XRD: STRUCTURAL ANALYSIS AT LIST

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OVERVIEW

Outline

• Introduction to structure and structural analysis

• XRD facilities at LIST

• Examples:
  • Powder analysis
  • Thin film analysis
  • Phase identification
  • Phase transformations
  • Stress analysis
  • Texture analysis and pole figures
  • X-Ray reflectometry
  • SAXS / WAXS

• Further developments
The crystal structure describes the atomic arrangement of a material.

When the atoms are arranged differently, a different diffraction pattern is produced (e.g., glass vs. cristobalite).
These three phases of SiO$_2$ are chemically identical.

The amorphous glass does not have long-range atomic order and therefore produces only broad scattering peaks.

Quartz and cristobalite have two different crystal structures:
- The Si and O atoms are arranged differently.
- Both have structures with long-range atomic order.
- The difference in their crystal structure is reflected in their different diffraction patterns.
Bruker D8 Discovery

• Cu Kα (and Mo Kα) X-ray sources
• Parallel beam configuration (Göbbel mirror)
• Point/line focused beam capabilities
• Energy Sensitive Detector and scintillator
• Eulerian cradle
• Hot stage

Mainly used for:
• Grazing incidence analysis
• Phase identification
• Rocking curves
• X-Ray reflectometry
• Residual stress analysis
• Texture analysis
Panalytical X’Pert Pro

Panalytical X’Pert Pro

- Cu Kα X-ray source
- Parallel beam as well as parafocusing beam configurations
- Possibility to use programmable slits
- Transmission configuration
  - Small Angle X-Ray scattering (SAXS)
  - Wide Angle X-Ray scattering (WAXS)
- Point/line focused beam capabilities
- 1D-Position Sensitive Detector
- Cryo-stage and hot stage
- Rel. Humidity chamber

Mainly used for:
- Powder analysis
- Phase identification
- X-Ray reflectometry
- Semi-quantitative as well as quantitative phase analysis
The incident angle, $\omega$, is defined between the X-ray source and the sample.

The diffraction angle, $2\theta$, is defined between the incident beam and the detector.

In the Bragg-Brentano geometry, the diffraction vector ($s$) is always normal to the sample surface.
For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract.

Basic assumptions of powder diffraction:
- For every set of planes, there is an equal number of crystallites that will diffract.
- There is a statistically relevant number of crystallites.
THIN FILM ANALYSIS

Grazing Incidence

- A larger incidence angle $\omega_i$ increases penetration depth
- Characterisation of thin films using XRD is possible

**XRD pattern of a bilayered coating on WC substrate (V. Hody)**

- $\omega_i = 0.5^\circ$: top layer
- $\omega_i = 3^\circ$

**BF-TEM image TiAlTaN 900°C (6 hrs)**

- Crystalline coating
- Substrate (blue index)

**Coating**

- Fixed $\omega_i$
- Incidence angle $\omega_i$ increases penetration depth
Temperature chambers:

- Hot stage characteristics:
  - From room temp. up to 1100°C
  - Vacuum (down to 10^{-2} mbar)
  - Controlled atmosphere (inert gas: H\textsubscript{2}, N\textsubscript{2}, Ar)

- Temperature chamber characteristics:
  - -193°C up to 450°C (in vacuum)
  - Ambient up to 300°C (in controlled atm.)
  - Rel. humidity generator:
    - between 5% and 90% at 25°C
Phase transformations in thin films

- X-ray diffraction spectra of an $\text{Al}_{0.48}\text{Ti}_{0.4}\text{Ta}_{0.12}\text{N}$ hard coating.
- Analysis in grazing incidence
- Heat treatment up to $950^\circ$ C, atm. pressure, air

The structure changes with temperature
Temperature induced phase changes in organic material

- 30 s, 25 °C: DoC = 48%
- 30 s, 190 °C: DoC = 0%
- 30 s, 140 °C: DoC = 0%
- 30 s, 130 °C: DoC = 45%

Change in degree of crystallinity (DoC) with temperature
STRESS ANALYSIS

Residual Stress Analysis

Experimental set-up
- Parallel beam configuration
- $\chi$-mode (Eulerian cradle)

Macrostrain / residual stress

$\sin^2 \Psi$ method

Intensity

For different values of $\chi=\Psi$

Biaxial or uniaxial stress

Triaxial stress

Texture

(Reference: www.stanford.edu/group/glam/xlab/MatSci162_172/LectureNotes/05_Stress&Texture.pdf)
TEXTURE ANALYSIS

Investigation of Texture

- Eulerian Cradle:
  - sample tilt: $0^\circ < \chi < 90^\circ$
  - sample rotation: $0^\circ < \phi < 360^\circ$

*Example: Texture on rolled metal sample*

Investigation of industrial processes by texture:
Pole figures are symmetrical around $\phi=0^\circ$ and $\phi=90^\circ$

-Powders, dispersions
-Liquid crystals, Gels
-Fibres, Single crystals

Presence of texture
DETERMINATION OF CRYSTALLITE SIZE

Crystallite Size and Microstress

As size of crystallite decreases, width of diffraction peak increases

Microstress can be introduced by:
- surface tension of nanoparticles
- morphology of crystal shape, such as nanotubes
- interstitial impurities

In case where microstress is small, crystallite size can be determined
Layer thickness determination by XRR

From fall in intensity and period of interference fringes

- Thickness of thin films and multilayers
- Surface and interface roughness

From $\theta_c$

- Material density

(Measurement by I. Infante Canero and Y. Fleming)

TiO$_2$ layer thickness: 28 nm

Si substrate

TiO$_2$ coating
QUANTITATIVE PHASE ANALYSIS

Quantification of crystalline phases and amorphous content

- Ways to estimate the amorphous phase content:
  - By estimating the Degree of Crystallinity (DoC)
  - By using a standard of known crystallinity (several methods)

(Scott A Speakman, Ph.D., http://prism.mit.edu/xray)
TRANSMISSION IMAGING: SAXS/WAXS

Small Angle X-ray Scattering vs. Wide Angle X-ray Scattering

- **SAXS provides:**
  - Shape of particles
  - Size of particles
  - Particles’ surface per volume

- **Particle characteristics:**
  - Liquid, solid or gaseous domains dispersed within a light matrix
  - \(1 \text{ nm} < \text{size} < 100 \text{ nm}\)
  - Concentration > 1 wt. %

- **WAXS provides:**
  - Crystal nature
  - Lattice parameters
  - Crystal Amount
  - Crystal Orientation

(picture by www.anton-paar.com)
Analysis of polystyrene/ZrO$_2$ (95/5) nanocomposite

1) Un-treated data

2) Corrections
   - background subtraction
   - absorption correction
   - desmearing

3) Modelling

   Spherical shape (model fitting)
   Average diameter: 650 Å
   Surface per volume: 0.136 Å$^{-1}$

4) Analysis using the model curve
Study of polymer/nanofiller interaction in the case of nanoclay

The increase in clay intersheet distance indicates an intercalation mechanism.
Structure changes due to load

- Coupling of tensile device and X-ray scattering
  - Identification of deformation mechanisms of soft materials in terms of chain orientation and damage

For more information, see Frederic Addiego’s presentation this afternoon
Thank you for your attention!