Lecture

Nanoceramics

An Overview of Nano Materials
Literature


Nanoparticles: From Theory to Applications
G. Schmid (Ed.), Wiley, 2004

Nanotechnologie, R. Clasen, Univ. Saarlands SS2011


http://www.nano.gov
http://www.understandingnano.com
http://www.nanotechproject.org/inventories/medicine
http://www.nanomedjournal.com
http://www.nanowerk.com

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Definitions

Nano material:

„A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.“

European Commission (18 October 2011)

Nano ceramic:

Ceramic materials comprised of particles of 100 nm or less, i.e. of nano materials.

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Parts:

- Overview of Nano Materials
- Ceramics
- Fabrication of Nano Materials
- Phenomena in Dispersed Systems
- Consolidation of Nano Powders
- Properties of Nano Ceramics
Overview of Nano Materials

„nano to macro“

- Water molecule: 0.1 nm
- Gold nanoparticle: 10 nm
- Virus: 20 nm - 1 µm
- Hair: 100 µm
- 1 cm
- Full stop: 1 mm
- Watermelon: 10 cm

https://chembam.com/definitions/nanotechnology/
Overview of Nano Materials

Surface-to-Volume ratio increases with decreasing size:

Material properties can change drastically:

- Melting point
- Magnetic properties
- Color
- Conductivity

... 

These changes can appear suddenly

https://chembam.com/definitions/nanotechnology/
Overview of Nano Materials

- Cluster in Inorganic Chemistry - Narrow Definition:
  Compounds with metal-metal bonds with at least 3 metal atoms

- Cluster – Extended Definition
  Small groups of atoms (often used for metal oxides)

- Nanoparticles
  Particle with nano-dimensions

Quantum dots are clusters of \(~10^4\) atoms with specific optical properties
Categorization:

**Nano-object:**

A material with one, two, or three external dimensions with a size of approximately 1 - 100 nm

• **Nanoplate**
  – one nm-scale dimension
  – Graphene, silicate clay (montmorillonite)

• **Nanofiber, nanotube, nanorod**
  – two nm-scale dimensions
  – cellulose, poly(lactic acid), carbon nano-tubes, gold

• **Nanoparticle**
  – three nm-scale dimensions
  – TiO$_2$, SiO$_2$, …
Overview of Nano Materials

Nano technology comprises:

- Nano electronics
- Nano medicine
- Nano machines
- Nano materials (such as nano ceramics)

Nano technology is a highly interdisciplinary field!
### Examples for application:

- **Functionalisation of surfaces:** „self-cleaning“ surfaces
- **Catalysis, chemistry and materials science:** catalytical nano particles
- **Energy transformation and storage:** carbon nano tubes as hydrogen storage
- **Construction:** reinforcement of building materials
- **Sensors and actuators:** Lab-on-a-Chip, logic and memory units
- **Life sciences:** Improving medical diagnosis, therapy pathways (cancer treatment, wound care)
- **Defense:** sensors for damage detection, water repellent uniforms
- **Automotive industry:** nano particles as fuel additives
- **Aviation:** low-weight, durable and temperature resistant coatings
## Overview of Nano Materials

Selected packaging materials that contain nano materials [Öko-Institut, TA-SWISS ]:

<table>
<thead>
<tr>
<th>Product</th>
<th>Substance</th>
<th>Composition</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packaging (Bayer)</td>
<td>Clay mineral (silicate)</td>
<td>Nano particles in polymer</td>
<td>Bottles, foils</td>
</tr>
<tr>
<td>Packaging (Honeywell)</td>
<td>Clay mineral (silicate)</td>
<td>Nano particles in polymer</td>
<td>Bottles with oxygen scavenger</td>
</tr>
<tr>
<td>Packaging (Nanocor)</td>
<td>Clay mineral (silicate)</td>
<td>Nano particles in polymer</td>
<td>Bottles</td>
</tr>
<tr>
<td>Packaging (Plactic)</td>
<td>Clay mineral (silikate)</td>
<td>Nano particles in bio degradable polymer</td>
<td>Trays</td>
</tr>
</tbody>
</table>

**Embedded nano particles increase:**
flame retardancy, thermal stability, peak heat release rate, fracture, and strength

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Overview of Nano Materials

Nano ceramics are a part of nano technology:

→ nano scale ceramics where at least one dimension is in nano scale, e.g. nano particles, fibers, tubes, rods, foils

→ macro scale ceramics made from nano scale particles

SEM images of the $(Y_{0.94}Gd_{2})O_5O_{12}:Ce_{0.06}$ bulk samples heat-treated at different temperatures (a) glass hot-pressed at 910 °C, (b) 1100 °C, (c) 1200 °C, (d) 1400 °C.
Overview of Nano Materials

Powder:

- consists of a large number of freely moveable particles
- dry
- particles are loosely contacted
- flow properties depend on the morphology and electrostatic charge
## Overview of Nano Materials

### Classification of solid matter by particle size:

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Name</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.1</td>
<td>nano powder</td>
<td>particles</td>
</tr>
<tr>
<td>0.1 - 1</td>
<td>ultra fine powder</td>
<td>particles</td>
</tr>
<tr>
<td>1 - 10</td>
<td>super fine powder</td>
<td>particles</td>
</tr>
<tr>
<td>10 - 100</td>
<td>granular powder</td>
<td>particles</td>
</tr>
<tr>
<td>100 - 3000</td>
<td>granular solid</td>
<td>granules</td>
</tr>
<tr>
<td>3000 - 10000</td>
<td>fragments</td>
<td>grains</td>
</tr>
</tbody>
</table>

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Limit of 100 nm

nano → mikro

0.0001 Micron  0.001 Micron  0.01 Micron  0.1 Micron  1.0 Micron  10 Micron  100 Micron  1,000 Micron  10,000 Micron

Gas Molecules → Tobacco smoke → Oil smoke → Viruses → Bacteria → Plant spores → Foundry dust → Lung damaging dust → Unsettling atmospheric impurities → Setting atmospheric impurities → Heavy industrial dust → Fumes → Dusts → Electron Microscope → X-rays → Ultra-Violet rays → Visible → Infra-Red → light

Fog → Mists → Rain

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## Overview of Nano Materials

Typical size of some nano-scale materials [Rao et al., 2004].

<table>
<thead>
<tr>
<th>Form</th>
<th>Size</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocrystals</td>
<td>Diameter of 1…10 nm</td>
<td>Metals, semiconductors, magnetic materials.</td>
</tr>
<tr>
<td>Nanowires</td>
<td>Diameter of 1…10 nm</td>
<td>Metals, semiconductor, oxides sulfides, nitrides.</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>Diameter of 1…10 nm</td>
<td>Carbon, layered metal.</td>
</tr>
<tr>
<td>Nanoporous solids</td>
<td>Pore diameter of 0.5…10 μm</td>
<td>Zeolites, phosphates, etc.</td>
</tr>
<tr>
<td>2-dimensional array</td>
<td>Several nm²...μm²</td>
<td>Metals, semiconductors, magnetic materials.</td>
</tr>
<tr>
<td>Surface and thin film</td>
<td>Thickness 1…1000 nm</td>
<td>Variety of materials.</td>
</tr>
<tr>
<td>3-dimensional structures (super lattices)</td>
<td>Several nm³...μm³</td>
<td>Metals, semiconductors, magnetic materials.</td>
</tr>
<tr>
<td>Nano Material</td>
<td>Function</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>UV absorber, photo catalyst</td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>UV absorber</td>
<td></td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>Hardness or to increase flow</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>Polychrome, catalyst</td>
<td></td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Supramagnet, catalyst</td>
<td></td>
</tr>
<tr>
<td>Carbon nano fibres</td>
<td>Increases mechanical stability, low weight</td>
<td></td>
</tr>
</tbody>
</table>
Overview of Nano Materials

nanocrystalline materials
metals, intermetallics, ceramics and composites.

Nano materials
Metals
Ceramics
Composite

Nano and micro materials
Metals and ceramics
Plastics and ceramics

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Metallic nano particles
e.g. Pt-, Au-, Cu- nano particles

Lycurgus cup (roman) contains Au and Ag nano particles.

Green color: light scattering by Ag
Red color: light absorption by Au

http://www.expeditionzone.com/start_hi.cfm?story=2370&business=&club=&member=

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Metallic nano particles

Au nano particles

Long-term stability of nano particles in glass

(Note: "Norwich, England, ca. 1480"). The ruby color is probably due to embedded gold nanoparticles

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Carbon nano particles

Damascus steel

Investigation via SEM showed the structure of damascus steel:

Cementite (Fe$_3$C) nanowires and carbon nanotubes are present in the steel. The patterns are caused by cementite grains on the surface.

The combination of metallic iron, cementite and carbon nanotubes results in superior properties of the steel.

Nano technology was used centuries ago without being aware of it
Overview of Nano Materials

Ceramic nano materials

e.g. SiO₂, Al₂O₃, TiO₂, ZnO, Mn₃O₄

Functional materials

White pigment:

TiO₂ nano particles with Rutil structure

TEM micrograph of Mn₃O₄ nanoparticles.

SEM images of the 'as precipitated' nanopowder (mean particle size = ca 280 ± 68 nm, sample of 103 particles) [J.A. Darr]

ZnO powder dispersion in a sunscreen (courtesy Elta Block).

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Ceramic nano materials

- e.g. SiO₂, Al₂O₃, TiO₂, ZnO, Mn₃O₄

Oxidic nano particles:
- Pigments, ceramics, membranes, structured catalysts, micro batteries
- SiO₂, Al₂O₃, CeO₂ nano particles: polishing
- TiO₂ and ZnO nano particles: UV absorber
- V₂O₅ and TiO₂ nano particles: catalysis

Al₂O₃, TiO₂ nano ceramics

Construction

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Magnetic nano materials

- Therapy
  - Drug delivery
  - Radiotherapy combined with MRI
  - Anemic chronic kidney disease
  - Hyperthermia/thermal ablation
  - Musculoskeletal system associated diseases

- Diagnosis
  - In vivo
    - MRI
  - In vitro
    - Sensing
    - Cell sorting
    - Bioseparation
    - Enzyme immobilization
    - Immunoassays
    - Transfection
    - Purification

applications of magnetic nanoparticles (NPs)
Magnetic nano materials

MAGNETIC NANOPARTICLES
Magnetic ceramic nanoparticles

the location and detection of viruses: a viral nanosensor.

Iron oxide particles (~50 nm in diameter) with a dextran coating are covered with antibodies. The antibodies are chosen for a specific virus (e.g., herpes simplex virus or adenovirus). When these specially coated nanoparticles are then exposed to the virus they will form clusters that would be large enough to be visible on a nuclear magnetic resonance (NMR) or magnetic resonance imaging (MRI) scan. This approach has already been demonstrated in the laboratory using viral particles in solution. The idea is that it might eventually be used to detect viruses in human body fluid or tissue.

Diagram of a viral-induced nanoassembly of magnetic nanoparticles.
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**Composites**

**Nano-composite:** mixture of different materials on nanoscale

for example: Co, Cr, Pt, SiO$_2$

recording media material: Co grain; 30 nm
CoCrPt alloys with SiO$_2$ or thin oxide

thin films of several layers sputtered onto a substrate.
(Al alloys or glass, thickness from 0.35 mm to 2 mm)
few magnetic layers - CoCrPt alloys with SiO$_2$

TEM image of a granular perpendicular recording medium.
The grains are separated from each other by a thin oxide region.
(Black lines illustrate the bit boundary) [Rachid Sbiaa]

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Composites

Increasing hardness

Nano-composite: mixture of different materials on nanoscale

Metallic nano particles in alloys
Dispersion hardening – nano particles are diffused into a metal to increase hardness
  e.g.  Co in Cu
       Cu in Al

Oxide and non-oxide ceramics in alloys
Light metals (Al, Mg) + carbides (B₄C, SiC), nitrides (BN, AlN), borides (TiB₂), oxides (Al₂O₃)
ceramic/metal composites
High strength steel:
Carbide precipitates with diameter of < 10 nm
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Nano-composite: mixture of different materials on nanoscale

Metal / metal oxide composite:

a porous oxidic base is covered with metallic particles with a size of 40-100 nm

Application: catalysis
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metallic nano particles with ceramic micro particles

e.g. Pt or Au nano particles on the matrix

Gold cluster on an oxidic base
metallic nano materials with polymers

Nanocrystalline film on polystyrene

PVP coated Pd nanocrystals

Cu

Au

Ag

Typical local roughness, 35 nm (rms)
metallic nano particles with polymers

Anti-Bacterial
FE-SEM: Zeiss(1550)-Clark
This image shows electrospun nylon 6 nanofibers decorated with surface bound Ag nanoparticles.

Immersing nylon 6 nanofibers into Ag colloidal solution with pH 5, Ag nanoparticles were assembled onto nylon 6 nanofibers via interaction between nylon 6 and protection groups of Ag nanoparticles. Future applications include antibacterial filtration.

Fiber Science and Apparel Design (Hong Dong)
Overview of Nano Materials

ceramic nano particles with polymers

e.g. MgO, Al$_2$O$_3$ or SiO$_2$ nano particles or carbon nanotubes as fillers in PE

SiO$_2$ nano particles are used as *thickening agents*, *fillers* or to increase mechanical toughness
ceramic nano particles with ceramic micro particles

SiO$_2$ nano particles as filler in concrete:

The amount of micro pores is decreased, this results in an increased hardness.

nanostructured matrix for the solid lubricant in combination with nanophased powder
Siegel classification of nano materials

Siegel classification:

- Clusters or powder (MD=0)
- Multi layers (MD=1)
- Ultra-thin grainy films (MD=2)
- Composites (MD=3)

Definition of nanomaterials following Siegel
Nanocrystalline materials can be classified into several groups according to their dimensionality: zero-dimensional atom clusters, one-dimensional modulated multilayers, two-dimensional ultra-fine-grained overlayers, and three-dimensional nanocrystalline structures.

A nanoparticle is a quasi-zero-dimensional (0D) nano-object in which all characteristic linear dimensions are of the same order of magnitude (not more than 100 nm).

Nanorods and nanowires are quasi-one-dimensional (1D) nano-objects.

The group of two-dimensional objects (2D) includes planar structures, nanodiscs, thin-film magnetic structures, magnetic nanoparticle layers, etc., in which two dimensions are an order of magnitude greater than the third dimension, which is in the nanometre range.
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Siegel classification

- Clusters (0D)
- Nanotubes, filaments and rods (1D)
- Films and layers (2D)
- Polycrystals (3D)
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Gleiter classification

Classification schema for nanocrystalline materials according to their chemical composition and the dimensionality (shape) of the crystallites (structural elements) forming the materials.

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Specific surface area of nano materials
Specific surface area

A large fraction of the atoms of a nano particle are surface atoms:

Diameter: 10 nm

Number of atoms: 30 000

Fraction of atoms on surface: 20%

At 5 nm diameter 40% are on the surface, at 2 nm 80% and at 1 nm 99%!

- melting point decreases
- defect density increases
- crystal structure can change
- band gap changes
fraction of atoms at the surface as a function of particle diameter ($d_p = 0.5$ nm).

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Number of atoms</th>
<th>Fraction at surface (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>2.0</td>
<td>64</td>
<td>99</td>
</tr>
<tr>
<td>5.0</td>
<td>1.000</td>
<td>50</td>
</tr>
<tr>
<td>10.0</td>
<td>8.000</td>
<td>25</td>
</tr>
<tr>
<td>20.0</td>
<td>64.000</td>
<td>12</td>
</tr>
</tbody>
</table>
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Surface atoms

A cube consisting of 27 atoms has
1 atom in the bulk
6 atoms at the faces
12 atoms at edges
8 atoms at corners
96% of atoms at surface

A cube consisting of 64 atoms has
87.5% of atoms at surface
Surface atoms

\[ N_0 = 8 + 6(n - 2)^2 + 3(4n - 8) \]

- \( n \): length of cube
- \( N \): number of atoms \((N = n^3)\)
- \( N_0 \): surface atoms
- \( N_0/N \): fraction of surface atoms
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Specific surface area

\[
\begin{array}{c|c|c}
\text{Dimension} & \text{Surface Area} \\
\hline
27 \text{ cm} & 0.44 \text{ qm} \\
0.1 \text{ cm} & 120 \text{ qm} \\
1 \text{ nm} & \text{ca. 12 qkm} \\
\end{array}
\]

Beispiel: 50 kg Quarz

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Surface area/volume relations for different reinforcement geometries

- **Particulate powder**: \( S/V = \frac{3}{r} \)
- **Fibrous material**: \( S/V = \frac{2}{r} + \frac{2}{l} \)
- **Hexagonal Platelet**: \( S/V = \frac{2}{0.866l} + \frac{2}{t} \)

Thostenson, E.T.; Li, C.; Chou, T.W.
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Specific surface area

\[ SSA = \frac{S_{\text{total}}}{m_{\text{total}}} \]

\[ S_{\text{part}} = \pi D^2 \quad S_{\text{total}} = n \times S_{\text{part}} \]

\[ m_{\text{total}} = V_{\text{total}} \times \rho \]

\[ V_{\text{part}} = \frac{4}{3} \pi \frac{D^3}{8} \quad V_{\text{total}} = n \times V_{\text{part}} \]

\[ SSA = \frac{n \times \pi D^2 \times 3 \times 8}{n \times \pi D^3 \times 4 \times \rho} = \frac{6}{D \rho} \]

\[ [SSA] = \frac{m^2 \times m^3}{m^3 \times kg} = \frac{m^2}{kg} \]

\[ SSA \sim \frac{1}{D} \]
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Surface atoms

Densely packed atoms result in a larger number of surface atoms.

Surface atoms bond to ubiquitous ions such as $\text{OH}^-$, $\text{H}_2\text{O}$ or $\text{O}^{2-}$. 

<table>
<thead>
<tr>
<th>Partikel-durchmesser [nm]</th>
<th>$\alpha$-$\text{Al}_2\text{O}_3$</th>
<th>$\text{ZrO}_2$ (monoklin)</th>
<th>$\text{ZrO}_2$ (tetragonal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>21,1</td>
<td>14,8</td>
<td>14,6</td>
</tr>
<tr>
<td>100</td>
<td>4,4</td>
<td>3,1</td>
<td>3,0</td>
</tr>
<tr>
<td>1,000</td>
<td>2,8</td>
<td>1,9</td>
<td>1,9</td>
</tr>
</tbody>
</table>
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- Surface atoms are in a higher energetic state
- This increases their suitability for absorption, heat exchange, sensing,…

Fig. 1.52: At the surface of a hypothetical two-dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other, the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

http://Materials.usask.ca
Overview of Nano Materials

Dependence of Material Properties on the Size of Nano Particles
### Overview of Nano Materials

Depending on the diameter, different properties are influenced:

<table>
<thead>
<tr>
<th>Property</th>
<th>Diameter Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic activity</td>
<td>&lt; 5 nm</td>
</tr>
<tr>
<td>Magnets get &quot;softer&quot;</td>
<td>&lt; 20 nm</td>
</tr>
<tr>
<td>Refraction</td>
<td>&lt; 50 nm</td>
</tr>
<tr>
<td>Electromagnetic phenomena</td>
<td>&lt; 100 nm</td>
</tr>
<tr>
<td>(&quot;supra paramagnetism&quot;)</td>
<td></td>
</tr>
<tr>
<td>Electric phenomena</td>
<td>&lt; 100 nm</td>
</tr>
<tr>
<td>(&quot;supra conduction&quot;)</td>
<td></td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>&lt; 100 nm</td>
</tr>
<tr>
<td>(increased hardness)</td>
<td></td>
</tr>
</tbody>
</table>


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Nanocrystalline materials may exhibit increased strength/hardness, improved toughness, reduced elastic modulus and ductility, enhanced diffusivity, higher specific heat, enhanced thermal expansion coefficient (CTE), and superior soft magnetic properties in comparison with conventional polycrystalline materials.

Sizes:
- Atom: 0.001 nm
- Nano granule: ~10 nm
- Boundary: ~1 nm
- Glide plane: 0.1 nm

Two-dimensional model of a nanostructured material. The atoms in the centers of the crystals are indicated in black. The ones in the boundary core regions are represented as open circles.

The chemical, optical, electrical, and magnetic properties of **nano particles** depend both on their size (1-10 nm) as well as their morphology (sphere, rod, leaves,…).

*Copper colloids* are catalitically active and are used to convert syngas to methanol.

*Titanium* dioxide nano particles can be used in solar cells, for the photochemical wastewater detoxification, as a UV-absorber and so on…

*CdSe* nano particles, so-called quantum dots, are used as fluorescent markers for in vivo measurements or in displays.
Mechanical Properties

Definitions

- Elasticity  - non permanent deformation
- Plasticity  - permanent deformation
- Strength    - ability to withstand load
- Ductility   - ability to be drawn into wire
- Malleability - ability to deform under compression
- Hardness    - resistance to abrasion, wear, scratch, cut
- Britteness  - fracture without warning
- Toughness   - amount of energy absorbed before rupture
- Stiffness   - to resist deformation Al v/s steel beam (sag)
- Resilience  - resist impact/shock, absorb energy up to elastic limits
- Fatigue     - under alternating stresses
- Creep       - slow & progressive deform at constant stress & at high temp
Mechanical Properties

Tensile Stress-Strain Diagram

- Elastic Range
- Plastic Range
- Elongation Until Failure
- Ultimate Tensile Strength
- Yield Point
- Proof Load (Typically 85-95% of Yield)
- Typical Clamp Load (75% of Proof Load)
- Failure (Fracture Point or Tensile Point)

Stress (Tension/Load) vs. Strain (Stretch & Elongation)
### Mechanical Properties

#### Table 1-2: Mechanical Properties of Metals/Alloys

<table>
<thead>
<tr>
<th>TOUGHNESS</th>
<th>BRITTLENESS</th>
<th>DUCTILITY</th>
<th>MALLEABILITY</th>
<th>CORROSION RESISTANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>White Cast Iron</td>
<td>Gold</td>
<td>Gold</td>
<td>Gold</td>
</tr>
<tr>
<td>Nickel</td>
<td>Gray Cast Iron</td>
<td>Silver</td>
<td>Silver</td>
<td>Platinum</td>
</tr>
<tr>
<td>Iron</td>
<td>Hardened Steel</td>
<td>Platinum</td>
<td>Aluminum</td>
<td>Silver</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Bismuth</td>
<td>Iron</td>
<td>Copper</td>
<td>Mercury</td>
</tr>
<tr>
<td>Zinc</td>
<td>Manganese</td>
<td>Nickel</td>
<td>Tin</td>
<td>Copper</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Bronzes</td>
<td>Copper</td>
<td>Lead</td>
<td>Lead</td>
</tr>
<tr>
<td>Lead</td>
<td>Aluminum</td>
<td>Aluminum</td>
<td>Zinc</td>
<td>Tin</td>
</tr>
<tr>
<td>Tin</td>
<td>Brass</td>
<td>Tungsten</td>
<td>Iron</td>
<td>Nickel</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Structural Steels</td>
<td>Zinc</td>
<td>Iron</td>
<td>Iron</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Misc.</td>
<td>Tin</td>
<td></td>
<td>Magnesium</td>
</tr>
</tbody>
</table>

*Metals/alloys are ranked in descending order of having the property named in the column heading.

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Examples of metals/alloys possessing certain mechanical properties
Mechanical Properties of Materials

Strength

Ply-bond

All chemical bonds are breaking

Shear

Glide plane

Two layers are moving → bonds are not broken
Yield strength $R_e$ of nano materials

A decrease in grain diameter results in a significant increase in strength

Large yield strength (highly elastic material)
- Material (crystals) without dislocations
- Material with dislocations and barriers for their movement

The extraordinary combination of both high strength and high ductility

Elasticity

Prof. Dr. Plewa
Dr. Baur
Normally, materials may be strong or ductile, but not at once. Nevertheless, some nanostructured materials retain its high strength and ductility under deformation.

The mechanisms of improving of ductility are an increase of grain boundary sliding and grain rotation.
Mechanic stress above the yield strength causes parts of the material to glide relative to others.

These dislocations can only move until they reach a grain boundary.

Plastizität
Mechanical properties of materials

Dislocations can only move until they reach a grain boundary. The boundaries present a barrier that cannot be passed by the dislocation. A so-called „dislocation pile-up“ occurs.

Hall-Petch relation:

\[ \tau_{gb} \approx k_y \cdot D^{-1/2} \]

Small grain diameters \( D \) result in smaller additional stress \( \tau_{gb} \).

The dislocation pile-up causes a high resistance towards deformation – hardness and strength increase.
Mechanische Eigenschaften von Nanomaterialien

\[ \sigma = \sigma_0 + k \cdot d^{-0.5} \]

Relationship between grain size and mechanical strength for PCA.

(Theo G M M Kappen)
Mechanical Properties

Festigkeit von nanokristallinem Eisen in Abhängigkeit von der Korngöße

\[ \sigma = \sigma_0 + k \cdot d^{-0.5} \]

Prof. Dr. Plewa
Dr. Baur
Nano crystalline TiO₂ (rutile) can be deformed plastically at temperatures between 600 and 800 °C.

Micro crystalline TiO₂ shows this creeping only at significantly higher temperatures close to the melting point (1830 °C).

This has been attributed to diffusion along grain boundaries.
In metallic nano materials hardness increases with decreasing ductability.

Nanostructured chips are typically 2-3 times as hard as bulk material

Kevin Trumble
Mechanical Properties

Intergranular processes
* Small scale sliding in the grain boundaries

Intragranular processes
* Dislocation nucleation and motion

Hardness

Amorphous Nanocrystalline Microcrystalline phase

$d_c = 10 \text{ nm}$ → Grain size

Schematic illustration of development of the hardness in materials with decreasing grain size $d$.

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>$5.8 \pm 0.5$</td>
<td>$145 \pm 20$</td>
</tr>
<tr>
<td>15</td>
<td>$6.5$</td>
<td>$170$</td>
</tr>
<tr>
<td>20</td>
<td>$6.7$</td>
<td>$150$</td>
</tr>
<tr>
<td>40</td>
<td>$6.8$</td>
<td>$180$</td>
</tr>
<tr>
<td>100</td>
<td>$5.7$</td>
<td>$130$</td>
</tr>
<tr>
<td>bulk (literature)</td>
<td>$12–17$</td>
<td>$200–220$</td>
</tr>
</tbody>
</table>

Room temperature hardness and elastic modulus values for nanocrystalline YSZ obtained from nanindentation studies.

Ductility is caused by easy movement of dislocations along the glide planes.
**Mechanical Properties**

**Summary**

- **Deformation**
  - **elastic**
    - reversible deformation
  - **plastic**
    - irreversible deformation
  - **super plasticity**
    - irreversible deformation

- **Distortion of the lattice**
- **Gliding of layers**
- **Movement of dislocations**
- **Movement of grain boundaries, dislocations and diffusion**

**Atomic bonds**

- Atomic bonds are not broken
- Atomic bonds are broken locally

Prof. Dr. Plewa
Dr. Baur
Mechanical Properties

Mechanism of superplasticity

Grain boundary sliding is an important mechanism for high temperature creep of nanomaterials (grain switching model)
Overview of Nano Ceramics

Most metallic materials are ductile and have high toughness. Most ceramic materials have a high hardness and brittleness.

Nano sized materials (<20 nm) of the same chemical composition:

- Metals: high hardness and brittleness
- Ceramics: high ductility and high toughness

- Ductility - ability to be drawn into wire
- Malleability - ability to deform under compression
- Hardness - resistance to abrasion, wear, scratch, cut
- Brittleness - fracture without warning
- Toughness - amount of energy absorbed before rupture
Electrical properties

A result of the large specific surface area of nano particles:

- electrical resistance is large compared to macrocrystalline materials

At diameters > 100 nm:
Electrons are mainly scattered at grain boundaries (number of grains is higher in nano ceramics)

At diameters < 100 nm additional electron scattering occurs at the surface of the wire. Resistance increases strongly.
Ion conductivity decreases with decreasing particle size.

Grain boundaries begin to play a large role:

- Transition from bulk-controlled ionic conductivity to GB-controlled ionic conductivity
- Diffusion processes in the boundary layer are dominating

Arrhenius plots of electrical conductivities of 8YSZ: Q. Li et al.

The nanocrystalline sample has a higher density than the microcrystalline samples, and high density should improve the electrical conductivity to some extent.
Magnetic Properties

Hysteresis behavior of the field $H$ to the magnetization $M$ of a ferromagnet:

- $H = 0$:
  - vanishing magnetization
  - full magnetization

- $H > 0$:
  - paramagnetic
  - ferromagnetic

Para- and superparamagnets show (fast) no hysteresis.

Authors:
- Prof. Dr. Plewa
- Dr. Baur
Area with identical magnetisation are called magnetic domains or Weiss domain.

The boundary is called Bloch wall.

A ferromagnetic material will have a magnetic moment even without an external magnetic field.

Interaction between electron spins favours parallel ordering.

At temperatures above the Curie temperature this ordering will be destroyed and the magnetic moment is lost.
Magnetic Properties

Diameter of magnetic domains: 10-100nm

→ Nano particles consist of a single magnetic domain!

→ Upon polarity reversal the whole particle will be affected

This requires significantly less energy as no interaction between magnetic domains occurs:

→ Hysteresis is much less pronounced
Magnetic Properties

(a) Comparison of the hysteresis loops for three applications of ferromagnetic and ferrimagnetic materials.

(b) Saturation magnetization and coercivity values for different magnetic materials. (by G.Y. Chin et al.)
Magnetic Properties

Single-domain ferromagnetic particles
The critical radius $r_c$ below which a particle acts as a single domain particle is given by

$$r_c \approx 9 \frac{(AK_u)^{1/2}}{\mu_0 M_s^2}$$

where $A$ is the exchange constant, $K_u$ is the uniaxial anisotropy constant, $\mu_0$ is called constant of permeability, and $M_s$ is the saturation magnetization.

Typical values for $r_c$ are about 15 nm for Fe and 35 nm for Co, for $\gamma$-Fe$_2$O$_3$ it is 30 nm, while for SmCo$_5$ it is as large as 750 nm.
Magnetic Properties

Single domain nano particles

Critical radii ($r_c$):

Fe – 15 nm, Co – 35 nm, Fe$_2$O$_3$ - 30 nm, SmCo$_5$ – 750 nm

Fe$_2$O$_3$ Nanoteilchen (Magnetit)
Magnetic Properties

Single domain particles:

- weak magnetic fields are sufficient to fully magnetize the material (low interaction of domains)
- removal of the field results in loss of magnetisation
- decreasing the particle size increases the softness of the magnet

→ „super paramagnetism“

Paramagnets show hardly any hysteresis even as macro particles!
Magnetic Properties

Super-paramagnetism

Qualitative illustration of the behaviour of the coercivity in ultrafine particle systems are the particles size changes.

J. Dutta & H. Hofmann:

Prof. Dr. Plewa
Dr. Baur
Magnetic Properties

Super paramagnetism
→ mainly a result of single domain particles

A ferromagnetic materials begins to behave like a paramagnetic material

The hematite particles with average size of 41 nm have almost no remnant magnetisation at zero magnetic field strength

Magnetisation measurement of subrounded hematite particles with 160 nm average size

Magnetisation measurement of subrounded hematite particles with 41 nm average size
## Optical Properties

### Colour and particle size of gold nanoparticles

<table>
<thead>
<tr>
<th>Shape</th>
<th>Size/nm</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>&lt;3</td>
<td>Pale blue</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Pink</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>Orange</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>Red</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>Dark magenta</td>
</tr>
<tr>
<td></td>
<td>100-150</td>
<td>Violet</td>
</tr>
<tr>
<td>Irregular</td>
<td>200</td>
<td>Light Blue</td>
</tr>
<tr>
<td>Ellipsoids</td>
<td>60x90</td>
<td>Purple</td>
</tr>
<tr>
<td>Aggregated</td>
<td></td>
<td>Blue</td>
</tr>
</tbody>
</table>

The colour of the gold image depends on the dimensions of the nanoparticles, which are controlled by the parameters of the photochemical process.

---

Prof. Dr. Plewa
Dr. Baur
The band gap of a material increases with decreasing particle size:

→ instead of bands discrete energy levels are observed
This change in the band gap can be utilized to tailor the emission wavelength of a particle.

As can be seen, the energy gap changes little for specimens with the grain size larger than 100 nm, but rapidly increases when grain size decreases below 30 nm.
Optical Properties
Change of the band gap in $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$

For example, the band gap of CdS was found to increase from 2.5 eV, the bulk value, to $>3.5$ eV as the particle diameter was decreased from 10nm to 1nm.
Transmission as a function of grain size

Krell et al., JACS (2003); Apetz & van Bruggen, JACS (2003)

Influence of residual porosity

Theoretical maximum ~ 66%

Wavelength (nm)

Transmission (%)

(001) sapphire

sub-μm Al₂O₃ (sintered) (0.8 mm thick)

~ 70% of maximum

sub-μm Al₂O₃

Transmission as a function of grain size

Prof. Dr. Plewa
Dr. Baur
Transmission as a function of grain size

Extinction or optical density

\[ E = \log \frac{I_0}{I} \]

Transmission as a function of particle size

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Dr. Baur
The color of a material depends on the size of the band gap.

Nano scale particles show narrow absorption and scattering.

Color depends on:
- particle morphology
- interaction between particle
- …
Emission color changes with particle size

The band gap increases with decreasing particle size

CdSe:
- 1.7 eV (red light) @ 20 nm
- 2.4 eV (blue light) @2 nm
different emission color by variation of particle size (CdSe 1 - 12 nm)
Scattering results in a weakening of the scattered light in the direction of propagation of the light.

Interaction between light and matter

small particles $d << \lambda$: **RAYLEIGH-scattering** (*elastical scattering*)  
* violet light ($400 \text{ nm}$) is $2^4 = 16$ times stronger scattered than red light ($800 \text{ nm}$)  
Example:  
- Setting/rising sun appears red  
- structures on the horizon appear blue  
- the sky appears blue, not black as blue light is scattered towards the observer

larger particles $d > \lambda$: **TYNDALL-scattering** ($d > \lambda$) or **MIE-scattering** ($d \approx \lambda$) – only very slight wavelength dependence, appears white  
Example:  
- Milk  
- Soap water  
- Droplets of oil in water  
- Foam  
- fine powder (salt, snow, gypsum), which are transparent in bulk
Rayleigh formula

Intensity of scattering is proportional to the wavelength by $I_{\text{scatt}} \sim \lambda^{-4}$

Intensity of scattering is linear proportional to the number of particles $I_{\text{scatt}} \sim N$

$$I_{\text{scatt}} = N \cdot \frac{I_0 \alpha^2 \pi^2}{\varepsilon_0^2 \lambda^4 r^2}$$

- $I_0$ Intensität des Primärlichts
- $\alpha$ Polarisierbarkeit des Teilchens
- $\varepsilon_0$ die elektrische Feldkonstante
- $r$ Abstand vom Dipolzentrum

If a material absorbs 100% light across the whole visible-light, it shows a completely black color. If only certain percentage across the entire visible-light region is equally absorbed, it is partially black or gray. If no light is absorbed across the entire visible-light region, the color is white. If the light across the entire visible-light region is not equally absorbed, certain color (e.g., yellow, brown, green) will be observed.
The intensity of the scattered light depends on:
- wavelength of incident light
- angle between incident and scattered light
- particle morphology
- physical properties of the substance

The dependence of the intensity of the scattered light on the particle size can be divided in three parts:

\[ \alpha = \frac{2 \cdot \pi \cdot r}{\lambda} \]

\( r \) – particle radius, \( \lambda \) – wavelength of incident light

1. **Case: \( \alpha > 10 \) and \( \lambda \ll r \):** Light diffraction dominates (Fraunhofer equation)

2. **Case: \( 0,1 < \alpha < 10 \) and \( \lambda \approx r \):** MIE – scattering (only slightly wavelength dependent)

3. **Case: \( \alpha \ll 1 \) and \( \lambda \gg r \):** RAYLEIGH- scattering

\[ \frac{I}{I_0} \sim \frac{r^6}{\lambda^4} \]

Small particles result in less scattering and small wavelengths are scattered more strongly.
Optical Properties

Nano scale phosphors

The surface is usually either amorphous or can be seen as a defect:
- the larger the surface area the higher the number of defects

Nano particles (1 to 100 nm) have a quantum yield of approximately 20%!

Some applications require nano particles anyway…
Optical Properties

Nano scale phosphors

Nano-Thin-Film Phosphor
Y2O3: Eu

- 50nm
- 60nm
- 160nm

light emission efficiency (cd/m²)

low-voltage (kV)

phosphors for field emission displays (FED) (H Murakami ULVAC, Inc.)

Prof. Dr. Plewa Dr. Baur
Optical Properties

Nano scale phosphors

Primet GaN nanoparticles (red) show a 20% increase in intensity over high purity bulk GaN micron sized particles.

Platelet GaN Nanopowder Synthesized by Primet
Optical Properties

Nano scale phosphors

Comparison of (a) UBV excitation and (b) emission spectra of 1000°C-annealed LaPO₄:Ce₆⁺, Tb⁻⁻₉₆ nano phosphor and commercial LaPO₄:Ce₆⁺, Tb⁻⁻₉₆ bulk phosphor. The excitation and emission spectra were collected with a detection wavelength of 544 nm and an excitation wavelength of 157 nm, respectively.

Quenching curves of nanopowder and bulk Y₂O₃ doped with different Tb concentrations. [Jacobsohn]

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Optical Properties

nano scale phosphors

Ce-doped Lu$_2$SiO$_5$
red-shift and enhanced Stokes shift

Normalized PLE (left curve) and PL (right curve) for nanophosphor LSO (1% Ce) and bulk LSO.

Michael Wayne Blair 2008

G. Stryganyuk
Optical Properties

nano scale phosphors

red shift for emission from nanocrystals.

PL excitation and emission spectra of ZnS:Mn ‘bulk’ (micrometer) and nanocrystalline (3-4 nm) powders. The maximum PL emissions occur at 582 and 598 nm for ‘bulk’ (micrometer size powder) and nanocrystals, respectively. The excitation maxima for PL emission are 342 and 308 nm for ‘bulk’ and nanocrystals, respectively.


if \( d_n \) then \( E_g \)

\( \lambda \) (Absorption) \( \downarrow \) red → blue

\( \lambda \) (Emission) \( \downarrow \) red → blue

\( \lambda \) (Reflection) \( \rightarrow \) blue → red
Optical Properties

nano scale phosphors


Prof. Dr. Plewa Dr. Baur
Luminescent nanocrystals (nanophosphors) can offer increased luminescence efficiency under certain circumstances:

A comparison of photoluminescence ($\lambda_{exc} = 266$ nm) of Eu:Y$_2$O$_3$/ZnS:Ag blend with different sizes of Eu:Y$_2$O$_3$ nanocrystallites.

A comparison of cathodoluminescence (90 kV) of Tb:Y$_2$O$_3$/Cr:Al$_2$O$_3$ blends with different size of Tb:Y$_2$O$_3$ nanocrystallites.