به نام خدا

مرکز دانلود رایگان
مهندسی متالورژی و مواد

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Small-angle x-ray scattering...
...and crystallisation processes

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Materials Physics
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Small-angle x-ray scattering

Anomalous SAXS

Nanoscale refractory analogue
- Gelation & Calcination
- Sintering
A small-angle x-ray scattering camera

e.g.: HMI SAXS beamline at Bessy, Berlin
Small-angle scattering vs. diffraction

\[ q = (4\pi/\lambda) \sin \theta \]

x-rays scatter from electrons

neutrons scatter from nuclei and magnetic moments

- scattering from atomic structures
- size of objects \( \sim \lambda \)
- small length scale \( \rightarrow \) large angle

- scattering from interfaces
- size of objects \( \gg \lambda \)
- large length scale \( \rightarrow \) small angle
SAXS and particle size
SAXS and particle size
What can we learn from a SAXS pattern?

Porod slope at larger $q$

$q^{-n}$ where $n$ represents the surface morphology

$n=4$: smooth
$3<n<4$: surface fractal
$1<n<3$: mass fractal

Guinier regime

Guinier radius is proportional to the particle size (radius of gyration of the particles)

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Resonant scattering and absorption

atomic scattering factor:
\[ f(q,E) = f_0(q) + f'(q,E) + jf''(q,E) \]

scattered intensity \( \sim f^2 = f_0^2 + 2f_0f' + (f'^2 + f''^2) \)

Side effects...
... not entirely unwanted!

• experiment at 18keV
  -> compressed \( q \) scale

• difference patterns reveal which features are due to edge element even if partial scattering functions cannot be computed

normal SAXS

correlations btw. edge element & others

correlations between labelled phases only
Chemical contrast

- photon energy calibrated to Zr foil at 17.993keV
- 8eV chemical shift of edge in unreacted sample
- edge shifts by several eV as reaction progresses

ASAXS:

3 energies below the edge
=> determine partial structure factors

but: chemical edge shift
Chemical contrast

- photon energy calibrated to Zr foil at 17.993keV
- 8eV chemical shift of edge in unreacted sample
- edge shifts by several eV as reaction progresses

Energy-dependent SAXS:

compare above/below edge

=> maximum contrast with little uncertainty w.r.t. chemical shifts

but: fluorescence

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Finding the resonance

1. Absorption measurement gives \( f'' \):

\[ f''(E) \sim E \mu(E) \]

2. Extend the measured range according to tabulated data

3. Kramers-Kronig transform gives \( f' \):

\[
f'(E) = \frac{2}{\pi} P \int_{E_1'}^{E_2'} \frac{E' f''(E')}{E^2 - E'^2} \, dE'
\]
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Precursors and ceramics under heat load

How do particles in a ceramic bond to the matrix?

- Annealing
- Reactive sintering
Small-angle x-ray scattering

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Making a sol-gel ceramic

1. Gelation.

\[ \text{Zr(OiPr)}_4 + 4 \text{H}_2\text{O} = \text{Zr(OH)}_4 + 4 \text{iPrOH} \]

In-situ SAXS experiment at Daresbury - 6.2
Making a sol-gel ceramic

1. Gelation.
\[ \text{Zr(OiPr)}_4 + 4 \text{H}_2\text{O} = \text{Zr(OH)}_4 + 4 \text{iPrOH} \]

2. Drying.
\[ \text{Zr(OH)}_4 = \text{ZrO}_2 \cdot 2 \text{H}_2\text{O} \]

3. Calcination.
\[ \text{ZrO}_2 \cdot 2 \text{H}_2\text{O} = \text{ZrO}_2 + 2 \text{H}_2\text{O} \]

Polymerisation precedes crystallisation.
Nuclei form at room temperature, crystallisation requires ~800°C to activate.
Small-angle x-ray scattering

Anomalous SAXS

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- Gelation & Calcination
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In-situ sintering experiments at Daresbury-6.2

- fast tunable monochromator
- energy up to 18keV (Zr-K edge)
- Rapid detector family
- pellet furnace (to 1100°C)

Each temperature step (17min) comprises:

- ramp at 12.5K/min (2min)
- equilibration (3min)
- 18.02keV experiment (5min)
- 18.05keV experiment (5min)
- 17.98eV experiment (90s)

Fig. from CC Tang et al., Nucl. Instr. Meth. Phys. Res. B222 (2004) 659

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In-situ sintering experiments at Daresbury-6.2
Porod slope at larger $q$

$q^{-n}$ where $n$ represents the surface morphology

$n=4$: smooth
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$1<n<3$: mass fractal

What can we learn from a SAXS pattern?

Guinier regime

Guinier radius is proportional to the particle size (radius of gyration of the particles)

$$I(q) = A \exp \left\{ \frac{R_g^2 q^2}{3} \right\} + C$$
Guinier radius: matrix softening & agglomeration
Porod slope: matrix softening & agglomeration

- Below edge: zirconia-air contrast
- Above edge: glass-air contrast
- High-T: zirconia-glass contrast

<table>
<thead>
<tr>
<th>Temperature (deg C)</th>
<th>Porod Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>3.8</td>
</tr>
<tr>
<td>400</td>
<td>3.6</td>
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<tr>
<td>450</td>
<td>3.4</td>
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<tr>
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<td>2.6</td>
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<tr>
<td>700</td>
<td>2.4</td>
</tr>
<tr>
<td>750</td>
<td>2.2</td>
</tr>
</tbody>
</table>
The Model – Yr model.
The Model - Yr model.

450°C

Different graphs showing changes in parameters like Guinier Radius, Porod Slope with Temperature.
The Model – Yr model.

- Guinier Radius, Rg (nm)
  - Temperature (deg C)
- Porod Slope
  - Temperature (deg C)

550°C

R_g

Glass

Pore

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The Model - Yr model.

650°C

Gurier Radius, $R_g$ (nm)

Temperature (deg C)

Porod Slope

Temperature (deg C)
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Summary: Energy-dependent SAXS

**Standard SAXS**
- characteristic length scales
- interface morphology
- but: messy in complex systems

**Difference SAXS above/below edge**
- chemical contrast
- but: fluorescence

**Anomalous SAXS**
- partial structure factors
- but: very sensitive to chemical shifts
Summary: Refractory ceramics

**Gelation**
Initial formation of a polymer network

**Calcination**
Polymerisation, then crystallisation

**Sintering**
glass grain surfaces becomes smoother near the softening point
pores consolidate

**Corrosion**
ZrO2 component of the refractory is less prone to corrosion by K⁺ than by Na⁺

**ZrO2 particles agglomerate inside the pores**
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