X-ray Diffraction for powder sample

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Today’s topics (AM)

- Features of Rigaku TTRAX III
- Basics of powder XRD
  - Feature of XRD
  - Evaluation item
- Texture analysis for bulk sample
  - Measurement and Process
- SAXS for nano-size sample
  - Principle and Optics
  - Application
Rigaku TTRAX III

- Horizontal goniometer
- High power X-ray source
- Parallel beam method
- In-Plane axis

Feature of TTRAX III

In case the sample isn’t set to horizontal….

- Hard-to-pack sample
- Semi-liquid sample
- Thin layer sample
In Horizontal goniometer

Hard-to-pack sample

Independent on sample condition

Thin layer sample

Semi-liquid sample

Feature of TTRAX III

High power X-ray source

Sealed-off X-ray tube
2~3kW

Rotating anode X-ray tube
10~18kW

Cooling water

Target

Be window

Feature of TTRAX III

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Geometry for powder sample

- **Focusing method**
  - Parallel Beam

<table>
<thead>
<tr>
<th></th>
<th>Focusing method</th>
<th>Parallel beam</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Systematic error</strong></td>
<td>1. Flat sample</td>
<td>Umbrella effect</td>
</tr>
<tr>
<td></td>
<td>2. Umbrella effect</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Adsorption effect</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. Eccentric error</td>
<td></td>
</tr>
<tr>
<td><strong>Intensity</strong></td>
<td>Strong</td>
<td>medium</td>
</tr>
</tbody>
</table>

Cross Beam Optics
Rigaku patented technology

BB and PB geometries are simultaneously mounted, aligned, and selectable.
Measurement of rough sample surface

Focusing method
Parallel beam

Sample: Zeolite

Hold of peak shape, peak position and FWHM

Free from Eccentric error (Parallel beam)
Bragg’s condition of diffraction

- The conditions for a reflected (diffracted) beam are given by the relation

\[ 2d \sin \theta = n \lambda \]

**Bragg’s equation**

- \( d \): Interplanar spacing
- \( \lambda \): X-ray wavelength
- \( n \): 1, 2, 3, \ldots

**X-ray diffuse scattering**

- Interaction of substance and X-ray: 2

- Scattering angle \((2\theta = 0\sim 10 \, \text{deg.})\)

- Intensity (a.u.)

- 0.1

- 1

- 10

- 100

- 1000

- 2\theta (deg.)
Reflection and interference

Two beams reflected on the surface and the interface interfere each other.

Interaction of substance and X-ray:

Evaluation item in powder sample

- Peak positions, d values: Phase identification, Lattice constant
- d shift: Residual stress, Solid solution
- FWHM: Crystal quality, Crystallite size, Lattice strain
- Intensity vs. Orientation: Preferred orientation, Fiber structure, Pole figure
- Integrated Int. of amorphous: Crystallinity
- Integrated Int. of crystal: Quantitative analysis

Intensity vs. Angle (2θ)
The powder diffraction pattern is characteristic of the substance. The diffraction pattern indicates the state of chemical combination.

### Basics of XRD

#### Phase Identification in X-ray diffraction
- The powder diffraction pattern is characteristic of the substance.
- The diffraction pattern indicates the state of chemical combination.

![Diffraction Pattern](image)

#### Basics of XRD

#### Quantitative analysis (RIR method)

The concentration of each phase is calculated by integrated intensity and RIR value.

**Polymorphs of TiO₂**
- Rutile (RIR: 3.40)
- Anatase (RIR: 3.30)
- Brookite

**Preparation**
Rutile: Anatase = 3:1

**Result**
- Rutile: 71.6 wt%
- Anatase: 28.4 wt%
Crystallite size

Polycrystal

There is one or multiple crystalline in one particle.

Small angle X-ray scattering

Crystallite size

The width of diffracted line

- Scherrer method
- Hall method

Debye ring

The width of diffracted line broaden in crystallite size less than 100nm (1000 Å)
Crystallinity

Plastic wrap

Change of lattice constant

Monitoring the change of lattice constant in real time → *in situ* measurement

\[ 2dsin \theta = \lambda \]

- **Al₂O₃**
  - 35.12° → 35.16°
  - 25.56° → 25.58°
  - 900°C → 25°C
**Basics of XRD**

**Stress and interplanar spacing**

Compressive stress: \( d'_1 > d'_2 > d'_3 > d'_4 \)

Tensile stress: \( d'_1 < d'_2 < d'_3 < d'_4 \)

Bragg’s condition of diffraction

\[ 2d \sin \theta = n \lambda \]

**Basics of XRD**

**Peak shift and sin^2 \( \psi \) diagram**

Normal line of sample surface: \( N \)

Normal line of lattice plane: \( N' \)

\[ 2 \theta (\text{deg}) \quad \text{Intensity (counts)} \]

\[ \text{sin}^2 \psi \]

\[ 2 \theta \]

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Calculation of stress value

\[ \sigma (\text{stress value}) = K \frac{\Delta 2 \theta}{\Delta \sin^2 \psi} \]

Slope of \( \sin^2 \psi \) diagram

\[ K (\text{stress constant}) = \frac{-E}{2(1+\nu)} \cos \theta_0 \cdot \frac{\pi}{180} \]

Material-specific value

\( [E: \text{young's modulus}, \ \nu: \text{poisson ratio}, \ \theta_0: \text{diffraction angle in stress free condition}] \)

Measurement of residual stress

- Iron plate

Before rubbing

After rubbing
Texture evaluation and pole figure analysis for bulk sample

Texture and substance

Nonoriented sample: brick, concrete, (powder)

Oriented sample: aluminium foil, iron plate, plastic bottle

Single crystal: silicon wafer, diamond, quartz
What is oriented sample?

The condition that a lattice plane faces to the same direction

- Metal orientation (rolled sample)
- Approximate equivalent to single crystal (Epitaxial film)
- Uni-axial orientation (fiber orientation)

2D image and $2\theta$ - I diffraction pattern

- Nonoriented
- Oriented
What is the purpose of texture?
Which plane is faced to Rolling direction and Normal direction?

Texture evaluation

Spherical projection method and Stereographic projection method

3D is described with 2D

Spherical projection method    Stereographic projection method
Texture evaluation

Pole figure

RD (Rolling direction)

TD (Transverse direction)

ND (Normal direction)

Sample behavior in Reflection method and Transmission method

Reflection method

Alpha: 5deg step
(ex. 15° → 20° → 25° → 30° → 35° → 40° → 45° → 50° → 55° → 60° → 65° → 70° → 75° → 80° → 85° → 90°)

Beta: 5deg step
(ex. 0 → 5° → 10° → 15° → 20° → 25° → 30° → 35° → 40° → 45° → 50° → 55° → 60°)

Transmission method

Beta rotation at each alpha angle
(ex. 15° → 20° → 25° → 30° → 35° → 40° → 360°)

Sample is moved centering around purple line
**Orientation analysis : step 1**

Pole figure of (111) in rolled Cu-Zn(70-30)

The angle between RD and each pole is estimated with Wulff net.

**Orientation analysis : step 2**

The angle between ND and each pole is estimated with Polar net.
Orientation analysis : step 3

Angle between plane in \((h_1k_1l_1)\) and \((h_2k_2l_2)\) of cubic crystal

<table>
<thead>
<tr>
<th>((h_1k_1l_1))</th>
<th>ND</th>
<th>((h_2k_2l_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>110</td>
<td>111</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>110</td>
<td>45</td>
<td>0</td>
</tr>
<tr>
<td>111</td>
<td>54.7</td>
<td>35.3</td>
</tr>
<tr>
<td>210</td>
<td>26.6</td>
<td>18.4</td>
</tr>
<tr>
<td>211</td>
<td>35.3</td>
<td>54.7</td>
</tr>
<tr>
<td>RD</td>
<td>65.9</td>
<td>73.2</td>
</tr>
</tbody>
</table>

Angle between plane in \((111)\) and \((110)\) = 35.5°, 90°

Angle between plane in \((111)\) and \((211)\) = 19.5°, 61.9°, 90°

Texture evaluation

Orientation analysis : step 4

Angle between plane of cubic

\((111)\) \((110)\) = 35.5°, 90° \(\rightarrow\) ND

\((111)\) \((211)\) = 19.5°, 61.9°, 90° \(\rightarrow\) RD

Rotate standard \((110)\) projection of cubic crystal 35° clockwise.

RD is \([1\bar{1}2]\)

This texture is \((110)[1\bar{1}2].\) \((hkl)[uvw]=h^*u+k^*v+l^*w=0\)

ND  RD
Texture evaluation

Process by stereographic objection figure

Rotate 35 degree

Standard (110) objection of cubic crystal

Small angle X-ray scattering for nano-size sample
Purpose of SAXS

- Particle size estimation (X-ray scattering)
  - Particle size
  - the distribution
- Phase identification (X-ray diffraction)
  - molecular structure

Small angle X-ray scattering

Principle of SAXS

X-ray Sample

Scattering angle

\( 2\theta = 0 \sim 10 \text{ deg.} \)

Scattering

\( 2\sin \theta = n\lambda \)

Diffraction

\( 2d \) (deg.)

\( (r/n) / \text{Angle} \)

0 0.1 100 1000

0 1 2 3 4 5

2d (deg.)
Small angle X-ray scattering

Particle information

- Particle size and particle distribution

Phase information

- Long-period structure

Slope of SAXS profile: Average size

Shape of SAXS profile: Breadth of distribution

Peak position of SAXS: Structure and Interval
Small angle X-ray scattering

Instrument for SAXS

- NANO-Viewer
  - Ultima IV
  - TTRAX III

NANO-Viewer

Point focus optics

- NANO-Viewer (2D-SAXS System)

  Semiconductor
  2D detector Pilatus100k

2D image

X-ray source

1st slit

2nd slit

3rd slit

2D detector

Sample

3 slits optics
NANO-Solver

- Automatic particle size & distribution estimation!

NANO-Solver

SAXS profile

- Size: 3nm
- Size: 60nm

Normalized dispersion: 10%
Relations of dispersion and profiles

- Dispersion: 10%
- Dispersion: 90%

Average diameter: 3 nm

Applications of SAXS

Particle size estimation (transmission mode)
**SAXS profiles and size distribution**

- Au nanoparticles

![Graphs showing SAXS profiles and size distribution for three samples.]

**Comparison of TEM image**

![Comparison of TEM images and their corresponding SAXS distributions for three samples.]

**Small angle X-ray scattering**

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Nano size of porous silica

- Mesoporous silica

![Graphs showing intensity vs. 2θ for small angle X-ray scattering]