ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY (ESEM)

Jean-Luc BIAGI
Electron Interaction with sample

- **Topography**
- **Chemical contrast**
- **EDX spectrum**

![Diagram showing electron interaction with a sample](image)

- **Primary Electron Beam**
- **Secondary Electrons** (nm range)
- **Backscattered Electrons** (several 10's of nm to 100 nm)
- **Auger Electrons**
- **Characteristic X-rays**
- **Samples Surface**
- **Volume of Primary Excitation**
- **1-3 μm Analysis Depth**
Features

- **Quanta FEG 200 (FEI) coupled with an EDS GENESIS XM 4i (EDAX)**

- Electron gun : Field Emission Gun (FEG)
  - Better beam stability (compared to a hot cathode)
  - High lateral resolution (a few nanometers)

- Versatile all in one SEM
  - **High vacuum** (down to 6e-6 mbar)
    - Common SEM mode
  - **Low vacuum (around 1 mbar)**
    - Low pressure gas inside the analysis chamber
    - Eliminate sample charging
  - **Extended Low Vacuum mode ESEM (0.1 to 30 mbar)**
    - Control of humidity conditions

- **Samples**
  - All types with minimum preparation
  - Max. dimensions / weight: 8cm × 8cm × 5cm / 1kg
Topographical / Morphological characterization

- Porosity in brass

High vacuum mode

Topographical contrast

Depth of field
Secondary $e^-$

Chemical contrast

Colour scale = $f$ (Z atomic)
Backscattered $e^-$
Characterization of non-conductive samples

- Tick on carbon tape

- No sample preparation
- Quick results
- Spatial resolution (tens of nm)
- Magnification of $\times 50\,000$ easily obtained
Elemental chemical analysis and mapping

Qualitative analysis: Ti, Zn, O
Elemental chemical analysis

Semi-quantitative analysis

Experimental result of EDS analysis

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Mo</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
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</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>0.7</td>
<td>2.8</td>
<td>18.9</td>
<td>1.5</td>
<td>64.1</td>
<td>0.2</td>
<td>11.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Standard ANSI 316 Stainless Steel

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Mo</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
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<tbody>
<tr>
<td>Wt%</td>
<td>0.5</td>
<td>2.4</td>
<td>18.5</td>
<td>1.6</td>
<td>64.3</td>
<td>0.1</td>
<td>12.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Transmission imaging (STEM detector)

- Ultrathin sections placed on copper-grid
- Better resolution than in classic mode

Ag nanoparticles

Nanotubes in a composite
DYNAMIC IN-SITU ANALYSES

In-situ materials testing: micro-tensile machine

Visualization of sample damage as a function of stretching

For more information, see Yves Fleming / Frederic Addiego’s presentation this afternoon

Micro-tensile machine
DYNAMIC IN-SITU ANALYSES

Material change under temperature effect

Temperature control: heating stage up to 1500°C

Temperature Profile:

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Ramp</th>
<th>Scale Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>473°C</td>
<td>20</td>
<td>0.000005</td>
</tr>
<tr>
<td>610°C</td>
<td>20</td>
<td>0.000005</td>
</tr>
<tr>
<td>625°C</td>
<td>10</td>
<td>0.000005</td>
</tr>
<tr>
<td>646°C</td>
<td>10</td>
<td>0.000005</td>
</tr>
</tbody>
</table>

Increase of temperature

Appearance of surface defects
DYNAMIC IN-SITU ANALYSES

Analysis under humid conditions

→ Temperature control
  ▪ Peltier cooling stage down to \(-25^\circ\text{C}\)

→ Humidity (RH) control
  ▪ Variation of humidity up to 100%

Peltier cooling stage

Temperature and/or RH control

Pressure & temperature conditions to maintain water in a liquid state in ESEM.
DYNAMIC IN-SITU ANALYSES

Analysis under humid conditions

- Gaseous Secondary Electron Detector GSED
- Peltier cooling stage
- View of the chamber in ESEM configuration

Cooling stage
Maximum sample size is limited to $6 \times 6 \text{ mm}^2$
DYNAMIC IN-SITU ANALYSES

Analysis under humid conditions

- Example 1: Hydration / Dehydration

Analytical parameters

- Pressure: 6 to 7 Torr
- Temperature: 5°C
- Humidity: 0 to 100 %
DYNAMIC IN-SITU ANALYSES

Analysis under humid conditions

- Example 2: silicon wafer coated with plasma-polymer

Due to coatings defects (cracks, uncoated area, thickness variation, ...), droplets are not of perfect circular shape.

Drops appear and increase in diameter randomly.
Example 3: carbon fibers

- As received, no surface treated

- Carbon fibre treated with a water-based solution containing a catecholamine at different concentrations

- Carbon fibre treated with a water-based polyelectrolyte solution then with an aged catecholamine solution during different time of treatment.

With courtesy to Arnaud Martin
**DYNAMIC IN-SITU ANALYSES**

Analysis under humid conditions

- Example 4: Liquid drops on the insect body

Pressure: 5.2 Torr - Temperature: 1°C - Humidity: 100%
Type of analyses

⇒ Topographical / Morphological characterization

⇒ Phase distribution / Elemental chemical analyses (EDS)

⇒ Transmission imaging (STEM detector)

⇒ Dynamic in-situ analyses

⇒ In situ materials testing (micro-tensile machine)

⇒ Temperature control (heating stage up to 1500°C)

⇒ Under humid conditions (ESEM)

  - Temperature control (Peltier cooling stage down to –25°C)
  - Humidity (RH) control (variation of humidity up to 100%)
SEM HITACHI SU-70 CHARACTERISTICS

Source: FEG gun

Equipment:
- Only High Vacuum
- Accelerating voltage range: 0.1-30kV
- SEM detectors (upper, lower)
  Multiple (SE/BSE) in-Lens
- Resolution at $15kV = 1nm$, $1kV = 1.6nm$
- Magnification: 30x - 800,000x
- EDS and WDS spectrometers
  (Oxford instruments)
- Samples: polymers (low energy), metals, composites, ceramics
- Size of specimen: up to $5cm \times 5cm \times 3cm$
- Rotation of sample $360^\circ$ and tilt $70^\circ$
Advantage of Wavelength Dispersive Spectrometry (WDS)

Overlap of Silicon K and Tantalum M lines are easily resolved using WDS (red spectrum) instead of EDS (green spectrum).

- Better sensitivity, better accuracy
- Requires (time-consuming) element per element calibration
<table>
<thead>
<tr>
<th></th>
<th>SEM HITACHI SU-70</th>
<th>E-SEM FEI Quanta FEG 200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate imaging performances</td>
<td>1 nm</td>
<td>Tens of nm</td>
</tr>
<tr>
<td>Modes</td>
<td>High vacuum only</td>
<td>High vacuum, low vacuum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(better for the analysis of insulating samples)</td>
</tr>
<tr>
<td>Sample size</td>
<td>5cm x 5cm x 3 cm</td>
<td>8cm x 8cm x 5cm / 1kg</td>
</tr>
<tr>
<td>Detectors</td>
<td>EDS, WDS</td>
<td>EDS only</td>
</tr>
<tr>
<td>Accessories</td>
<td></td>
<td>Mechanical strain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Relative humidity (Wet SEM)</td>
</tr>
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→ High performance SEM
→ Highly flexible SEM
False colour images of the surface of a material after ageing in tropical conditions

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