size distribution, number density of small vacancy clusters (FIM)

Transmission Electron Microscopy (TEM)

- **Principle**: Interaction between incident electron beam and a thin sample
- **Raw data**: Images in transmission of the sample (2D), spectra containing chemical information (EDS, EELS)
- **Microstructural information**: size distribution, number density of dislocation loops, voids and precipitates
  - Grain size
  - chemical mapping (EDS, EELS), information about composition of different phases, intergranular segregation
Ex: Genesis platform

Zeiss – XB 540 SEM (EBSD, EDS, FIB)

Jeol ARM 200F (double corrected, EELS, EDS, ADF, HAADF...)

Cameca LEAP 4000X HR

Specific environment for radioactive materials
Field Ion Microscopy

- **Sample:**
  - in the shape of a thin needle (< 50nm),
  - cooled down cryogenic temperature (20-80K),
  - under low pressure (~10^{-5} mbar) of image gas (H, He, Ne),
  - submitted to high voltage (1-11kV).

\[ E = \frac{V}{\beta R} \sim 10 - 50 \text{ V/nm} \]

- **Field ionization of the image gas**

\[ G = \frac{L}{(m + 1)R} \]

\[ G \sim 10^6 - 10^7 \]

- **Field evaporation of the surface atoms**
Increment in depth from the number of evaporated plans

3D reconstruction of the volume:
- high lateral and depth resolution
- ~100% detection efficiency
- No/poor chemical information

Grain boundary in W

3D reconstruction of W

Dark contrast from nano-voids in irradiated W

C. Hatzoglou

B. Claes
Atom Probe Tomography

- Same principle than FIM but
  - No image gas \((P\sim 10^{-11}\text{mbar})\)  
    \(\Rightarrow\) Field evaporation of surface atoms
  - Position sensitive detector  
    \(\Rightarrow\) Localisation of atom position
  - Time of flight mass spectrometry  
    \(\Rightarrow\) Identification of the chemical nature

\(\Rightarrow\) 3D reconstruction of the analysed volume, at atomic scale

A. Etienne, n-irradiated 16MND5
APT – tof mass spectrometry

- Assuming the whole potential energy if converted into kinetic energy:

\[ \frac{m}{n} = 2eV \frac{t_f^2}{L^2} = kV \frac{t_f^2}{L^2} \]

- Evaporation pulse (laser or electric) is applied to the sample
  \[ \Rightarrow \text{measurement of time-of-flight between pulse and arrival on detector} \]

- Results are collected on a mass spectrum
**APT – 3D reconstruction**

**Position sensitive detector + inverse projection**  ➜ Position of each atom at the surface

For each detected atom, the reconstructed volume is incremented by $V_{at}/Q$

Knowing the analysed surface, it allows to reconstructed the 3rd dimension

**Magnification**

$$G = \frac{L}{(m + 1)R}$$

$G \sim 10^6 - 10^7$
Solute clusters:
- composition: 2.6%Mn – 3.8%Si – 6.3%Ni – 5.3%Cu (Fe)
- number density: 3.7x10\(^{23}\) m\(^{-3}\)
- size distribution

Segregation along dislocations:
- composition: 0.95%Mn – 1.1%Si – 2.4%Ni – 0.31%Cu – 3.9P – (Fe)
- density: 1.1x10\(^{14}\) m\(^{-2}\)
A. Akhatova: intergranular segregation in Fe-P-C model alloy

\[ GP \ 35^\circ[104](16-1)/(33-1) \]

\[ \text{Distance, nm} \]

\[ X_{P}^{GB} = 0.13 \]

\[ X_{C}^{GB} = 0.40 \]

L. Zhang: P segregation at carbide-matrix interface in RPV weld
Visible features
- Solute clusters and precipitates (0.5 – 50 nm): composition, number density, size distribution, shape, 3D repartition, volume fraction
- Segregation on crystal defects (dislocations, loops, GB...): density, composition, Gibbs excess...
- Matrix: chemical composition

Performance
- detection efficiency: 35 to 80%
- detection limit: down 10 at. ppm in best cases
- spatial resolution: ~ 0.2 nm in depth – 0.5-1nm laterally
- Analysed volume: ~50x50x200 nm³

Limitations
- trajectory aberrations resulting from difference in evaporation field can induce bias atom positioning (shape of particles, chemical composition)
Transmission electron microscopy

- **Sample:**
  - in the shape of a thin foil (<100nm in thickness),
  - under secondary vacuum (~$10^{-5}$-10^{-7}$ mbar),
  - illuminated by electron beam (several $10^{\text{th}}$ to $100^{\text{th}}$ of keV).

- **Interaction electron-matter**
  - diffraction, mass-thickness, phase contrasts
  - energy loss, X-ray emission

- **Image in transmission that can reach atomic resolution**
  - information about phases, grain size, crystal defects...
  - Chemical analysis possible with specific detectors

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S. Rouland

A. Etienne

C. Hatzoglou
A parallel beam of electrons can be diffracted by a family of reticular planes \((hkl)\) in Bragg conditions

- **Electron non-diffracted** converge to the center or the focal plane
- **Diffracted electrons** by the same plane family converge to the same point of the focal plane.

\(\implies\) **Diffraction pattern in the focal plane**

Each electron coming from a same point of the sample converge on same point of image plane forming the **image into image plane of the objective**
• The contrast is obtained by mean of contrast aperture located in the focal plane of the objective. This aperture allows to select electrons from direct beam or from one of the diffracted beam.

→ Deficit or excess of electrons at the location of diffracting zones that appear more or less bright.

• The area selection aperture is located in the image plane of objective lens. It allows to select electrons coming from a give, area.

→ selection of the imaged area
TEM - Example

FP7 Longlife, D3.3 – RPV steel, n-irradiated at high dose (M. Mayoral)

heterogeneous distribution of dislocation loops

Mn Ni Si Cu

$y = 0.0806x^{0.7427}$

$R^2 = 1$
• Elastic scattering of results from interaction of incident electrons with electronic cloud or atom nucleus.

• It increases with:
  - Atomic number (Z)
  - Thickness of the sample

⇒ Through areas with high atomic number, electrons are more diffused (Z contrast)
Scanning TEM

- The incident beam is focused on a point of the sample (probe)
- The probe (<1nm) is scanned on the sample
- For each location, different signals can be collected to form the image
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Contrast in STEM

Contrast on image is obtained thanks to annular detectors

High Angle Annular Dark Field (HAADF) detector

- Heavy elements appear bright (Z-contrast)

Low Angle Annular Dark Field (ADF) detector

- Crystal defects bright (diffraction contrast)

Bright Field (BF) detector

- Crystal defects and areas rich in heavy elements appear dark
Example

O. Startev et al, SOTERIA WP3

HAADF image of RPV steel

⇒ PAGB, lath boundaries and carbides
Chemical analysis

Inelastic interaction between incident electrons and electron clouds

Energy Dispersive Spectrometry (EDS)

Electron Energy Loss Spectrometry (EELS)

chemical mapping – Chemical composition (in transmission)

STEM EDS on n – irradiated high Ni weld

STEM BF

STEM EDS

matrix

MnNiSi clusters

⇒ correlation between crystalline et chemical information
(S)TEM – Performances and limitations

Visible features
- Crystalline defects (GB, dislocations, dislocation loops, voids...): Size distribution (> 1 nm), number density
- Precipitates: Size distribution (> 1 nm), number density, chemical information (2D)
- Segregation: chemical information

Performance
- Detection limit: ~ 1% (EDS)
- Spatial resolution: ~ 0.2 nm
- Analysed volume: <100 nm in depth x several μm²

Limitations
- 2D image in transmission
Needs of very thin samples for FIM, APT and TEM (foil or needle)

Electropolishing

- APT needle: double layer, μ-loop
- TEM foil: twin jet

- "High" quantities of matter – can be a limitation for radioactive samples
- No control on the sample exact location
- Limited to metals
Sample preparation

- Focused Ion Beam milling:
  - Sputtering of sample atoms using ion beam (FIB)
  - Imaging using electron beam (SEM)

- Lift out

- Annular milling (neeles)

- TEM foil milling

- Reduce the amount of matter needed
- Applicable to all kinds of materials
- Control on the sample location
- Ga implantation!
<table>
<thead>
<tr>
<th>Technique</th>
<th>Sample shape</th>
<th>Analysed volume</th>
<th>Crystal defects</th>
<th>Segregations</th>
<th>Precipitates Solute clusters</th>
</tr>
</thead>
</table>
| 3D-FIM    | thin needle  | 50x50x200nm³    | - dislocation, GB visible  
- voids (0.5-few nm): SD, ND | / | - visible in some cases |
| APT       | thin needle  | 50x50x200nm³    | - visible if segregated | - shape, CC, ND | - SD (0.5-50nm), ND, CC, shape |
| (S)TEM    | thin foil    | 20-100nm thick several μm² | - GB  
- dislocation (D)  
- loops, voids, SFT (ND, SD) if > 1nm | - intergranular segregation: concentration profile | If size > 1nm  
- 2D chemical mapping  
- crystalline structure  
- information about CC |
| PAS       | well polished plate | 0-0.5mm depth several mm² | - V-type (from mono-V to nm voids): Size and chemical env. | / | / |
| SANS      | bulk         | cm³             | /               | /            | - SD (1-100nm), \( f_v \), CC range |

\( CC = \) chemical composition / \( SD = \) Size distribution / \( ND = \) number density / \( CC = \) chemical composition  
\( f_v = \) volume fraction
Thank you for your attention

http://gpm.labos.univ-rouen.fr/
http://genesis.univ-rouen.fr/

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Positons (emitted by the desintegration of a radioelement) go through the sample.

After thermalisation, positons diffuse into the material where they can:
- be trapped by vacancy-type defects
- Annihilate with electrons from the material

Annihilation results in the emission of 2 photon in opposite directions.
Life time $\Rightarrow$ size of vacancy clusters
Doppler shift probes the local electron momentum

Doppler shift, \( \Delta E \) is proportional to electron momentum, \( p_L \)

\[ \Rightarrow \text{Depends of the chemical environment} \]
- Mono-energetic neutron beam goes through a bulk sample
- Scattered intensity as a function of scattering angle contain information about size distribution, shape and volume fraction of features

\[ \vec{I}(\vec{q}) = f_p(\Delta \rho_{nuc}^2 + \Delta \rho_{mag}^2 \sin^2 \alpha) \left| F_p(\vec{R}, \vec{q}) \right|^2 S(\vec{q}) \]

- A-ratio contains information about chemical composition of features