Outline Course „Ceramic Nanotechnology“

1. Introduction: Applications, Goals and Challenges
2. Powder Synthesis and Conditioning
3. Particle Interactions in Colloidal Systems
4. Characterization of Nano- and Micro Particles
5. Properties of Suspensions
6. Stabilization of Suspensions and Additives I
7. Stabilization of Suspensions and Additives II
8. Colloidal Processing and Rheology
9. Shaping Ceramics I: Bulk Materials
10. Shaping Ceramics II: Foams
11. Shaping Ceramics III: Thin Films
12. Sol – Gel Technology: From Molecules to Advanced Ceramics
13. Selected Applications of Ceramic Nanotechnology
14. Summary
From Powder to Advanced Ceramics

- Colloid Crystals
- Surface Micro Patterning
- Surface Coatings
- Bulk Materials

Requirements for Ceramic Powder Synthesis

- Exact fixation of chemical composition
- Production of specific particle sizes and particle size distributions
- High sintering activity
- Economic synthesis: broad application/usability of powders
- Environment-friendly and energy saving processes

<table>
<thead>
<tr>
<th>Properties / Requirements</th>
<th>Impact on finished part</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle size</td>
<td>microstructure</td>
<td>→ &lt; 1 μm</td>
</tr>
<tr>
<td>particle size distribution</td>
<td>homogeneity</td>
<td>→ narrow ± 10 %</td>
</tr>
<tr>
<td>particle shape</td>
<td></td>
<td>→ uniform</td>
</tr>
<tr>
<td>low impurity level in powder particles</td>
<td>microstructure composition</td>
<td>→ low ppm range</td>
</tr>
<tr>
<td>phase composition</td>
<td></td>
<td>→ defined</td>
</tr>
<tr>
<td>absence of large size secondary phases</td>
<td>crack formation/crack propagation</td>
<td></td>
</tr>
<tr>
<td>absence of agglomerates/aggregates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Processing properties</td>
<td>surface properties e.g. of colloid surface</td>
<td></td>
</tr>
</tbody>
</table>

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Ceramic Nanotechnology – L4
www.bioceramics.uni-bremen.de
How to Characterize Nano and Micro Particles?

- Density
- Morphology
- Diameter & Size Distribution
- Specific Surface Area
- Surface & Bulk Composition
- Crystal Phase

Outline Lecture

- Particle Morphology and Size
  - Density
  - Definition Particle Size
  - Methods
- Other Particle Properties
  - Crystal Phase
  - Zetapotential / IEP
  - Elemental Composition
  - Interfacial Tension
Overview Methods Particle Size Measurements

Method | Resolution
---|---
Sieving | > 20 μm
Light Scattering | 1 nm - 5 μm
Laser Diffraction | 50 nm – 1000 μm
Coulter – Counter („Electrozone Sensing“) | > 1 μm
Microscope (Optical / SEM / TEM) | 1 nm – 100 μm
Centrifuge Sedigraph with X-Ray Detection | 10 nm – 1000 μm
Acoustic Spectroscopy | 50 nm – 1000 μm
What is Porosity / Density?

<table>
<thead>
<tr>
<th>Masse:</th>
<th>19.65 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gesamtvolumen:</td>
<td>10.0 cm³</td>
</tr>
<tr>
<td>Geschlossene Porosität:</td>
<td>0.5 cm³</td>
</tr>
<tr>
<td>Offene Porosität:</td>
<td>2.0 cm³</td>
</tr>
<tr>
<td>Theor. Dichte:</td>
<td>2.62 g/cm³</td>
</tr>
<tr>
<td>Scheinbare Dichte:</td>
<td>2.46 g/cm³</td>
</tr>
<tr>
<td>Rohdichte:</td>
<td>1.96 g/cm³</td>
</tr>
</tbody>
</table>

Gesamtporosität = geschlossene + offene Porosität \[2.5\text{cm}^3\]

Theor. Dichte = Masse / (Gesamtvolumen - Gesamtporosität) \[19.65\text{g} / 7.5\text{cm}^3\]

Scheinbare Dichte = Masse / (Gesamtvolumen - offener Porosität) \[19.65\text{g} / 8\text{cm}^3\]

Rohdichte = Masse / Gesamtvolumen \[19.65\text{g} / 10\text{cm}^3\]

Measuring the Density: Liquid or Gas Pycnometry

\[\rho_p = \frac{G_1 - G_0}{(G_3 - G_0) - (G_2 - G_1)} \cdot (\rho_F - \rho_L) + \rho_L\]

\(\rho_F\) = Dichte der Flüssigkeit
\(\rho_L\) = Dichte der Luft

\(G_0\) = leer
\(G_1\) = mit Pulverteilchen
\(G_2\) = mit Pulverteilchen gefüllt mit Flüssigkeit
\(G_3\) = gefüllt mit Flüssigkeit
What is “Particle Size”?

- $d_{eq}$: equivalent diameter
  - 2-dimensional: circle with equivalent area as projection area of particle
  - 3-dimensional: sphere with similar total volume as particle

- $X_F$: Feret diameter
  - Distance between 2 tangents to the particle contour

- $X_{F_{\text{min}}}$: smallest feret diameter
- $X_{F_{\text{max}}}$: largest feret diameter

Particle Size Distribution Modes

- Normal or Gaussian Distribution
- Bimodal Distribution
Cumulative and Differential Particle Size Distribution

The MEDIAN Diameter is called D_{50}.

Example Bimodal Distribution

D_{Median} \approx 30 \, \mu m

D_{Mean} \approx 27 \, \mu m
Different Particle Size Definitions

Numerical distribution (each particle contributes)

\[ \bar{D}_N = \frac{\sum n_i \cdot D_i}{\sum n_i} \]

Volume distribution: the contribution to the mass is mostly caused by the bigger particles.

\[ \bar{D}_V = \frac{\sum n_i \cdot D_i^3}{\sum n_i} \]

Different Measurement methods can result in different results!

Comparison number/volume distribution

Number distribution

Volume distribution

Emphasis on small particles due to their large number.

Particles are weighted according to their volume.
Light Microscope / SEM / TEM

Size Range
> 1 µm
> 10 nm SEM
> 1 nm TEM

Advantage
Morphology directly observable
No assumptions need to be made

Disadvantage
SEM/TEM expensive
Poor Statistics

The National Bureau of Standards has stated that at least 10,000 separate images (not particles) need to be measured for statistical accuracy in image analysis.

Sieving

Size range
> 20 µm

Advantage
very cheap

Disadvantage
Not suitable for submicron and nano particles
Low resolution

"Sieving Towers" on a vibrating device
Scattering of light by particles. Detector, shown in red, measures angles and light intensities.

The diffusion coefficient $D$ of the moving particles is obtained from the fluctuating scattering pattern. From the diffusion coefficient the hydrodynamic radius $R_H$ is calculated.

1. The scattered lights from each particle reach the detector together
2. They interfere mutually.
3. As the particles move, the intensity of the scattered lights are changed with time.

### Particle Size: Light/Laser Scattering

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 nm - 5 µm (Light)</td>
<td>Small particles measurable</td>
<td>Expensive, small particles may be concealed</td>
</tr>
<tr>
<td>50 nm - 5 µm (Laser)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Coulter Counter (“Electro sensing Zone”)

Particles suspended in a weak electrolyte solution are drawn through a small aperture, separating two electrodes between which an electric current flows. The voltage applied across the aperture creates a "sensing zone”. As particles pass through the aperture (or "sensing zone"), they displace their own volume of electrolyte, momentarily increasing the impedance of the aperture. the pulse is directly proportional to the 3-dimensional volume of the particle that produced it.

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 100 µm</td>
<td>In situ usable</td>
<td>Small particle range</td>
</tr>
</tbody>
</table>
**Particle Size: X-Ray Sedigraphy**

Particles falling in a liquid medium. Yellow line coming from the left represents the X-ray source. Not all the X-rays reach the detector. Amount of X-rays adsorbed by the sample represents the mass of particles at specific size.

**Size Range**
10 nm – 100 µm

**Advantage**
Wide size range, Particle Size and Distribution are measured

**Disadvantage**
Particles to be measured should not be X-ray transparent

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**X-Ray Disc Centrifuge (XDC)**

Spinning Disc

X-Ray Source

Detector

---
X-Ray Disc Centrifuge (XDC)

\[ I_i = I_0 \exp(-BC(t_i)) \]
\[ D_s^2 = \frac{18\eta_t \ln(r_i / S)}{\omega^2(\rho_p - \rho_f)t_i} \]

Acoustic Spectroscopy: Ultrasound

Size Range
10 nm - 1000 µm

Advantage
Fast technique that can be applied in situ without altering the system.

Disadvantage
Only mono - and bimodal characterization possible.

Sound Absorption as a function of Frequency is measured.

[Adapted from Meier L., Zürich]
BET Measurement: Specific Surface Area

From the amount of gas adsorbed on the surface the surface area is calculated.
Assumption: Monolayer Formation (Langmuir type of adsorption).

BET Apparatus

Gas Adsorption Method:
Mostly N₂ used

Calculation Particle Diameter:

\[ D = \frac{6}{A_{BET} \cdot \rho_{Particle}} \]

Detection Range
> 0.2 m²/g

Advantage
Best technique to determine the Specific Surface Area

Disadvantage
Particle Size Distribution not measurable
BET Surface vs Particle Diameter for SiO$_2$

\[
D = \frac{6}{A_{\text{BET}} \cdot \rho_{\text{Particle}}}
\]

General Note: Repeatability/reproducibility of Particle Size Measurements

Relevance of Factors in repeatability and reproducibility

“Novices in the size-measurement field must understand that most errors in size measurement arise through poor sampling and dispersion and not through instrument inadequacies.”

Outline Lecture

• Particle Morphology and Size
  - Density
  - Definition Particle Size
  - Methods

• Other Particle Properties
  - Crystal Phase
  - Zetapotential / IEP
  - Elemental Composition
  - Interfacial Tension

Characterization of other Particle Properties

<table>
<thead>
<tr>
<th>Method</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Ray Diffraction (XRD)</td>
<td>Crystal Phase</td>
</tr>
<tr>
<td>X-Ray Fluorescence (XRF)</td>
<td>Elemental Composition</td>
</tr>
<tr>
<td>Colloidal Vibration Potential (CVP)</td>
<td>Zetapotential / Isoelectric Point</td>
</tr>
<tr>
<td>Pendant Drop Method (PDM)</td>
<td>Interfacial Tension (Hydrophilicity / Hydrophobicity)</td>
</tr>
</tbody>
</table>
X-Ray Diffraction (XRD): Determination of Crystal Phase

Outputs
Detection of crystal structure
Crystallite size from peak broadening with Scherrer Equation

Counts/s vs. 2θ

X-Ray Fluorescence (XRF): Determination of Elemental Composition

Outputs
Detection of Single Elements and their Ratio

Typical XRF Spectra
Principle X-Ray Fluorescence (XRF)

1. An electron in the K shell is ejected from the atom by an external primary excitation x-ray, creating a vacancy.

2. An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the L or M shell.

The Colloidal Vibration Potential (CVP) Technique: Zetapotential and IEP

- Ultra sound frequency = 3 MHz
- Particle deflection

\[ CVP = C' \varphi \cdot \mu_e \cdot \frac{\rho_p - \rho_m}{\kappa^* \cdot \rho_m} \cdot \frac{Z_g - Z_s}{Z_g + Z_s} \]

Information about: Zetapotential and Isoelectric point (IEP)

- Accuracy: ± 0.15 pH
- ± 1 mV
Zeta Potential of selected Oxides and the IEP

**Definition Isoelectric Point (IEP):**

pH where the Zetapotential equals Zero.

Pendent Drop Method: Hydrophilicity / -phobicity

**Task**

Determination of the interface and surface tension of liquids

**Output**

Measurement of the static interfacial or surface tension as a function of time or of temperature

Measurement of the adsorption/diffusion coefficients of surfactant molecules in oscillating/relaxing drops

**Typical measuring range**

0.05 ... 1000 mN/m

\[ p_o + \Delta \rho g z = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]

where \( \gamma \) is the fitting parameter and the resulting surface tension
Interfacial tension measurement

\[ p_0 + \Delta \rho g z = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]

where \( \gamma \) is the fitting parameter and the resulting surface tension.

Surface tension measured for Oxide Particle Suspensions
(at pH 7 in water/air, "pendant drop method")

[Rezwan K., Diss. ETH 2005]
Surface Tension measured for Oxide Particle Suspensions

Interpretation

Surface tension decreases in the following order:
SiO₂ > TiO₂ > Al₂O₃ > ZrO₂

hydrophobicity

decrease surface tension

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