Imaging and Microanalytical Capabilities of the Swagelok Center for Surface Analysis of Materials (SCSAM)

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Fall Break Short Course
Oct. 27th, 2014
Swagelok Center for Surface Analysis of Materials
SCSAM: A Multi-user Analytical Facility

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The Case School of Engineering administers the Swagelok Center for Surface Analysis of Materials (SCSAM) for the entire Case Western Reserve University community.

SCSAM is a multi-user analytical facility providing instrumentation for materials characterization and surface and near-surface chemical analysis.

The facilities in SCSAM are available to campus users, MatNet (Materials Network of Ohio) associates and industrial clients for solving a variety of research, development and failure analysis problems.

- Hitachi S-4500 FEG Scanning Electron Microscope (SEM)
- FEI Helios Dual Beam Focused Ion Beam (FIB) FEG -SEM
- FEI Nova Nanolab Dual Beam Focused Ion Beam (FIB) FEG -SEM
- FEI Quanta 3D Dual Beam FIB- ESEM System
- FEI Tecnai F30 300 keV Scanning Transmission Electron Microscope
- Zeiss Libra 200 keV Analytical Transmission Electron Microscope
- Fischione Model 1040 NanoMill TEM specimen preparation system
- Gatan Ilion Ion Polisher
- Physical Electronics PHI nanoTRIFT V TOF-SIMS
- Physical Electronics PHI-680 Scanning Auger Microprobe System
- Physical Electronics PHI-5600 X-ray Photo-Electron Spectrometer (XPS/ESCA)
- Olympus FV-1000 Laser Scanning Confocal Optical Microscope
- Bruker Discover D8 X-Ray Diffractometer (Co target)
- Scintag X-1 Advanced X-Ray Diffractometer (Cu target)
- Rigaku B/MAS 2200 X-Ray Diffractometer (Cr target)
- Agilent 200 Nano-indenter
- Veeco DI Atomic Force Microscope (AFM) with Hysitron Nano-indenter
- RHK 7500 UHV Variable Temperature Scanning Probe System
Short Course Agenda*

Day 1
1:30-2:15—Arthur Heuer—Introduction
2:15-3:15—Amir Avishai—SEM/EDS
Break
3:30-4:00—Wayne Jennings—TOF-SIMS
4:00-4:45—Jonathan Cowen—XRD/EBSD
4:45 General discussion

Day 2
1:30-2:00—Amir Avishai—FIB
2:00-2:45—Danqi Wang—TEM
2:45-3:15—Richard Tomazin—AFM/Nanoindentation
Break
3:30-4:45—Wayne Jennings—XPS/AES
4:45 General discussion and wrap-up

* pdf’s of all presentations can be found on SCSAM’s web site: http://engineering.case.edu/centers/scsam/
Surface Analysis*

Irradiation with X-rays: X-ray Photoelectron Spectroscopy (XPS/ESCA) - 10µm spatial resolution

Irradiation with Ions: Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) - 100 nm spatial resolution

Irradiation with Electrons: Auger Electron Spectroscopy (AES) - 15 nm spatial resolution

*Top 2 or 3 atomic layers
PHI-680 Scanning Auger Microprobe

PHI 5000 Versaprobe XPS/ESCA Small Spot System
Chromium GI*-XPS 2p Signal from Passive Film on Carburized 316L SS Polarized at +200 mV for 1 hr in 0.6M NaCl Solution

*A glancing angle of 20 degrees was used throughout this work.
Varying the nitrogen activity can produce widely varying N depth profiles. Note the marked concentration dependence of the N diffusivity.
PHI TRIFT V TOF-SIMS*

*100 nm spatial resolution
High Mass Resolution: $^{26}\text{Mg}$ and $^{26}\text{Al}$
Oxidation of Ni-Base Alloys
Ni20Al5Cr-0.05Hf-0.05Y
1100°C for 50h, TOF-SIMS 3D Reconstruction

Aluminum  Nickel  Chromium  Yttrium  Hafnium

~1µm
300µm

NiCrAl-Spinel
Voids/HfO₂
α-Al₂O₃
Ni$_{20}$Al$_{5}$Cr-0.05Hf-0.05Y
1100°C for 50h, TOF-SIMS 3D

Aluminum  Nickel  Chromium  Yttrium  Hafnium

~1µm

300µm

NiCrAl-Spinel
Voids/HfO$_2$
α-Al$_2$O$_3$
(removed to show Y-phases)

Y-rich phases
Ni20Al5Cr-0.05Hf-0.05Y
1100°C for 50h, TOF-SIMS 3D

Aluminum  Nickel  Chromium  Yttrium  Hafnium

Hf is only seen below the spinel layer

Y-rich phases are continuous between spinel and Al₂O₃!!

Voids/HfO₂

α-Al₂O₃ (removed to show Y-phases)

~1µm

300µm
Thyroid Tumor Cells

Phosphocholine ($\text{C}_5\text{H}_{15}\text{PNO}_4$)
Electron Microscopy in the Swagelok Center: Useful Signals Generated from Electron–Matter Interaction

It is essential that specimens for TEM be extremely thin, i.e., ideally a few tens of nms or less. This allows the energetic electron beam to pass through the specimen and generate useful signals. For SEM, this requirement does not exist, but it is necessary for the sample surface to be electrically conductive to minimize effects of charging.
Electron Microscopes: Transmission (TEM) and Scanning (SEM)

Zeiss Libra 200FE TEM

FEI Helios 650 Dual Beam FIB/SEM
Operation of a Scanning Electron Microscope

Schematic diagram illustrating the essential components (left) and the scanning system (right) of a SEM. Note that an array of useful signals can be collected and analyzed by use of different detectors. Chemical microanalysis with the EDS (energy dispersive (X-ray) spectroscopy) detector is very widely used.
Microanalysis of a Cast Iron

[Images of various microanalysis results showing the distribution of elements such as Fe, Cr, and Si across the material sample.]
A FIB instrument showing the Ion and Electron columns and the specimen inside the vacuum chamber. FIBs are extensively used for TEM specimen preparation and 3D reconstruction.
Hitachi S-4500 FE-SEM

FEI xT Nova Nanolab 200 Dual-Beam FIB
3D Video of Mitochondria in an Optic Nerve Axon

2µm
in situ Lift Out
Site-Specific TEM Sample Preparation Procedure

1. Embed in epoxy under vacuum.

2. FIB

3. Final thinning

4. TEM lamella

- electrolyte
- cathode
- anode

Cells
Electrolyte-Cathode Interface

YSZ electrolyte

LSM-YSZ* cathode

*LSM – La\(_{1-x}\)Sr\(_x\)MnO\(_y\);
YSZ - Y stabilized ZrO\(_2\)
EDS Analysis-elemental maps

Superimposed map

Secondary MnO\textsubscript{x} phases (green regions) formed in electrode
EELS Analysis-valence state

O-K edge results show the presence of precipitates in 2 valence states
Combination of EDS and EELS techniques

Reveals formation of a mixture of phases with Mn in 2 valence states
Scintag Advanced X-Ray Diffractometer System

- Conventional theta-theta scan
- Rocking curves and sample-tilting curves
- Grazing angle X-ray diffraction (GAXRD)
- High-temperature (1600 °C) camera enables in situ studies
- DMSNT software package is used to control the diffractometer, to acquire raw data and to analyze data
- JCPDS database and searching software for identifying phases

XRD scans obtained from a carburized 316L austenitic stainless steel at different depths below the surface, obtained after successive removal of well-defined layers from the surface by electropolishing. The scan at the bottom was obtained from an untreated 316L stainless steel specimen.

The XRD scans show that the carburized case is single phase, extends to a depth of ~20 microns, and that the lattice parameter of the carburized material has expanded by ~3 % (the smaller 2 theta values indicate larger d spacings).
Tissue Regeneration in the Shell of the Giant Queen Conch, *Stombus gigas*

Schematic Drawing of Conch Shell

site of wound repair

abiotic glass
Schematic Drawing of Crossed Lamellar Architecture: “Ceramic Plywood”

Layers: 0.5-2 mm thick

First order lamellae
5-60 μm thick; many μm wide

Second order lamella
5-30 μm thick; 5-60 μm wide

Third order lamella with twins
60-130 nm thick; 100-380 nm wide

Twins
10-20 nm wide

Large top face
End face

Side face
Fracture Surface
X-Ray Diffraction Patterns; the CaCO$_3$ is the Aragonite Polymorph
Petrographic section viewed through crossed polarizers. Inner layer is on the left, middle layer is on the right.
X-ray diffraction patterns taken during wound repair
TEM Images of Lamellar Microstructure

First Order Lamellar Interface  Second Order Lamellar Interface
TEM image of “end-on” second order lamella. Note the globular matrix.
High resolution TEM image showing twin boundary in a third order lamella.
Conclusions

SCSAM is the best-equipped academic analytical characterization facility in the US, if not the World.