Materials Science at the ESRF
What is (Structural) Materials Science?

- Effect of structure on materials properties
- In particular, **micro** and **nano**-structure
- more particularly, defects in that structure

Materials Science = Real systems
- Spatial resolution
- In operando conditions (time resolution)
- Characterization of heterogeneity


Strain distribution in a jet engine turbine blade
Strain

Strain: \( (a_{\text{nano-structure}} - a_{\text{Bulk}}) / a_{\text{Bulk}} \) [%]

... intimately related to **physical properties & functionality** of nano-materials (optical, electronic, magnetic, mechanical...)

**Its origin:**
epitaxial growth on a substrate

surrounding matrix

interfaces with other materials or phases (core-shell, stacking faults ...)

**shaping procedures:** cutting, etching, rolling
ESRF Structure of Materials

Surfaces, Interfaces and Bulk

Techniques: X-Ray Diffraction, Scattering, Imaging, etc.

- **ID01**: Surface diffraction
  - Coherent diffraction imaging
  - Nano beams

- **ID03**: Catalysis
  - Surface scattering

- **ID15**: Buried interfaces
  - Liquid surfaces
  - Bulk diffraction
  - Fast tomography
  - Diffraction tomography

- **ID11**: Nano beams
  - Grain mapping
  - Chemical crystallography
  - Fast powder diffraction

- **ID31**: High resolution powder diffraction
  - 6 – 62 keV
Total Nano-Characterisation

Scale Gap: New Science

- Molecular Structure
  - Charge distribution
  - Crystal Structure
- Intra-granular structure
- Inter-granular interactions
- Bulk Structure

Crystallography
Reciprocal space

Mapping
Position space

10 pm 1 Å 1 nm 10 nm 100 nm 1 μm 10 μm 100 μm 1 mm 10 mm
Length Scale and technique

- Small Angle Scattering
- Diffuse Scattering
- Pair Distribution Function
- Imaging

Levels:
- Atomic
- Nano (<100nm)
- Nano (>100nm)
- Micro
- Macro

Techniques:
- Wide Angle Diffraction
- Reflectivity
- Scanning Beams
Reciprocal Space

Crystallography : Easy

Amorphous: Getting Easy

Barboiu et al JACS 2003
High Resolution Powder diffraction (ID31):
Structure solution for a metal-organic framework (MIL-100).

\[ a = 72.9 \text{ Å} \quad V = 387,420 \text{ Å}^3 \]
\[ Fd-3m \quad Z = 68 \text{ atoms} \]

Structure solution from computer simulations

The computationally designed trimeric building block chelated by three carboxylic functions

PDF analysis (ID11, ID15, ID31)

Pair Distribution Function analysis allows atomic scale information to be obtained in even crystallographically-challenged materials, e.g.

- glasses,
- quasicrystals,
- nanoparticles, nanocrystals,
- disordered and heavily defective materials,
- aperiodic materials, etc.
$F(Q) = Q[S(Q) - 1]/\text{nm}^{-1}$

$Ho_{11}Mg_{15}Zn_{74}$

Real-space fit of model

$\text{Ho}_{11}\text{Mg}_{15}\text{Zn}_{74}$
Multicrystal Crystallography (ID11)

Get complete data sets with small rotations:
• Fast
• Low dose

Sample preparation is “straightforward”
• Polycrystalline samples from everyday life
• Samples changing during the experiment

Want techniques to be usable by anyone

Example:
• Photochemistry
Photochemistry

Work of J Davaasambuu and S Techert, MPI Gottenburg

Light driven [2 +2] cycloadditon of 2–Benzylidene Cyclopentanone
Photochemistry

Work of J Davaasambuu and S Techert, MPI Göttingen

Light driven [2 +2] cycloaddition of 2-Benzyldiene Cyclopentanone
Monomer Refinement

- **Monomer: 12 grains found**

<table>
<thead>
<tr>
<th>Grain</th>
<th>R(int),%</th>
<th>R(sigma),%</th>
<th>Goof</th>
<th>R1,%</th>
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<tbody>
<tr>
<td>1</td>
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<td>2.8</td>
<td>1.07</td>
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<td>6.2</td>
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<td>1.02</td>
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<td>3</td>
<td>5.2</td>
<td>2.6</td>
<td>1.05</td>
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<tr>
<td>4</td>
<td>7.8</td>
<td>4.1</td>
<td>1.03</td>
<td>6.55</td>
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<tr>
<td>5</td>
<td>5.8</td>
<td>6.8</td>
<td>1.04</td>
<td>6.60</td>
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</table>

Orthorhombic, Pbca
a=8.59Å, b=10.61Å, c=31.10Å
Intermediate Refinement

- **Intermediate Phase:** 16 grains found

**Orthorhombic, Pbca**
- $a=8.58\text{Å}$, $b=10.76\text{Å}$, $c=30.79\text{Å}$

<table>
<thead>
<tr>
<th>Grain</th>
<th>$R(\text{int}),%$</th>
<th>$R(\text{sigma}),%$</th>
<th>Goof</th>
<th>$R_1,%$</th>
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<tr>
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<td>11.5</td>
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<td>1.06</td>
<td>15.30</td>
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The poor $R_1$ is due to the incompleteness of the reaction
Two Phase Refinement

- Refinement of Intermediate Phase including Dimer: 16 grains found

Orthorhombic, Pbca
a=8.58Å, b=10.76Å, c=30.79Å

<table>
<thead>
<tr>
<th>Grain</th>
<th>R(int),%</th>
<th>R(sigma),%</th>
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<th>R1,%</th>
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</table>

Two phase refinement brings R1 back to 6%!
single crystal quality fit from polycrystalline data taken during a 1\textsuperscript{st} order transition
Time resolved studies (ID11, ID15, ID31)

5 ms data
Three Way Catalysts (ID15)

Diminish polluting emissions from gasoline engine powered vehicles

Remove from exhaust gasses
- Carbon Monoxide (CO)
- un-burnt Hydrocarbons (HC)
- Oxides of Nitrogen (NO\(_x\))

TWC converter simultaneous tasks
- Oxidize CO to CO\(_2\)
- Oxidize HC to CO\(_2\) and H\(_2\)O
- Reduce NO\(_x\) to N\(_2\)

TWCs main components
- Support (Al\(_2\)O\(_3\))
- Catalyst (Pd, Pt, Rh nanoparticles)
- Promoter (CeZrO\(_4\) nanoparticle)

TWC operation for optimum performances
- engine running with air / fuel = 14.6 – 14.8 (by weight)
- exhaust gas oscillating (1-3Hz) between excess fuel and excess oxygen conditions

More in detail

Oxidation reactions with O\(_2\):

CO + ½ O\(_2\) → CO\(_2\)
HC + ½ O\(_2\) → CO\(_2\) + H\(_2\)O
HC + ½ O\(_2\) → CO + H\(_2\)O
H\(_2\) + ½ O\(_2\) → H\(_2\)O

Oxidation/reduction reactions with NO:

CO + NO → ½ N\(_2\) + CO\(_2\)
HC + NO → N\(_2\) + H\(_2\)O + CO\(_2\)
HC + NO → N\(_2\) + H\(_2\)O + CO
H\(_2\) + NO → ½ N\(_2\) + H\(_2\)O
H\(_2\) + 2 NO → N\(_2\)O + H\(_2\)O
5/2 H\(_2\) + NO → NH\(_3\) + H\(_2\)O
2 NO + 2 NH\(_3\) + ½ O\(_2\) → 2N\(_2\) + 3 H\(_2\)O

Water–gas shift reaction:

CO + H\(_2\)O → CO\(_2\) + H\(_2\)

Reforming reactions:

HC + H\(_2\)O → CO\(_2\) + H\(_2\)
HC + H\(_2\)O → CO + H\(_2\)
Role of Pd nanoparticles in CO dissociation?

From literature

2CO + O₂ + Pd → 2CO₂ + Pd
2NO + 2CO + Pd → N₂ + 2CO₂ + Pd

No CO dissociation on Pd

4%wt Pd / Al₂O₃ catalysts during CO/NO cycles (period 27.7 s) at 673°K

MS

DRIFTS

Surface species on Pd

XRD

2%wt Pd

4%wt Pd

The European Light Source
Summary

- Contrary to what believed, CO dissociates on Pd

- C diffusion into Pd lattice $\rightarrow$ PdC$_x$

- Under NO, PdC$_x$ disappears quickly to form NCO

- CO linear to bridge ratio changes indicating a size/shape change probably due to C storage

*M. A. Newton et al., J. Am. Chem. Soc. 132, 4540 (2010)*
*A. Kubacka et al., J. Catal. 270, 275 (2010)*
Combined XRD-IR-MS

SHORT PERIOD
Pd lattice parameter does not change
CeZrO₄ lattice parameter does change

LONG PERIOD
Towards the end of CO phase Pd changes as if CeZrO₄ were not present
Conclusions

Combining XRD–IR–MS new interplay between Pd and CeZrO$_4$ have been discovered:

1. *Inhibition of formation of PdC$_x$ phases during CO cycle through Oxygen release*
   
   CO dissociation is still occurring (formation of Pd(CN))
   
   BUT
   
   CeZrO$_x$ provides Oxygen to the adsorbed C atoms to efficiently produce CO$_2$

2. *Enhanced reducibility of nano-CeZrO$_4$ phase when in contact with Pd*
   
   contact with Pd nanoparticle promotes CeZrO$_4$ oxygen transfer

3. *Increased structural stability during redox cycles*
   
   Pd nanoparticles do not change shape

Phase diagram of Pd surface during CO oxidation for different CO/O$_2$ pressure ratios. R. van Rijn et al., PCCP, in press. (ID03)
In-situ characterisation of bainite growth (ID31)

In-situ characterisation of bainite growth [60 keV]

Evolution of diffraction peaks $\gamma\{111\}$ and $\alpha\{110\}$

- **Inter-plate austenite**
  - carbon-rich, larger lattice parameter, lower 2$\theta$, broadened peak (small grains / large strains)

- **Original austenite**
  - bulk carbon content sharp peak (large grains / low strains)

- **Bainitic ferrite**
  - broadened peak (small grains / large strains)
Residual austenite

Bainitic ferrite and films of austenite

\( \gamma_B \)

\( \alpha + \gamma_F \)

1 \( \mu m \)
Spatial Resolution

Resolution is tied to
- Beam size
- Detector Resolution
- Stability
- Reconstruction algorithms; use of additional information

- For 2 dimensional direct (transmission or reflection) mapping, the resolution is ultimately equivalent to the beam size.
- Beam size depends on the focusing optics and the source
- Upgrade → much improved source will give a huge improvement in focusing capability
Diffraction Mapping – Direct Mapping in 2d

- Powder Diffraction
- Spatial resolution determined by
  - Beam size
  - Accuracy of translations
  - Metrology of beam
  - = O(100 nm)
- Multi-dimensional Map
- Phases
- Strain
- Stoichiometry
- Microstructure
- ...

X-ray microscopy images during microprofiling along the thickness through the width of bent glassy Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ ribbon showing shear band creation on the compression side only.

Yavari et al., PRL 2012
Gergaud et al, in preparation
Yavari et al., Scripta Metall 2008
Region of interest:

Detector image (Rec. Space)

Si(004) peak

Raster scan of a 30x30 μm² Region

Detector image (Rec. Space)
...refers to the use of diffraction of coherent x–rays & mathematical algorithms – rather than lenses, to retrieve the image of the sample with nm resolution in a model–free way.
Surface Diffraction (ID03)

In-situ studies of the structure and morphology of surfaces either under static conditions (surface crystallography) or in situ during surface processes (heterogeneous catalysis, surface reactions, growth, ...)

**Techniques:**
- Surface X-ray diffraction
- Grazing incidence small angle scattering
- X-ray reflectivity
- Anomalous diffraction (including DAFS)
- Coherent diffraction

**Optics:**
- Energy range 5–28 keV
- Typical focal size 20x20 μm² with $10^{13}$ ph/s
- Min focal size 3x3 μm² with $10^{12}$ ph/s

Coherent diffraction from a gold nanorod

PRB 77 (2008) 153412
Structural determination of the adsorption of organic molecules on metal surfaces. The case of C$_{60}$ on the Pt(111) surface and the role of surface vacancies.

HIGH ENERGY MICRO-DIFFRACTION (ID15)

Studies of buried interfaces and liquid surfaces/interfaces

Optics for liquid-liquid interface studies
Si(111)/Si(311) crystals

GIANT METAL COMPRESSION AT LIQUID SOLID (Pb-Si, In-Si) SCHOTTKY JUNCTION

SELF ASSEMBLY OF Au NANOPARTICLES

3nm DT-Au amorphous film

5nm DT-Au ordered monolayer
3d reconstruction methods

- **X-ray Absorption & Phase Contrast**
  - Z contrast 0.1 µm
  - 3D morphology

- **X-ray Fluorescence**
  - Elemental contrast 0.1 µm
  - 3D chemistry

- **X-ray Diffraction**
  - 3D crystal phases
  - Or grain distributions
  - 3D crystal phases

**Structural phase**
**Or crystal Contrast 3-5 µm**

**Golosio et al, APL**

Courtesy of P. Bleuet

*P. Bleuet et al., Nature Materials 7, 468 - 472 (2008)*
Fast Tomography

Year

10min

4h

10s

1s

10ms

50ms

100000

10000

1000

100

10

1

0.1

0.01

1999 2001 2003 2005 2007 2009
ON THE FORMATION OF VOIDS IN Nb$_3$Sn

“INTERNAL TIN” SUPERCONDUCTING WIRES (ID15)

C. Scheuerlein, M. Di Michiel, A. Haibel


Destructive metallographic techniques: erratic and misleading due to irregularities of strands

*In-situ* combined diffraction and tomography study
Elongation of voids at 280°C
Agglomeration of globular voids during isothermal step at 340°C
Strong increase of small interfilament voids during isothermal step at 540°C
• Agglomeration of voids up to 200°C

• Void growth through density changes; strong correlation with Cu₃Sn content

• Strong increase of small interfilament voids during isothermal step at 540°C but no phase transitions

• Isothermal holding steps at 340 and 540°C are counterproductive
XRD-CT (ID15, ID22)

- Spatial resolution is defined by the X-ray beam size $\Delta y$
- Temporal resolution depends on
  - sample size / $\Delta y = N$
  - detector exposure time $1/f$
- Acquisition time per slice
  - $\sim N \times N / f$
  - easily many hours if $N$ big!
- XRD-CT was not applied to dynamical samples until 2010
- First experiment on phase evolution during catalyst body preparation
**DIFFRACTION TOMOGRAPHY**

**PHASE TRANSFORMATIONS DURING PROCESSING OF SUPERCONDUCTING COMPOSITES**
by C. Scheuerlein (CERN), S. Jacques (Manchester), A. Beal (Utrecht), and M. Di Michiel (ID15)

High resolution XRD-CT scans performed in short time
An application where XRD-CT replaces standard absorption and phase tomography
DIFFRACTION TOMOGRAPHY

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High resolution XRD-CT scans performed in short time
An application where XRD-CT replaces standard absorption and phase tomography
Friedrich and Knipping (Laue)
Make a powder into a bunch of single crystals we could index

1000 micron beam + turning
Make a powder into a bunch of single crystals we could index

1000 micron beam
Make a powder into a bunch of single crystals we could index

900 micron beam
Make a powder into a bunch of single crystals we could index

800 micron beam
Make a powder into a bunch of single crystals we could index

700 micron beam
Make a powder into a bunch of single crystals we could index

500 micron beam
Make a powder into a bunch of single crystals we could index

400 micron beam
Make a powder into a bunch of single crystals we could index

300 micron beam
Make a powder into a bunch of single crystals we could index

200 micron beam
Make a powder into a bunch of single crystals we could index

100 micron beam
Make a powder into a bunch of single crystals we could index

50 micron beam
Make a powder into a bunch of single crystals we could index

30 micron beam
Determine grain centres and orientation matrices

Grain positions, orientations, lattice parameters all simultaneously refined from low resolution multi-crystal data

“grain boundaries” from Voronoi calculation: if the grain centre falls in the middle of the reconstructed grain, perhaps nothing is missing.

Vaughan et al., in progress
Adding orientational information

The axes are placed at the crystal centre (this is for one layer).

Rotations after each step

Depicted are the Rodrigues vectors of subsequent rotations after straining a sample
Layer by layer maps

These are constructed using only grains with a match above and/or below
High Resolution Grain map

A combination of detectors allows the high resolution map to be constructed while we characterize simultaneously:

- Grain Shape
- Grain Position
- Crystal Structure
- Strain State

For each crystal independently

Reconstructed by
C. Gundlach, ESRF
S. Schmidt, Risø

Schmidt et al., Science (2007)
Gundlach et al., in progress
Vaughan et al (2010)
Poulsen et al (2010)
Acquisition of both the diffraction and extinction data allows the measurement of grain distributions, orientations and strain state in materials **without density contrast**.
Diffraction Contrast Tomography

Algebraic reconstruction methods allow the calculation of 3-dimensional grain maps with micron-level precision – resolution is determined currently by detectors.

Combining Grain Mapping with Tomography

Grain map from diffraction contrast tomograph to identify grain shapes and orientations

Conventional tomograph to identify crack

To relate crystal orientations to crack propagation

Collaboration between Manchester University and ESRF

Improving resolution of map with microscopy

There are not any good tricks to improve the resolution of the diffraction, but imaging can be improved magnifying the projections.

**Aim:**
Reconstruct grain map from far/near field diffraction data
Refine map with magnified DCT extinction data and/or “normal” tomography data from very distant detector
Diffraction/ Full-Field Nanoscopy Setup

Condensing Optics

Sample

Objective

High Resolution Diffraction Detector

Low Resolution Diffraction Detector

High Resolution Imaging Detector

$\chi_s$  
$O(0.5 \text{ m})$

$\chi_d$  
$O(50 \text{ m})$
1. CDI from single objects
Shape and strain of single nano-objects. Beam larger than sample.

2. Holographic approach
Phase encoded in the diffraction amplitude: no need for inversion algorithms. Beam larger than sample.

3. Ptychographic approach
Redundance of information from overlapping areas. Reconstruction of sample and probe. Beam smaller than sample.

4. Wave–front investigation
The knowledge of the x-rays probe used for each experiment. Disentangling contributions from sample and probe. More accurate determination of phase.

Referenced articles:
- Phys Rev Lett 104 165501 (2010)
- Nature Commun. 2 568 (2011)
- Optics Express 19 19223(2011)
Mathematical algorithms?

\[ I(\vec{q}) = \left| FT\left\{ \rho(\vec{r}) e^{i\Phi(\vec{r})} \right\} \right|^2 = |F(q)|^2 \]

Real Space

\[ G(r) = \rho^C(r) e^{i\Phi^C(q,r)} \]

Reciprocal Space

\[ F^N(q) = f(q) \cdot e^{i\Phi^N(r,q)} \]

Finite support condition

\[ G(r) = \rho^R(r) e^{i\Phi^R(q,r)} \]

\[ F^N(q) = \sqrt{I^M(q)} \cdot e^{i\Phi^N(r,q)} \]
3D reconstruction

- Inversion of the 3D intensity matrix in a *single* inverse Fourier Transform
- Plot of the 3D object in an orthogonal space

(a) (c) (d)

Comparison with AFM
Measurement of several diffraction patterns obtained for different but overlapping illumination areas

\[ y(r, R) = O(r - R) \times P(r) \]

- \( y(r) \) the exit wave,
- \( P(r) \) the illumination function,
- \( O(r) \) the object function,
- \( R \) the displacement of the beam

Faulkner et al. PRL 93 (2004); Rodenburg et al. APL 85 (2004)
Allow Total Characterisation

- Molecular Structure
  - Charge distribution
- Crystal Structure
- Intra-granular structure
- Inter-granular interactions
- Bulk Structure

Crystallography
- Reciprocal space
- New Science

Direct space
Thanks for slides and support

Dina Carbone (ID01)
Tobias Schulli (ID01)
Roberto Felici (ID03)
Andy King (ID11)
Wolfgang Ludwig (ID11)
Marco Di Michele (ID15)
Andy Fitch (ID31)
ESRF Structure of Materials

Surfaces, Interfaces and Bulk

Techniques: X-ray Diffraction, Scattering, Imaging, etc.

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<tr>
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<th>Tobias Schulli</th>
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<td>Surface diffraction</td>
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The European Light Source