Ceramic Nanotechnology
Lecture 10
Powder Synthesis and Conditioning

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➢ Class Outline „Ceramic Nanotechnology"

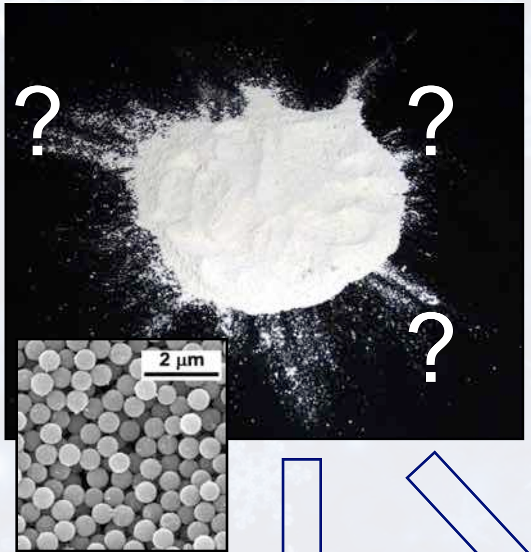
Nanotechnology: Background, Theory, Methods

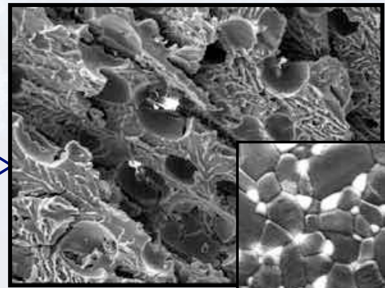
Selected Examples from the Frontier of Science

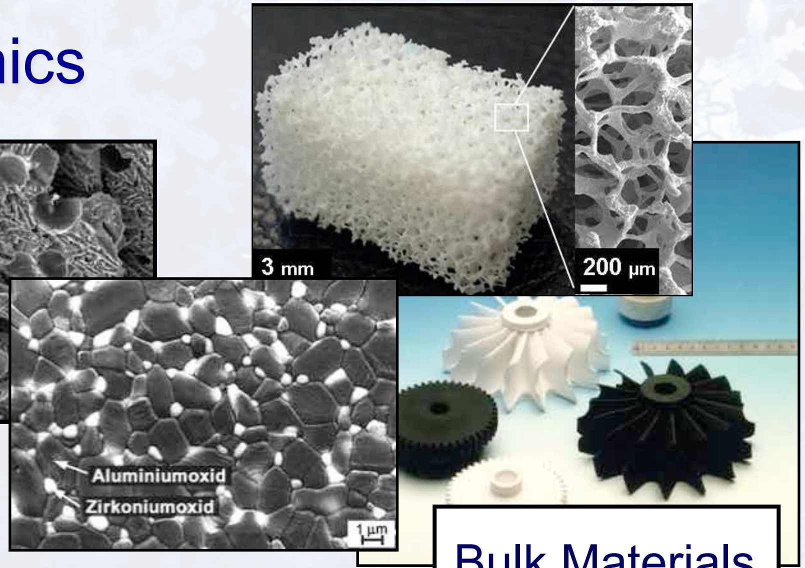
Applications in Ceramics

Am 8.11. findet <u>keine</u> Vorlesungen statt!
Stattdessen wird eine Wiederholungstunde direkt vor den Prüfungen angeboten.

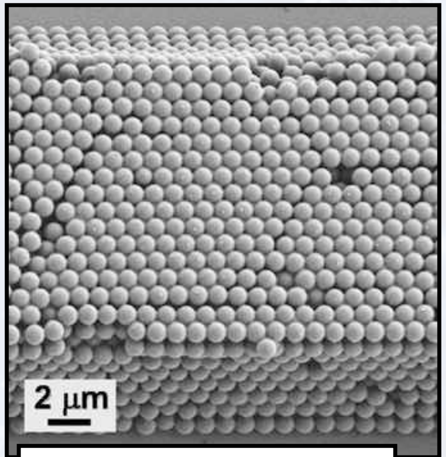
➢ From Powder to Advanced Ceramics





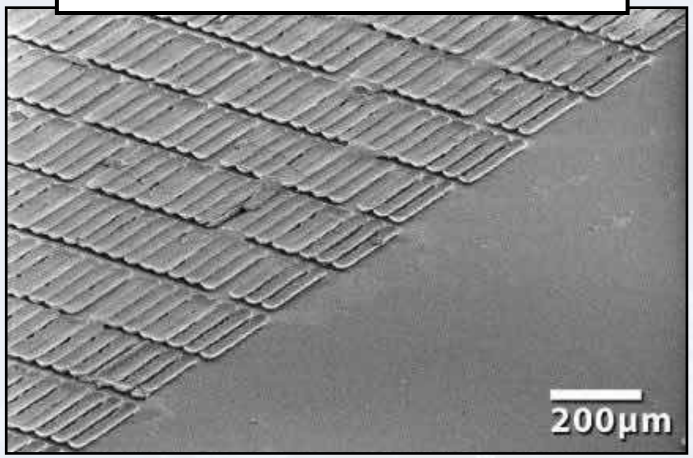


Bulk Materials

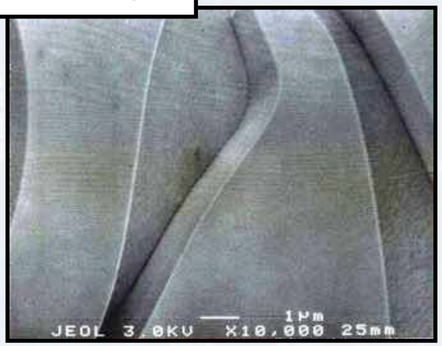


Colloid Crystals

Surface Micro Patterning



Surface Coatings



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➢ Producing Ceramic Bulk Components





Powder → **Bulk-Processing** → **Shaping** → **Green-/White-machining** → **Sintering** → **Post-processing** → **Ceramics**

Powder
- Raw Materials

Bulk-Processing
- Mixing
- Grinding
- Pelletizing
- Dispersing
- Plastisizing (additives)

Shaping
- Pressing
- Casting
- Extruding
- Spraying

Green-/White-machining
- Milling
- Turning
- Drilling
- Sawing

Sintering
- Firing

Post-processing
- Sanding
- Lapping
- Polishing

Ceramics
- Product

Shaping

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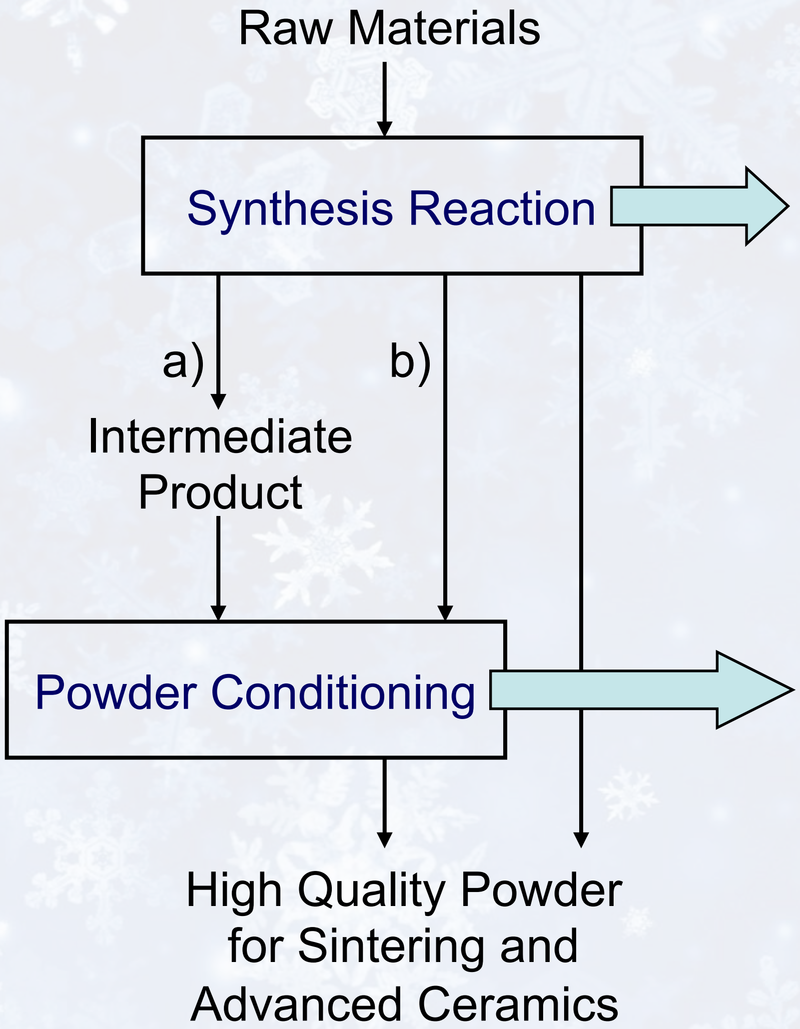
➢ Flow Chart Powder Synthesis



- **Solid State Reactions**
- **Gas-Solid Reactions**
- **Gas Phase Reactions**
- **Precipitation from Solutions**

a)
- Calcination
- Thermal Decomposition
- Crystallization

b)
- Mechanical Processing (e. g. grinding)
- Chemical Processing (e. g. washing)
- Thermal Processing (e. g. oxidation)

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➢ 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

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

➢ Important powders worldwide (> 100 tons/year)

Oxides	Al_2O_3, ZrO_2, ZrO_2-Y_2O_3, Y_2O_3, TiO_2 SiO_2
Nitrides	AlN, BN, Si_3N_4, TiN, Ti(C,N)
Carbides	B_4C, SiC, TiC
Borid	TiB_2
Others	$MoSi_2$, $BaTiO_3$

➢ Additives in Ceramic Processing (English)

Additive	Function
Ceramic powder	Matrix
Sintering additive	Densification aid
Solvent	Dispersion
Deflocculant	Control of surface charges and pH, dispersion
Dispersing agent	Deagglomeration
Wetting agent	Reduction of the surface tension of the solvent
Antifoaming agent	Avoidance of bubbles
Preservative	Avoidance of bacteria cultures
Binder	Green strength
Plasticizer	Flexibility
Softener	Flexibility
Lubricant	Reduce die and internal friction, mold release

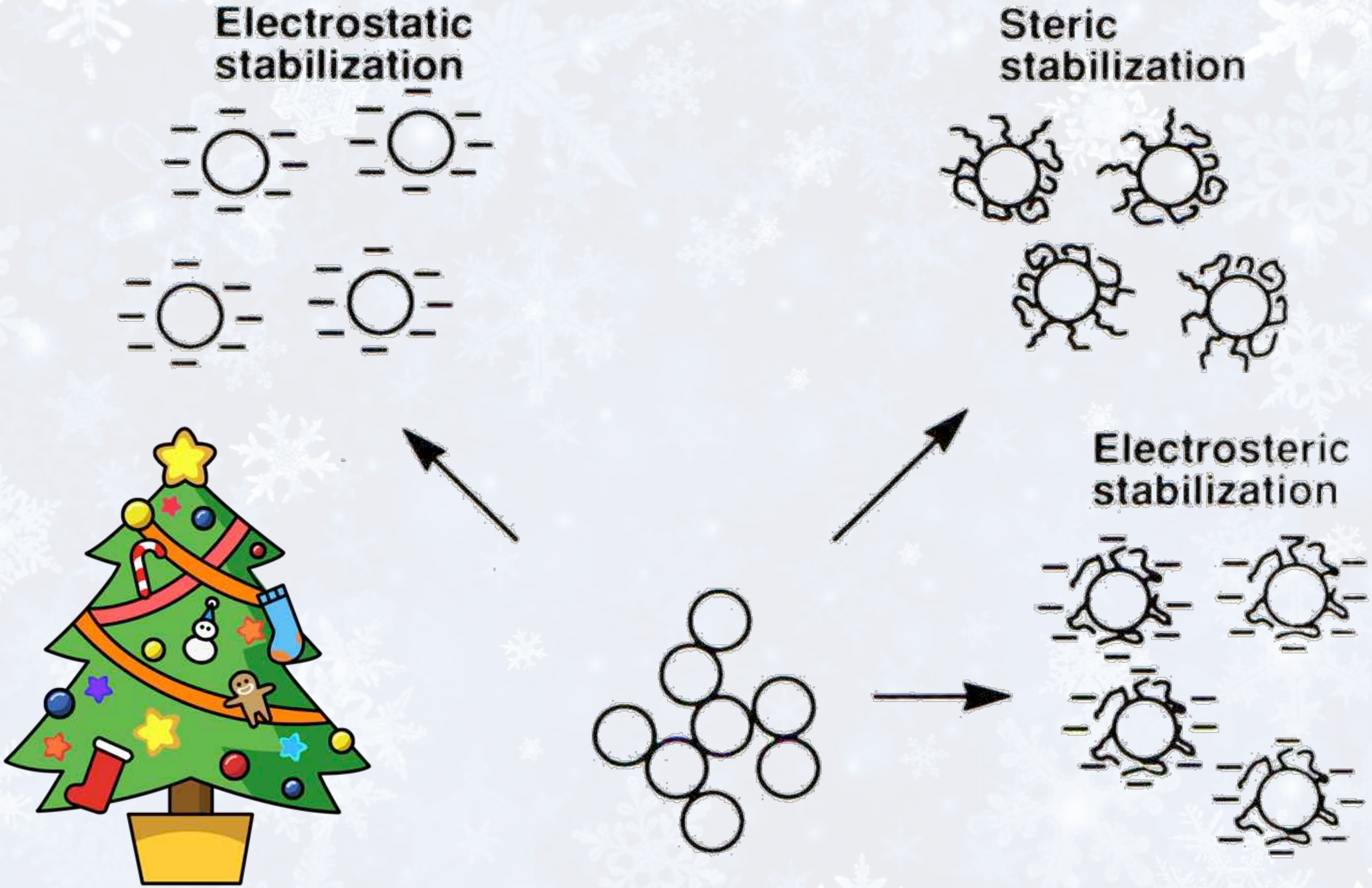
➢ Additives in Ceramic Processing (German)

Komponente	Funktion
Keramisches Pulver	Matrix
Sinteradditiv	Verdichtungshilfsmittel
Lösungsmittel	Dispersion
Verflüssiger	Kontrolle von Oberflächenladungen und pH-Wert, Dispersion
Dispergiermittel	Deagglomeration
Benetzungsmittel	Reduzierung der Oberflächenspannung des Lösungsmittels
Entschäumer	Verhinderung der Blasenbildung
Konservierer	Vermeidung der Enstehung von Bakterienkulturen
Binder	Grünfestigkeit
Plastifizierer	Flexibilität
Weichmacher	Flexibilität
Trenn- und Gleitmittel	Reduzierung von Haftkräften

➢ Types of Additives

Additive	*Function*	*Examples*
Dispersant	Allows the preparation of concentrated suspensions	*Citrate, polyacrylate and phosphate salts (0.05 – 1 wt%)*
Binder	Increases the mechanical strength of green compacts to allow handling before the sintering process	*Polyvinyl alcohol (PVA), polyethylene glycol (PEG), hydroxyethyl cellulose (HEC) and clay particles (1 – 5 wt%)*
Plasticizer	Increase the plasticity of the binder at the pressing temperature	*Water, polyethylene glycol (PEG) and glycerol (0.1 – 1 wt%)*

➢ Concepts of Stabilizing Colloidal Ceramic Particles in Liquids



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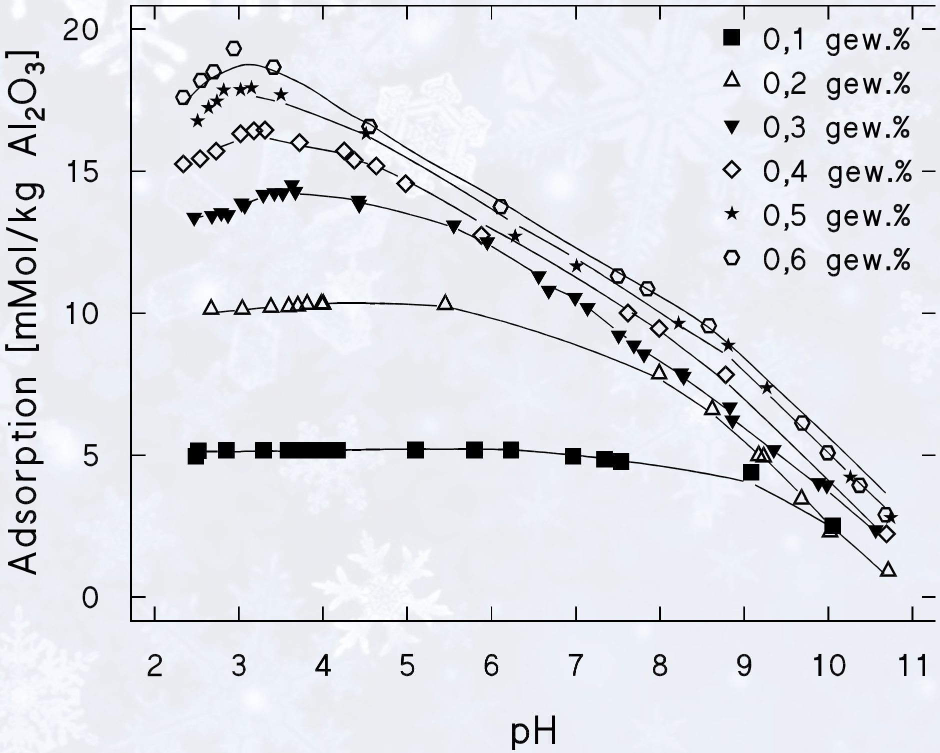
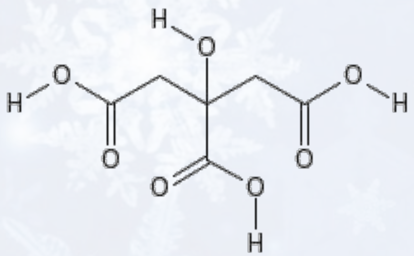
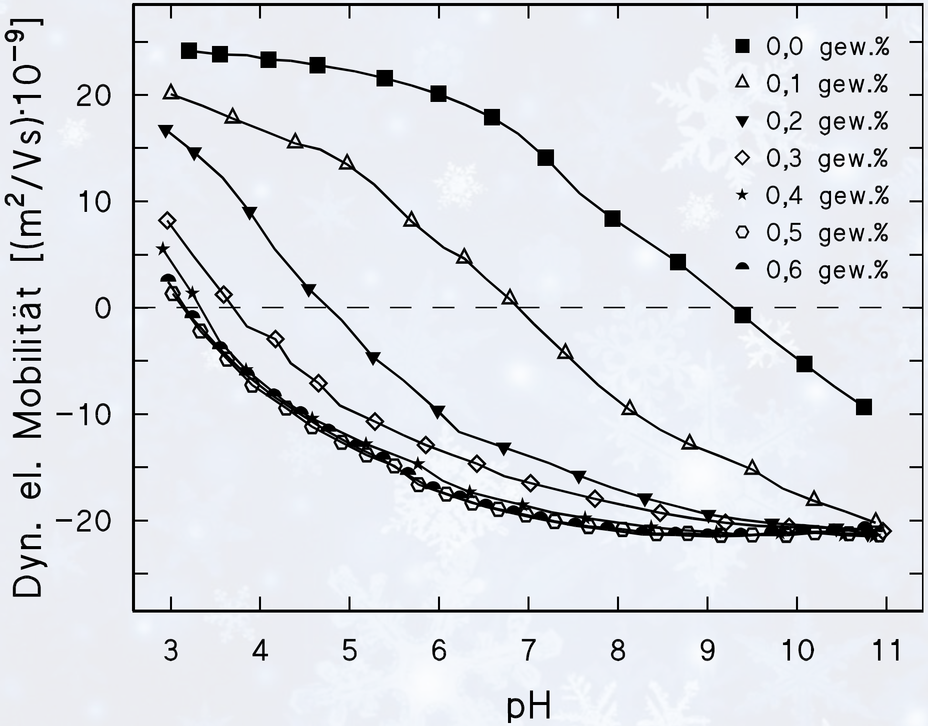
➢ Adsorption behavior of citric acid as f(concentration)



Isothermal Adsorption Curve for Citric Acid on Al_2O_3



Change of Al_2O_3 IEP with increasing Citric Acid amounts



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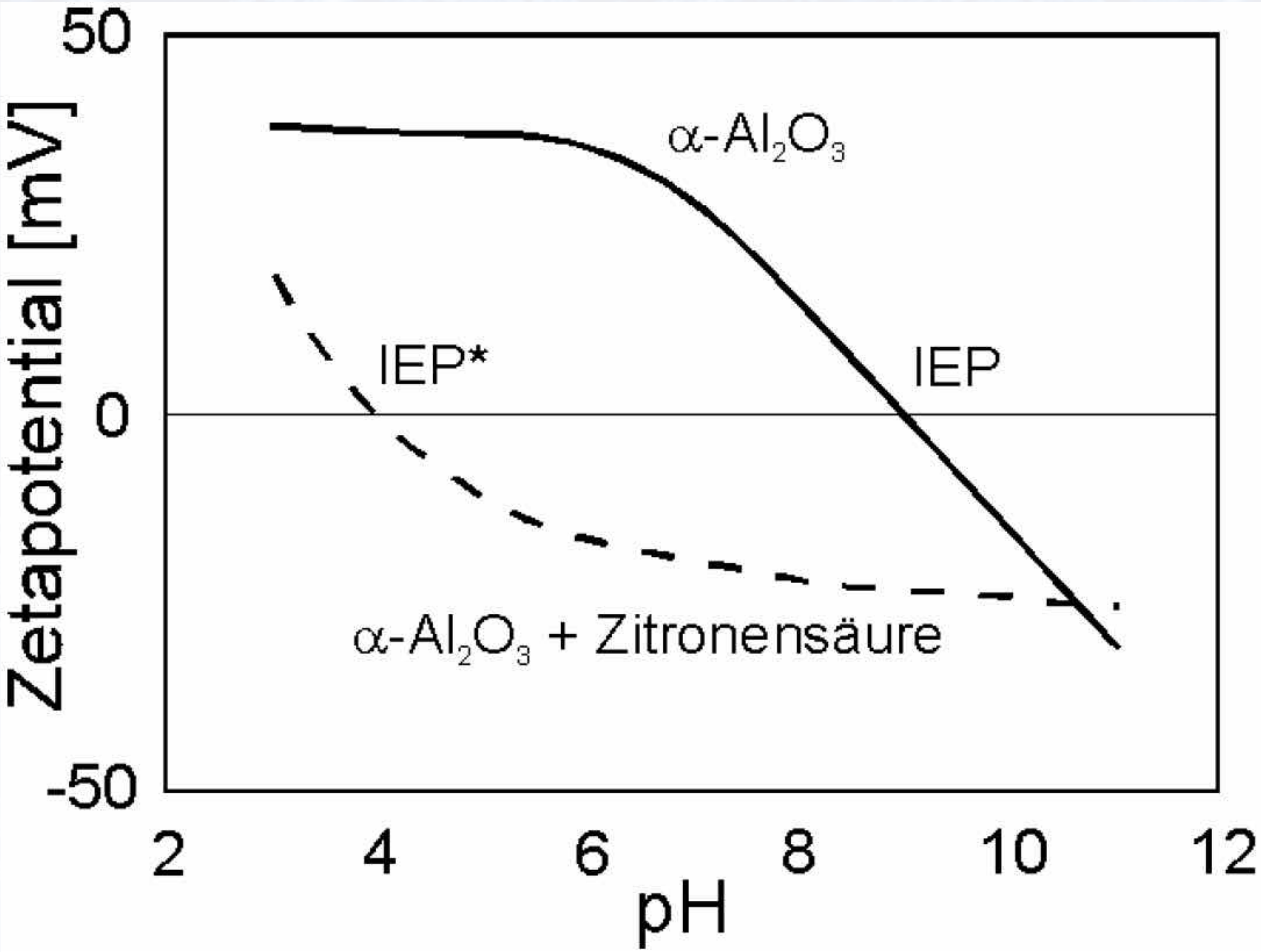
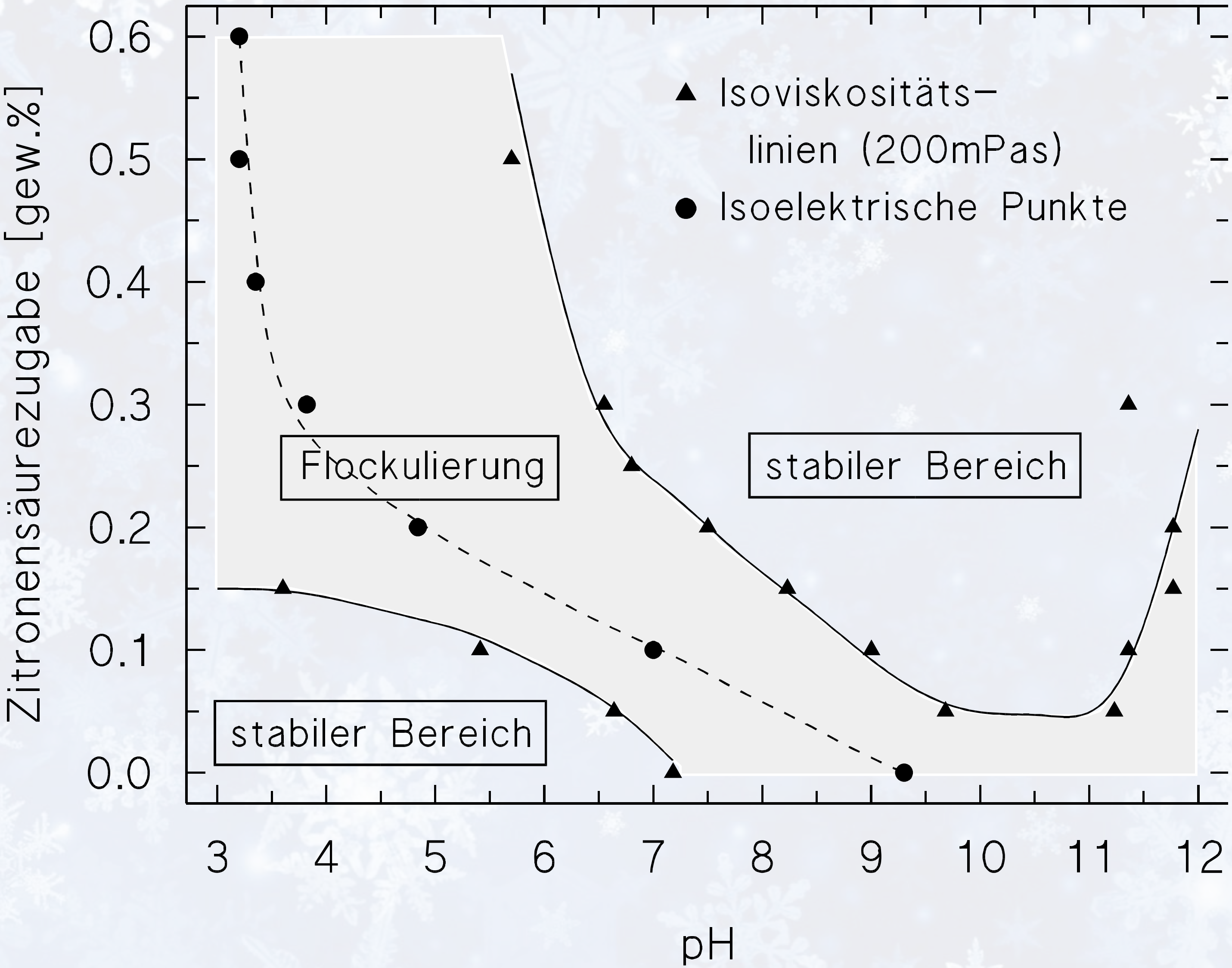
➢ Change of Al_2O_3 IEP by Citric Acid Adsorption



➢ Viscosity as a function of citric acid concentration



Citric acid addition to Al_2O_3 suspension demonstrating the impact on IEP and viscosity.

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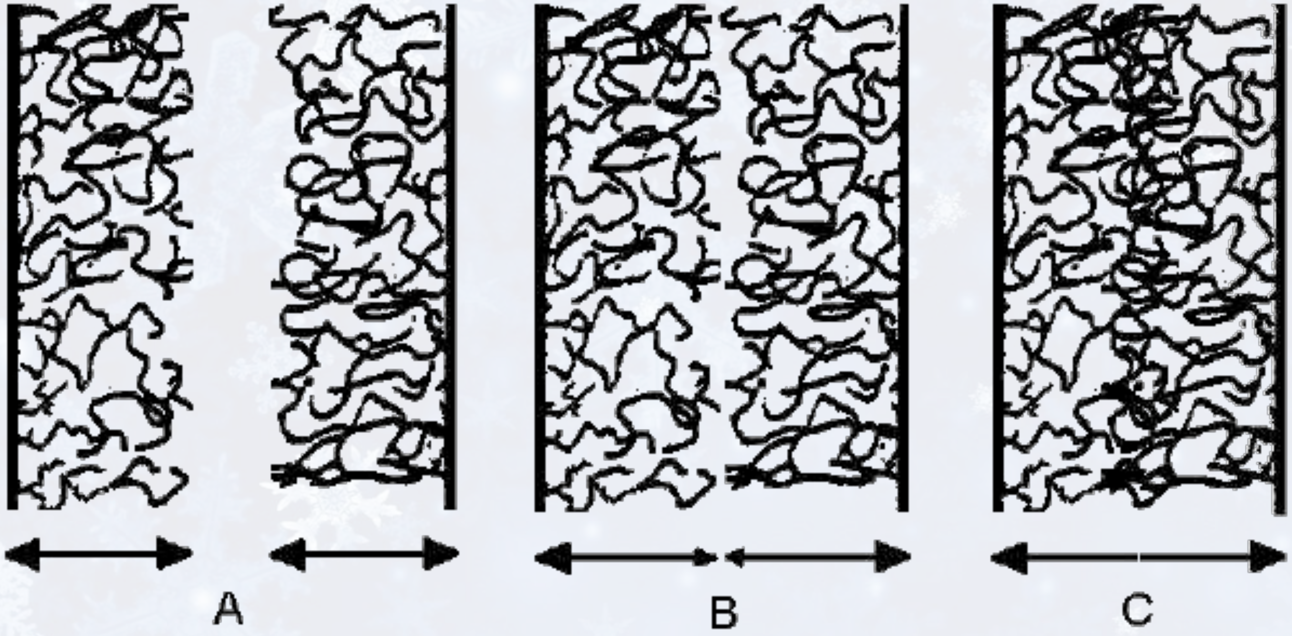
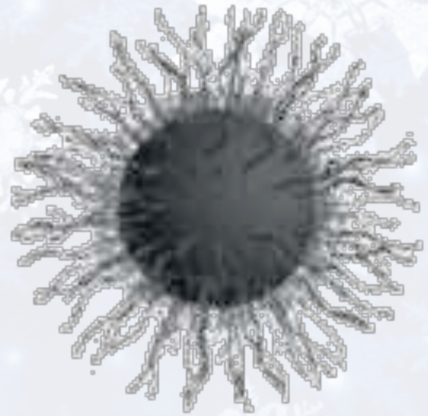
➢ Stabilization of Suspensions via Steric Hindrance





Steric Interactions between Polymer layers adsorbed on Particle Surfaces:

A – No Interaction
B – Small Repulsion
C – Interpenetration: Strong Repulsion

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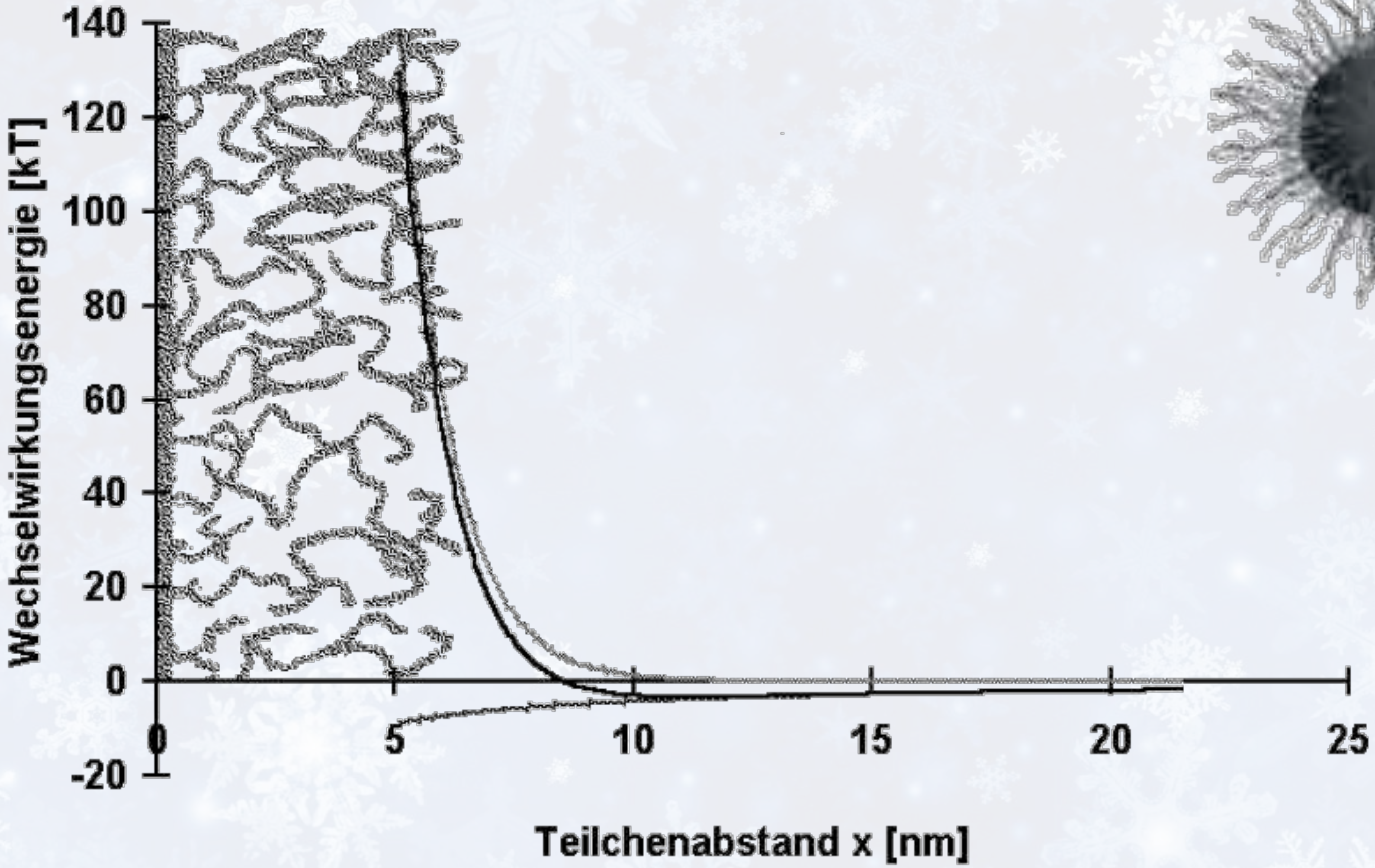
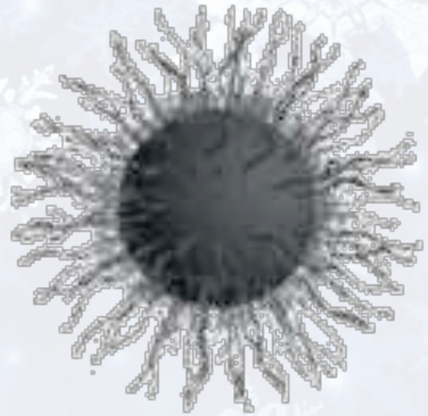
➢ Increase of Repulsion via Steric Hindrance





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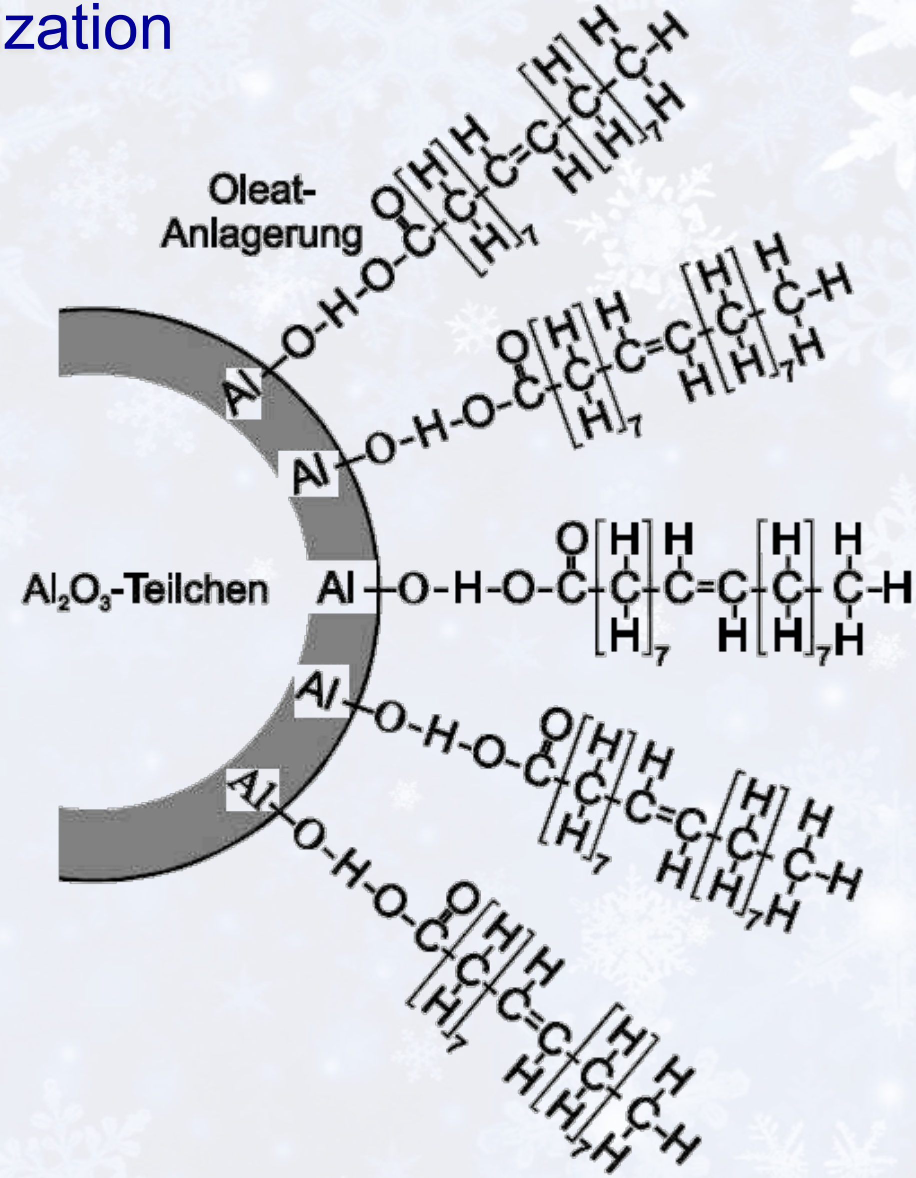
➢ Example: Steric Stabilization

Steric Stabilization of Al_2O_3 by Oleat Molecules in hydrophobic media.



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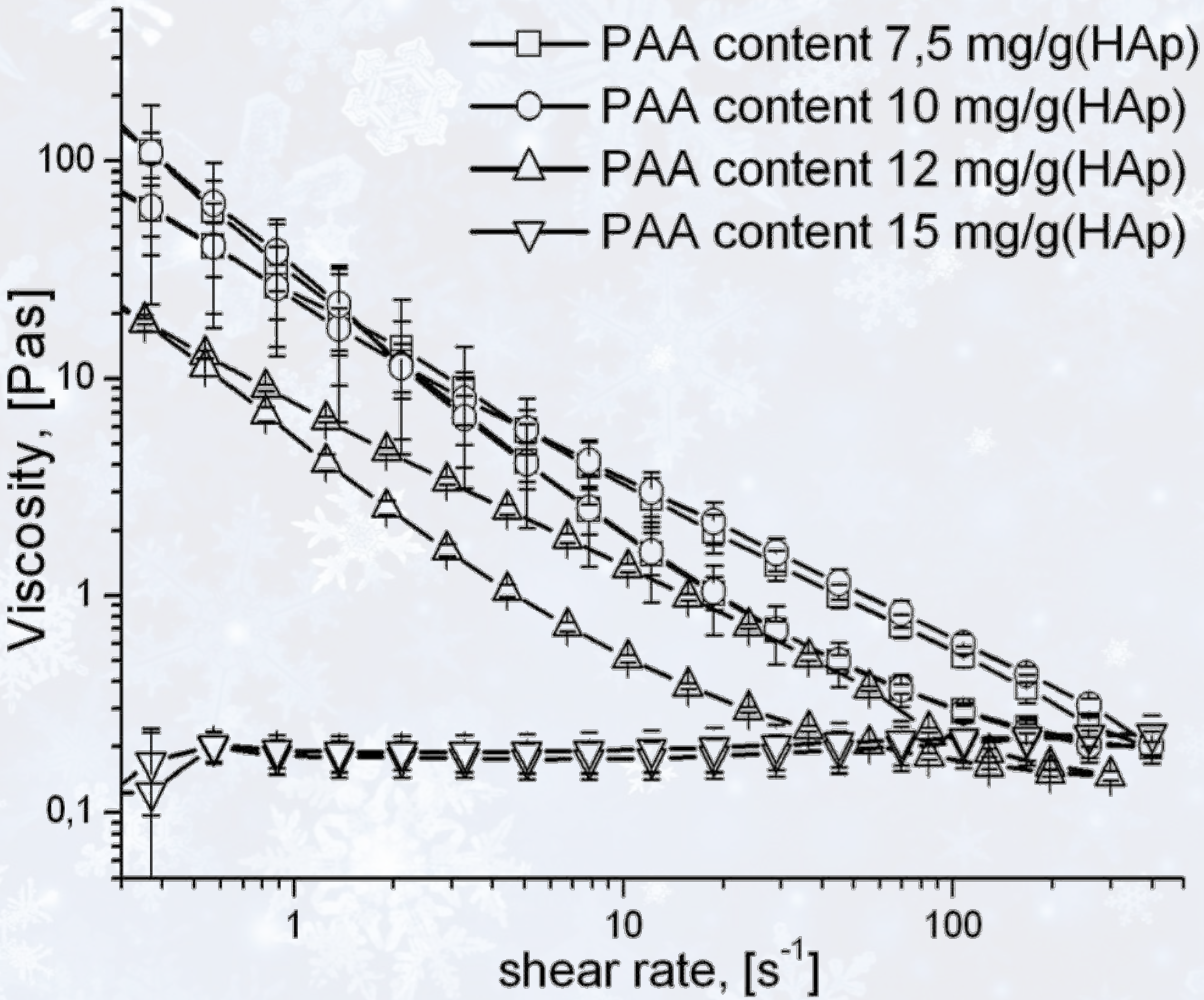
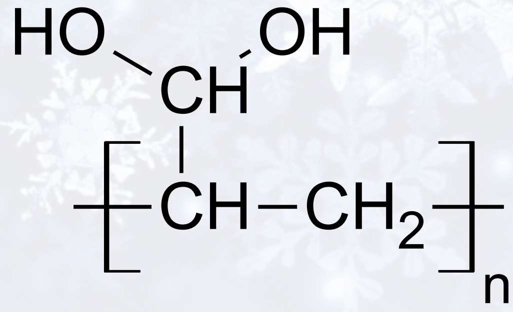
➢ Example: Electrosteric Stabilization of Hydroxyapatite by PAA





Poly Acrylic Acid
(PAA, n>5)

With increasing PAA amounts the viscosity of the hydroxyapatite suspension drops due to electrosteric stabilization.

➢ Examples Additives in Aqueous and Non-Aqueous Media

Solvents	Binders	Plasticizers	Deflocculants	Wetting agents
		Non-aqueous:		
Acetone Ethyl alcohol Benzole Bromochloro- methane Butanol Diacetone Ethanol Isopropanol Methylic isobutylketone Toluol Trichlorethylene Xylol	Celluloseacetate Butyrate resign Nitrocellulose Petroleum resign Polyethylene Polyacrylate ester Polymethyl- methacrylate Polyvinyl-alcohol Polyvinyl-butyral resign Polyvinyl-chloride	Butylbenzyl- phtalate Butylstearate Dibutylphtalate Dimethylphtalate Methylabietate Mixed Phtalate esters (Hexal-, octyldecyl- alcohol) Polyethylenglycol Polyalkylenglycol Polyalkylenglycol derivates (Triethylen- glycolhexoat) Trikresyl- phosphate	Fatty acids (Glyceryl-tri-oleate) Natural Fish oils (Menhaden) Synthetics (Benzene sulfonic acids)	Alkylarylpolyet her alcohol Polyethylengly colethylether Athylphenylgly col Polyoxyethyle nacetate Polyoxethylen- esther
		Aqueous:		
Water (with antifoaming agents based on resigns)	Acrylic polymer Acrylic polymer emulsion Ethylenoxide polymer Hydroxyethylen- cellulose Methylcellulose Polyvinylalcohol TRIS. Isocyaminate Resign based sliding additives	Butylbenzyl- phtalate Ethyltoluol- sulfonamide Glycerine Polyalcylenglycol Triethylenglycol Tri-N-butyl- phosphate	Complex vitreous phosphates Condensed arylic sulfoic acid Natural sodium salt	Non-ionic octylphenoxy- ethanol

➢ Types of Organic Surfactants (attention: bad nomenclature)

organic deflocculants

anionic

Molecules (M<500 g/mol)
- **aliphatic carboxylic acids** (citric acid)
- **aromatic carboxylic acids** (mellitic acid)
- **aliphatic sulfonic acids** (Tiron)

Phosphonic acids

Polymers
- **Polyacrylic acid** (Darvan 7)
- **Polymethacrylic acid** (Darvin C)
- **Biopolymers (**alginic acid)

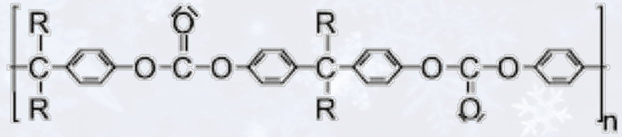
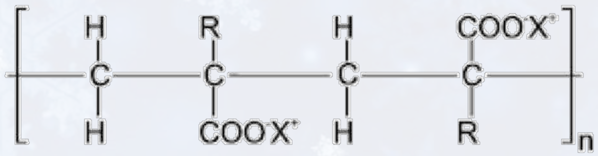
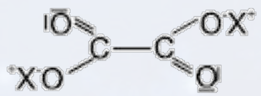
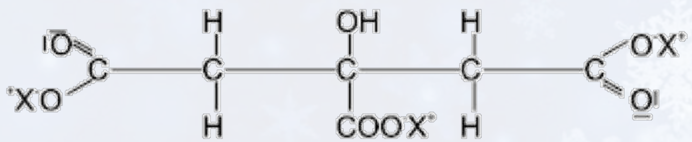
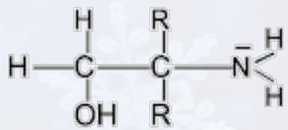
Phosponic acids

cationic

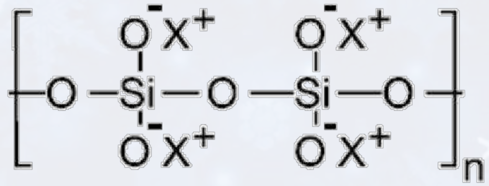
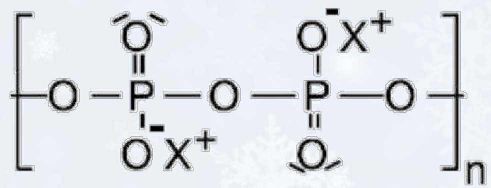
Molecules (M<500 g/mol)
- **quarternary alkyl-ammonium-chlorides** (hexadecyltrimethyl-ammoniumchloride)
- **Aminoxides** (Tetradecyldimethylaminoxides)

Polymers
- **Polyethylenimine**
- **Polydiallyldialkyl-ammoniumchloride**

➢ Overview of some Organic Additives

Organische Dispergiermittel	X=Na, K, NH_4; R=C_kH_{2k+1} mit k=0,1,2,3,...	
Polycarbonate		steric
Polyacrylate (*k=0*) und -methacrylate (*k=1,2,3,...*)		electrosteric
Oxalate		electrostatic
Citrate		electrostatic
Alkanolamine (Aminoalkohole)		electrostatic

➢ Overview of some Inorganic Additives

Anorganische Dispergiermittel	X=Na, K, NH_4
Polysilicate	
Polyphosphate	

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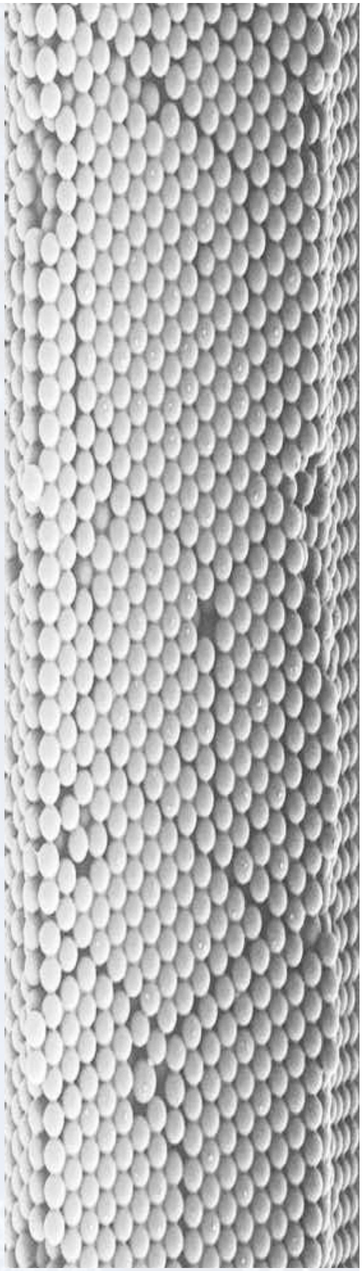
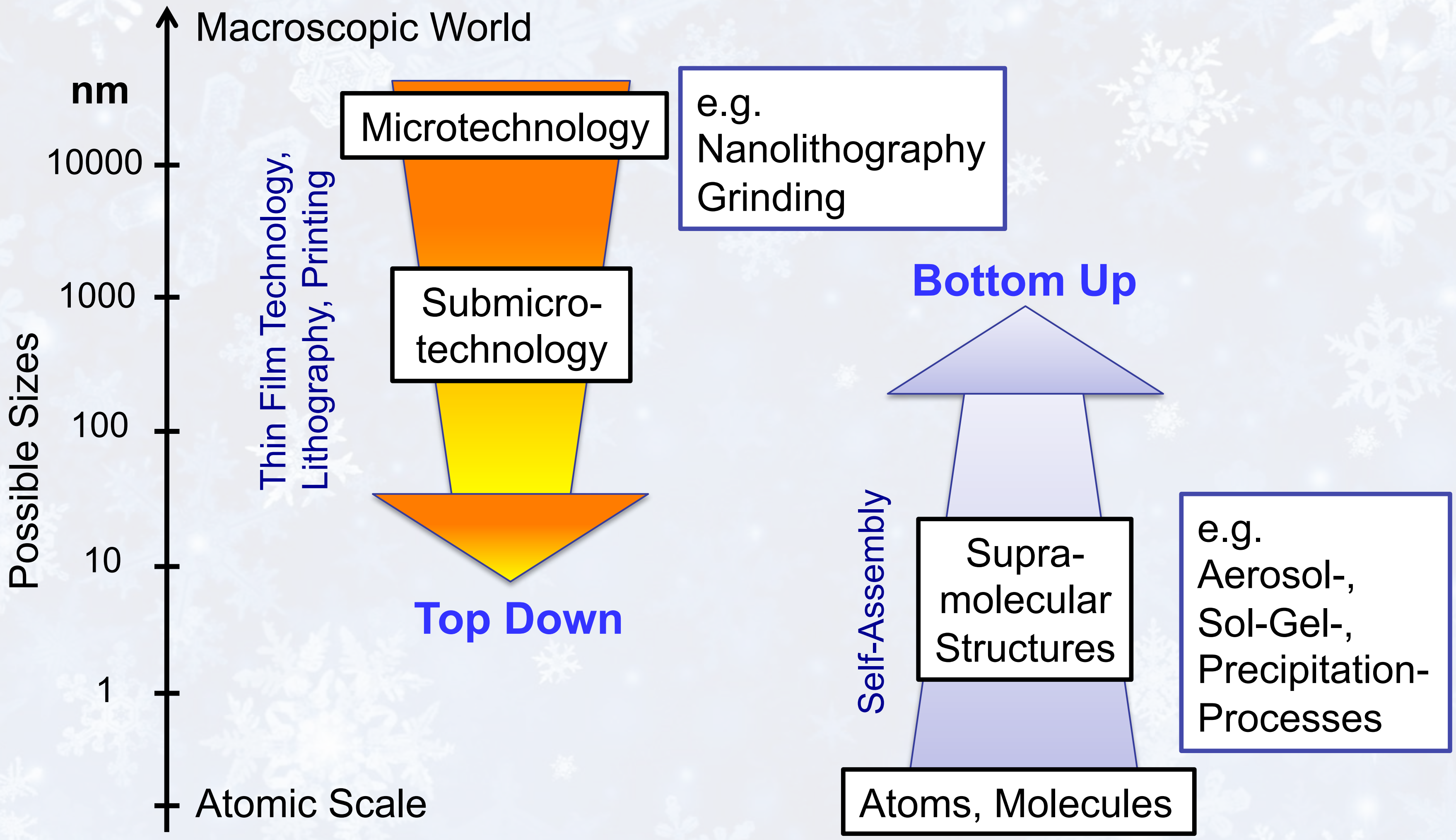
➤ Course Outline

- **Physical/Mechanical Preparation Methods**
- **Solid State Reactions**
- **Gas-Solid Reactions**
- **Gas Phase Reactions**
- **Precipitation from Solutions**

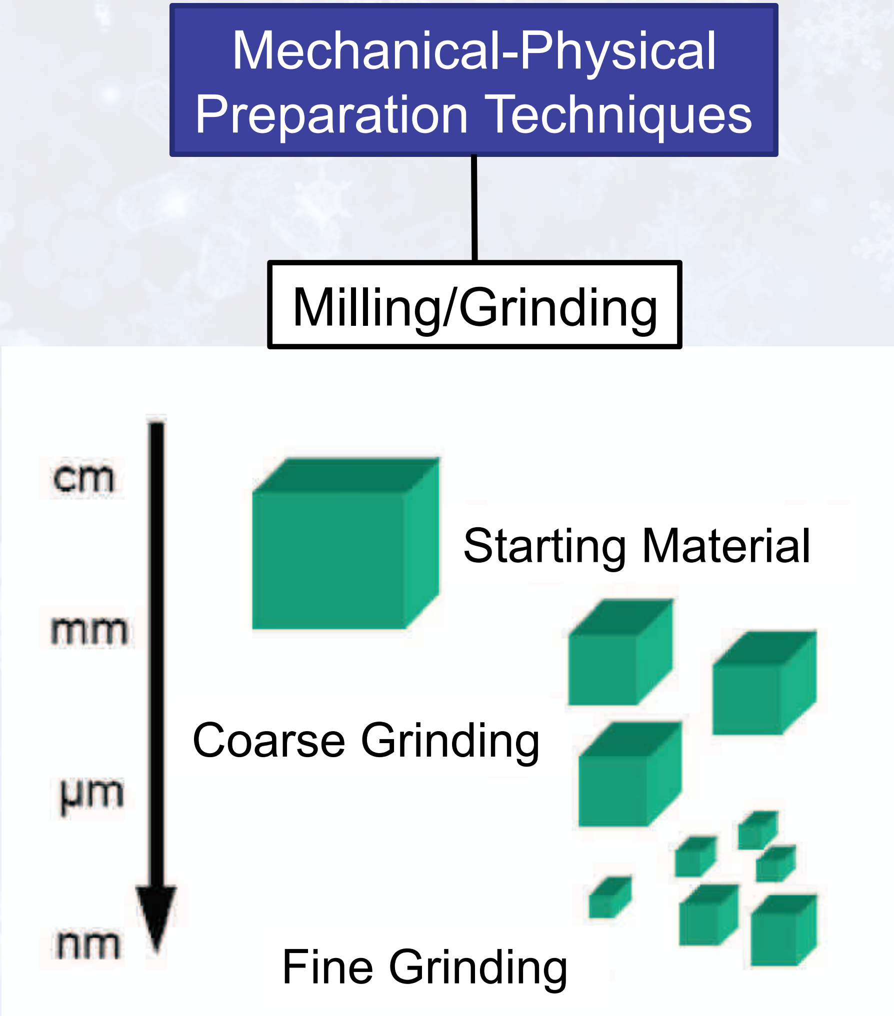


➢ Nanoparticle Synthesis: Principles



http://epub.oeaw.ac.at/ita/nanotrust-dossiers/dossier006.pdf

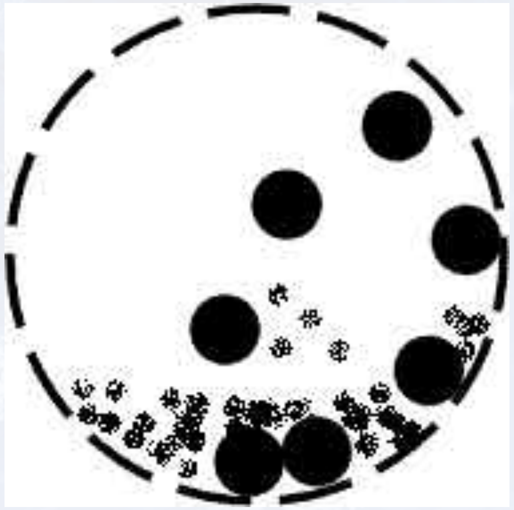
➢ Mechanical Attrition: Milling/Grinding



Top-Down-Process

➢ Ball Mill

- Particles sizes > 5 nm
- Polydisperse

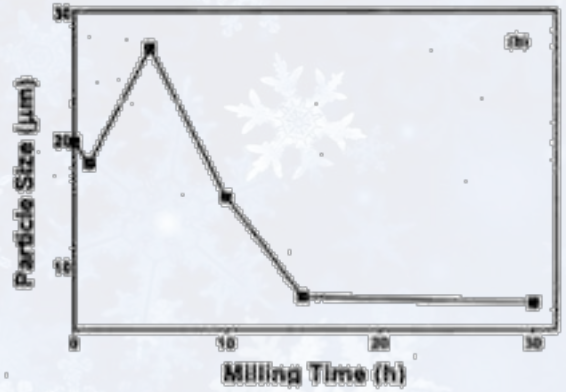


Problem: Contamination

- impurities in starting powders,
- vials and grinding media,
- milling atmosphere,
- control agents added to the powders.

➢ Milling

(a)



(b)

Change of average particle size as a function of milling time for MA Fe-20at.%Co powders by (a) fixed r.p.m. operation and (b) cyclic operation. Y. D. Kim et al., Mater. Sci. Eng. A 291, 17 (2000).

Grind Limit:

- Increasing resistance to fracture.
- Increasing cohesion between particles, with decreasing particle size causing agglomeration.
- Excessive clearance between impacting surfaces.
- Coating of the grinding medium by fine particles that cushion the microbed of particles from impact.
- Surface roughness of the grinding medium. Bridging of large particles to protect smaller particles in the microbed.
- Increasing apparent viscosity as particle size decreases.

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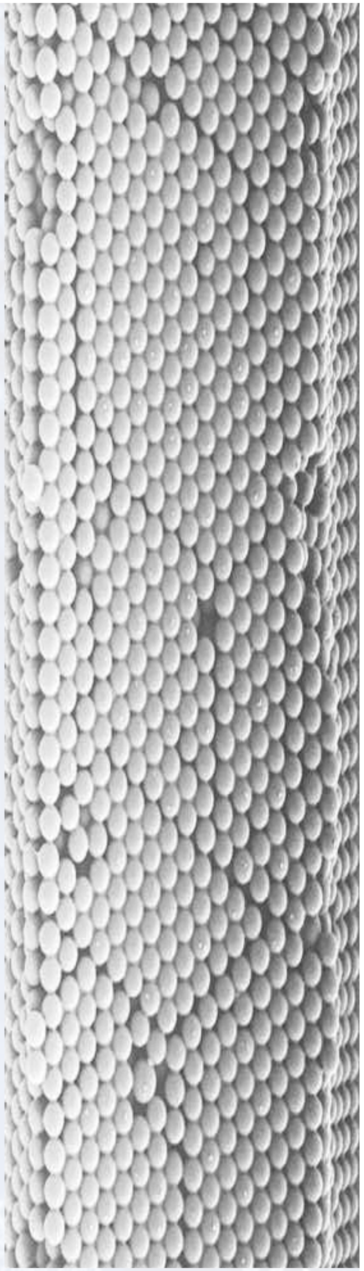
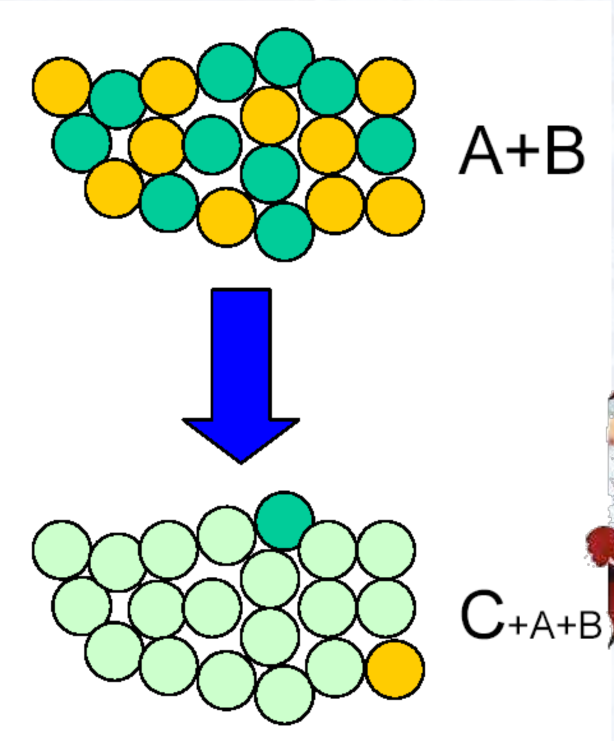


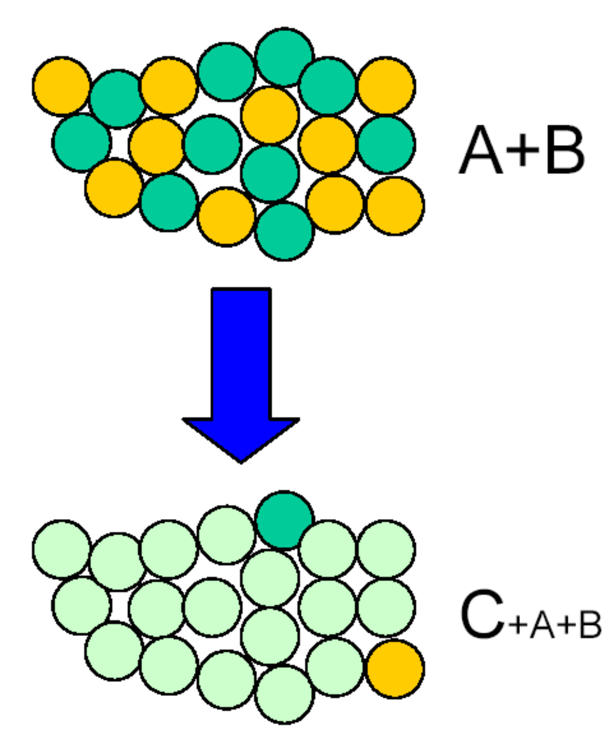
➢ Solid State Reactions

a.k.a.: dry media reactions

- Diffusion controlled
- Solventless
- Heat dependent
- Slow (kinetic constraints)
- Mixing is critical



➢ Solid State Reaction Example 1



Mixing of Powder, Calcination at temperatures typically over 1000 °C.

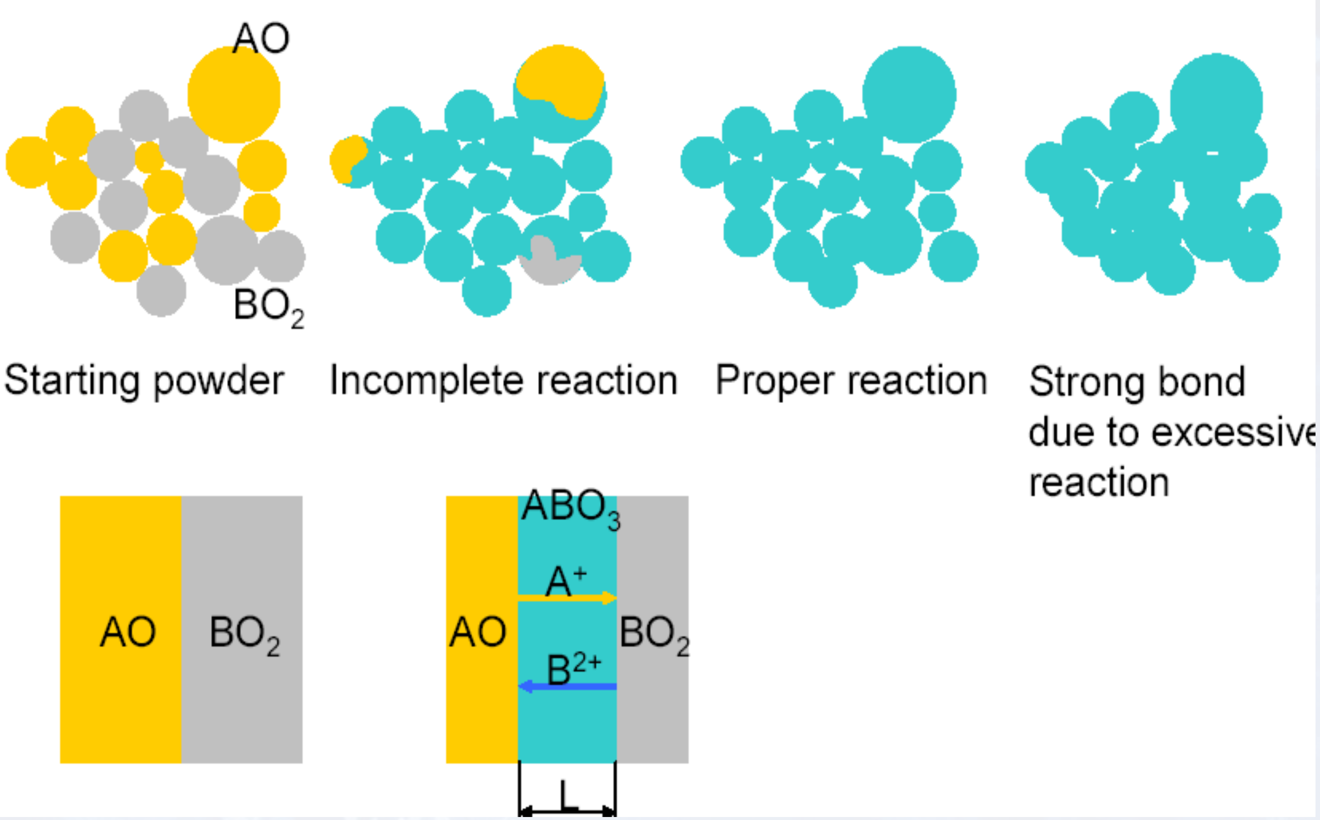
Example Chemical Equation:

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$$

Bariumtitanate $BaTiO_3$:
Very important for capacitors and piezoelectric ceramics

[*Graule, T. J., Gauckler L. J., ETH Zürich*]

➢ Optimization of the Solid State Reaction



Reaction depends on

- Compaction or filling state as reaction occurs at contact points between two phases

- Temperature diffusion coefficient = f(T); $D = D_o \exp^{(-Q/RT)}$

How to improve solid-state reactions?

- smaller particle size
- good mixing
- narrow particle-size distribution
- good compaction between particles
- reaction at relatively high temperature
- repetition of milling/mixing steps

[*Graule, T. J., Gauckler L. J., ETH Zürich*]

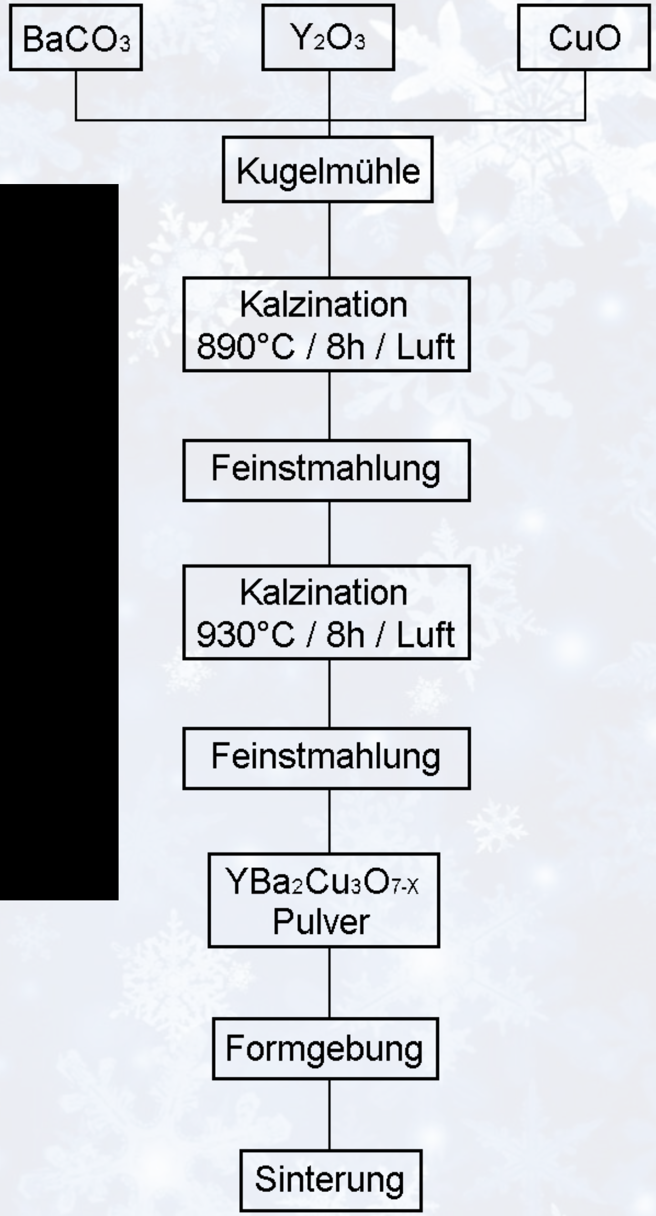
➢ Solid State Reaction Example 2

http://www.youtube.com/watch?v=94-Z2QgHI-s&feature=related

Superconducters: the Meissner effect

Synthesis of a high temperature superconductor (YBCO)

$$Y_2O_3 + BaCO_3 + CuO \rightarrow YBa_2Cu_3O_{7-x} + CO_2$$



[*Graule, T. J., Gauckler L. J., ETH Zürich*]

➢ Summary Solid State Powder Synthesis

Advantages

- Simple apparatus (ball milling, rotary evaporator, simple furnace)
- Inexpensive precursors and processes (cost-effective)
- Wide variety of element combinations (acetates or nitrates as precursor materials)

Disadvantages

- Wide particle-size distribution
- Coarse particle size (≥ 1 µm; typically not for nanopowder synth.)
- Contamination during mixing and milling
- High temperatures required for reaction (especially when the particle size is large or when the mixing is insufficient)
- Compositional fluctuation due to incomplete reactions
- Difficult to control the particle shape

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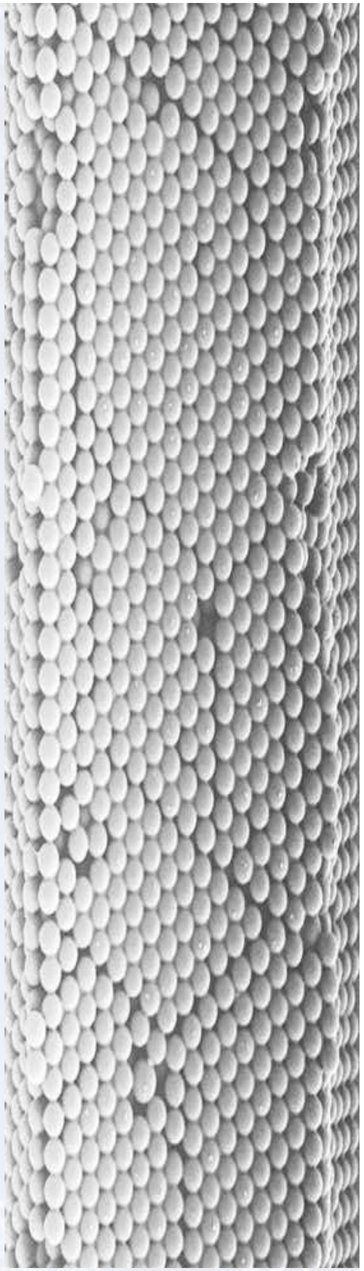
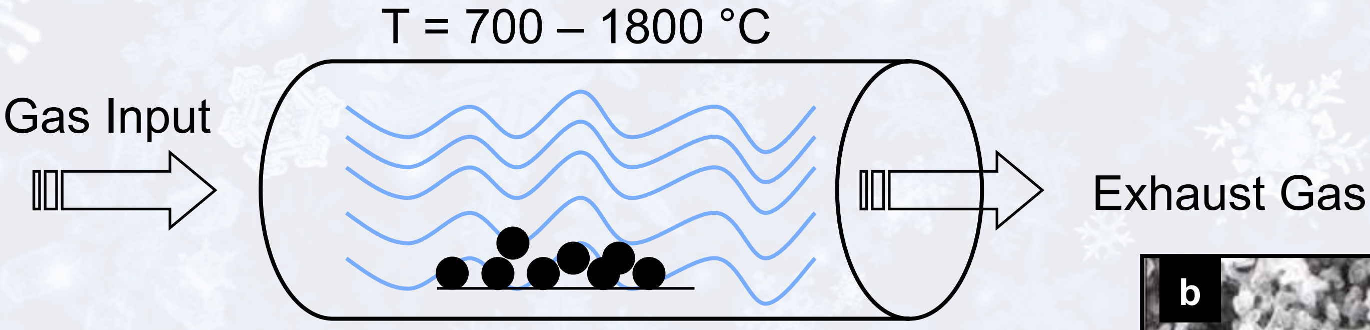


➤ Gas-Solid Reactions



Monolithic or Powder

↓

Products

↓

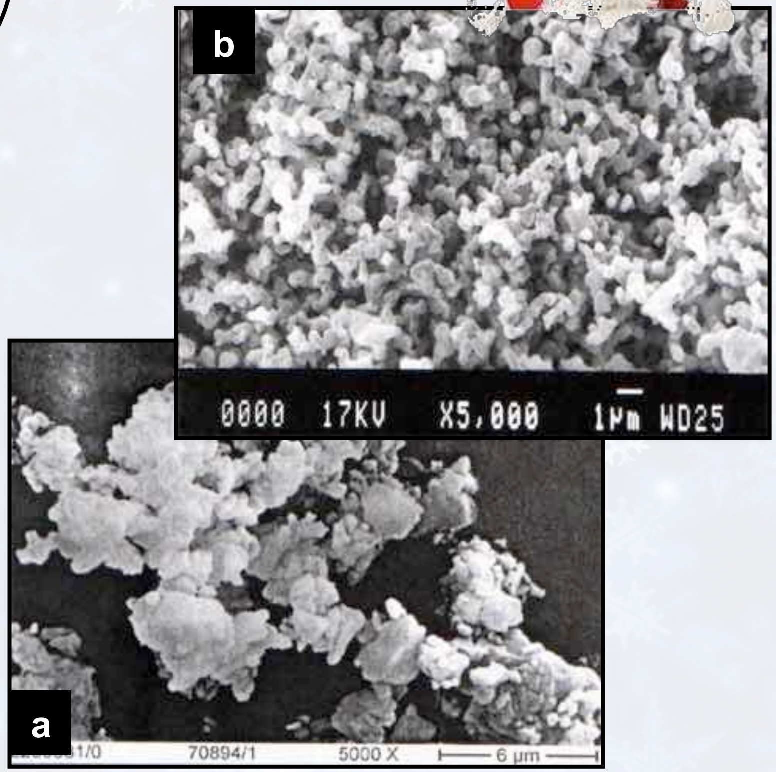
Grinding

Examples

a) $2\ Al + N_2 \rightarrow AlN$ (T > 700 °C)

b) $Al_2O_3 + 3\ C + N_2 \rightarrow 2\ AlN + 3\ CO$ (T > 1550 °C)

c) $Si + 2N_2 \rightarrow Si_3N_4$ (T> 1100 °C)



AlN Particles

Disadvantage

In the case of monolithical materials: grinding necessary, hence relatively coarse particles.

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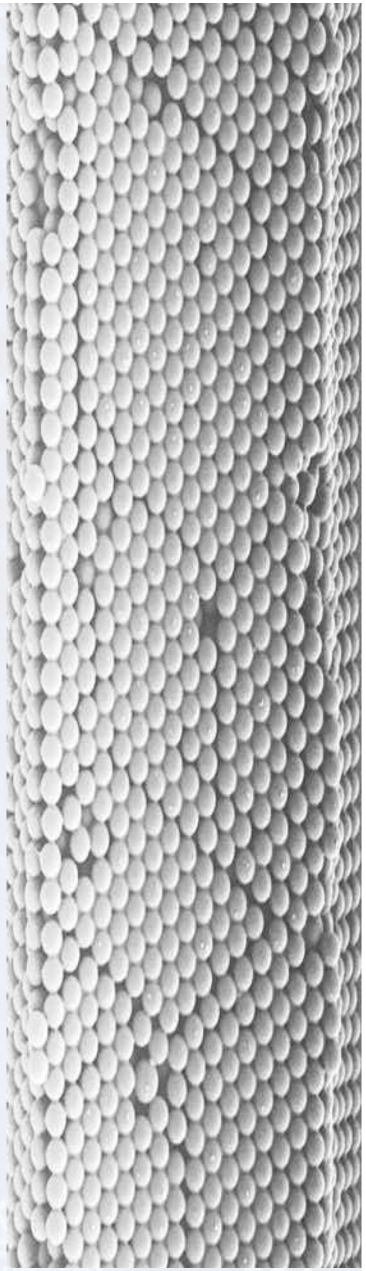
- **Gas Phase Reactions**
- Precipitation from Solutions



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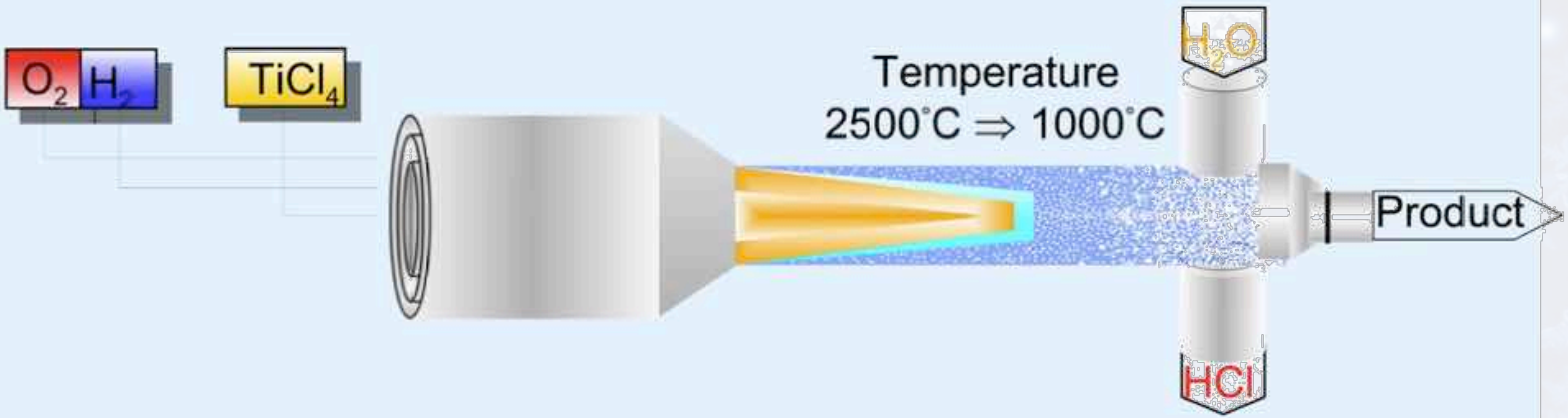
➢ Gas Phase Reactions: Flame Pyrolysis

[Evonik]



$SiCl_4$	⟶	AEROSIL® 200, 300, etc.
Various Metal Halides: $TiCl_4$	⟶	AEROXIDE® P25
$AlCl_3$	⟶	AEROXIDE® Alu C

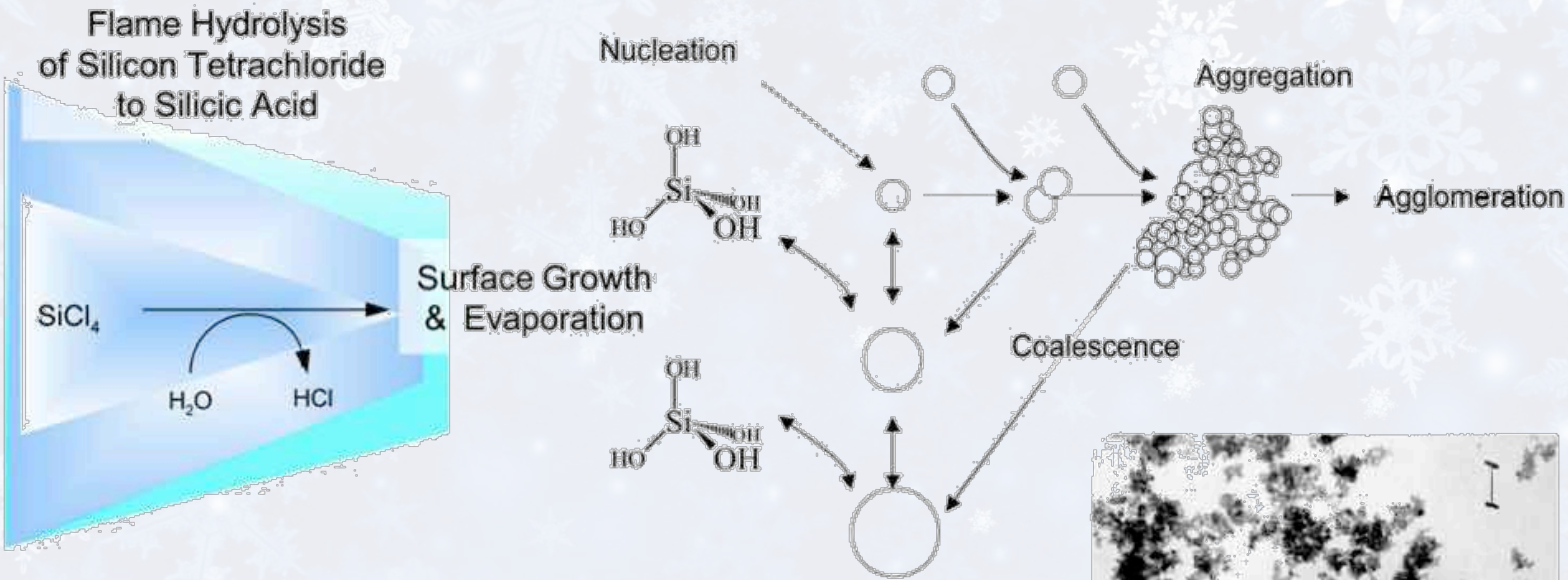
Examples

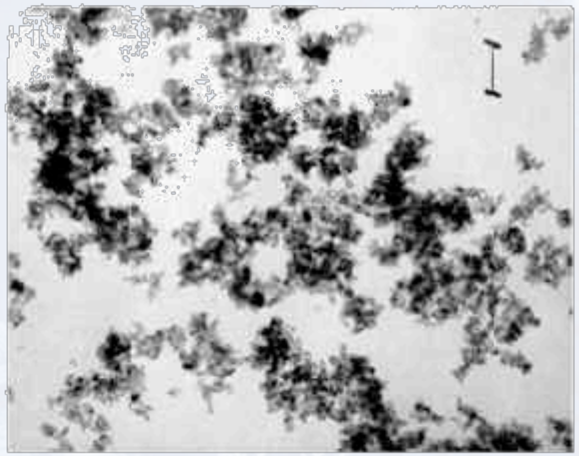
$CH_3SiH_3 \rightarrow SiC + 3\,H_2$

$SiCl_4 + 2\,H_2 + 2\,O_2 \rightarrow SiO_2 + 4\,HCl$ (e. g. Aerosil)

$TiCl_4 + 2\,H_2 + O_2 \rightarrow TiO_2 + 4\,HCl$ (e. g. Titanweiss)

➢ Flame Pyrolysis: Particle Formation





Aggregation represents fusing or sintering including coalescence into a larger particle

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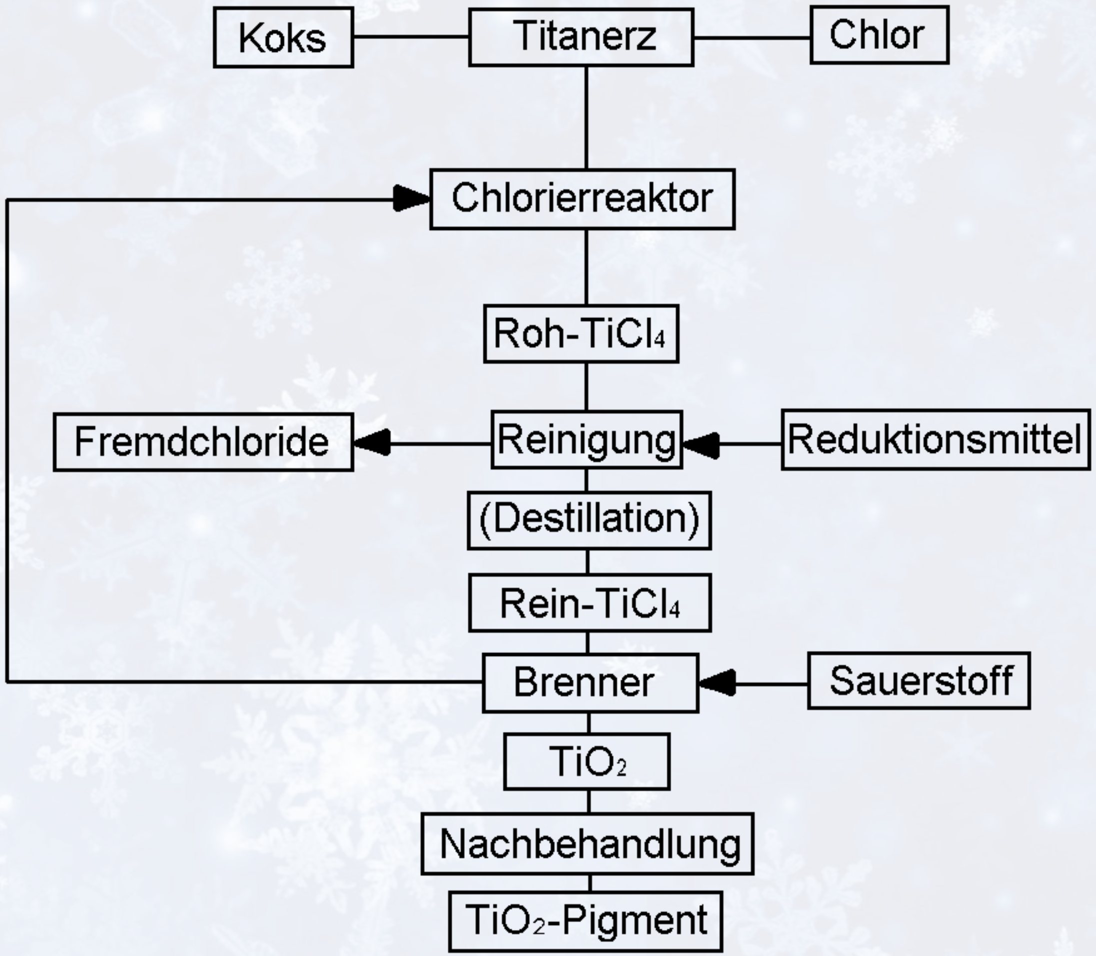
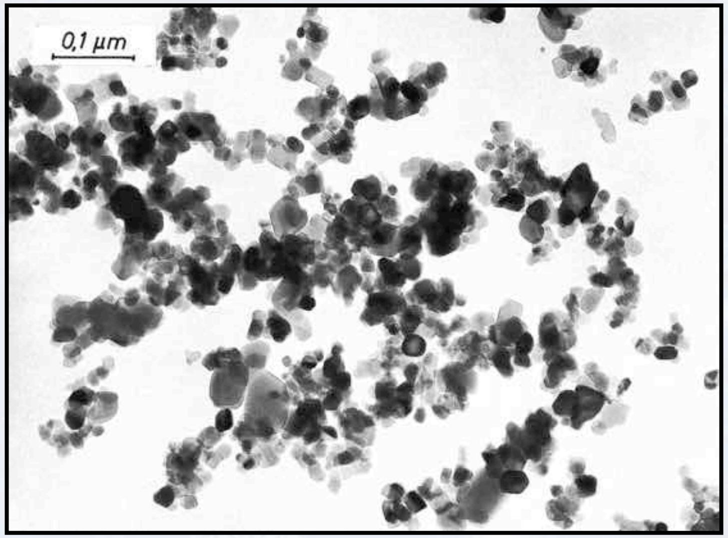
➢ Decomposition Reaction: Production of TiO_2

Highly used process („Titanweiss“), millions of tons / year:

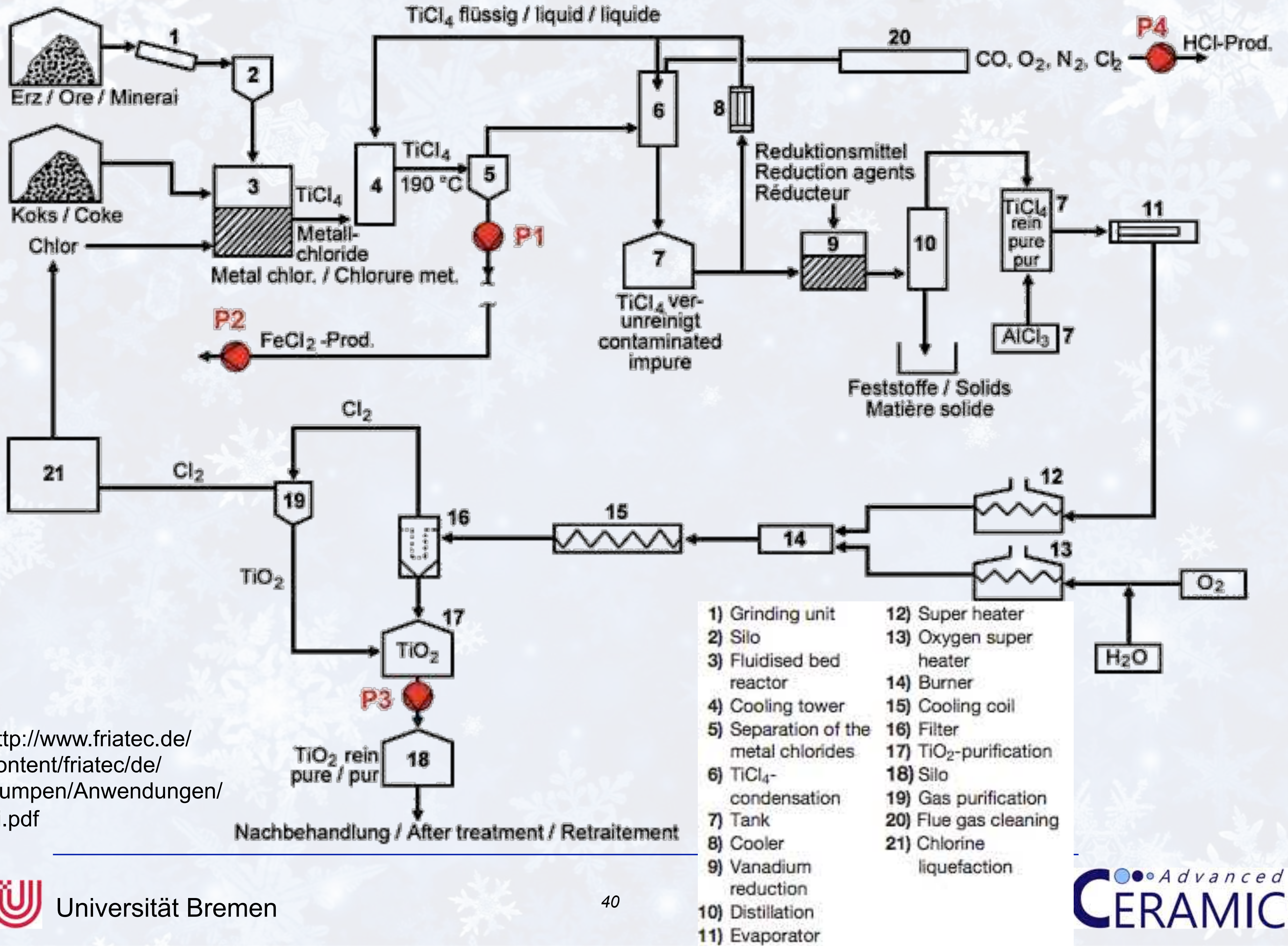
$TiCl_4 + 2\,H_2 + O_2 \rightarrow TiO_2 + 4\,HCl$





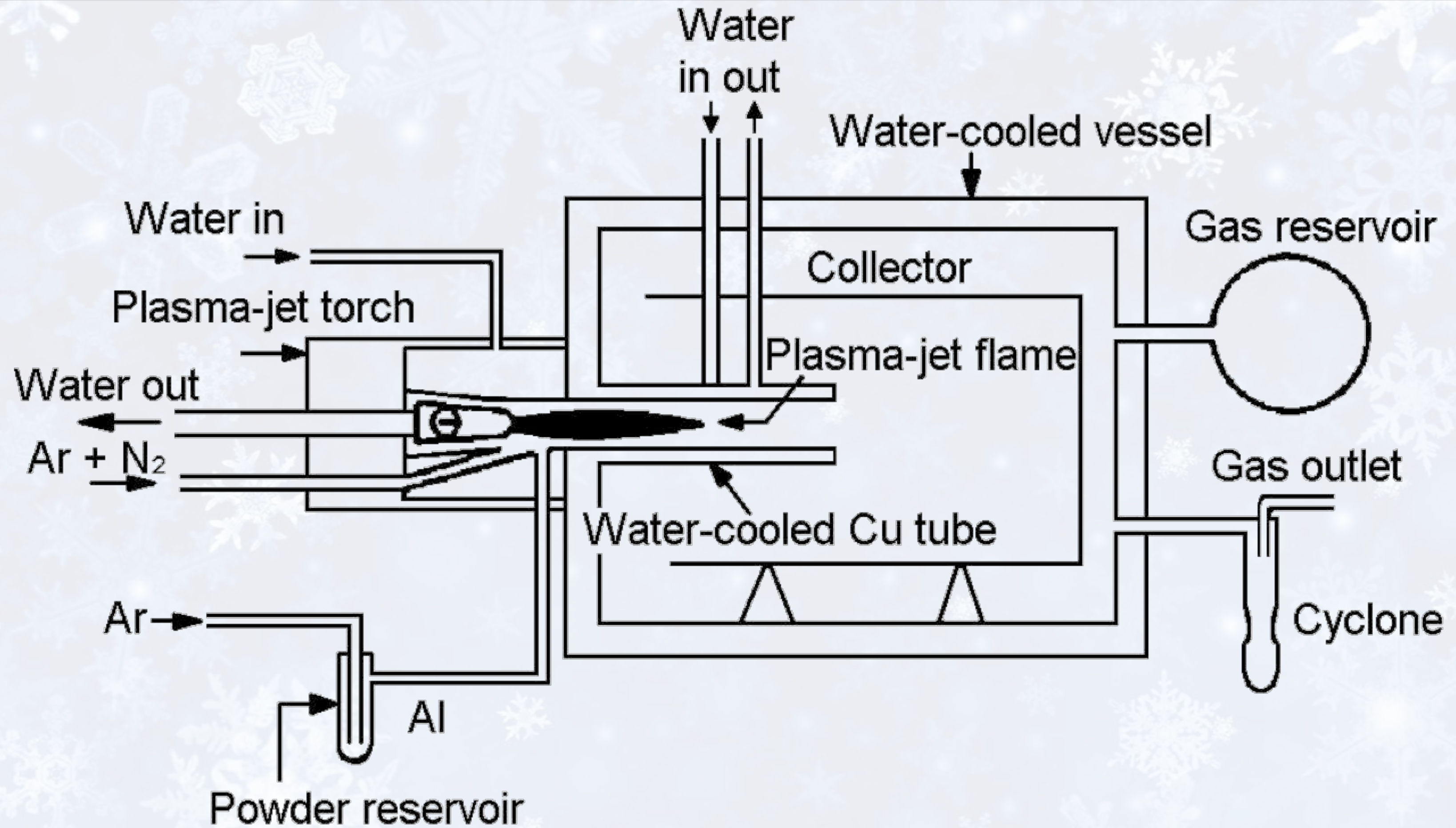
TEM image of TiO_2

➢ Decomposition Reaction: Production of TiO_2



http://www.friatec.de/content/friatec/de/Pumpen/Anwendungen/Ti.pdf

➤ Gas Phase Reactions: Plasma Process

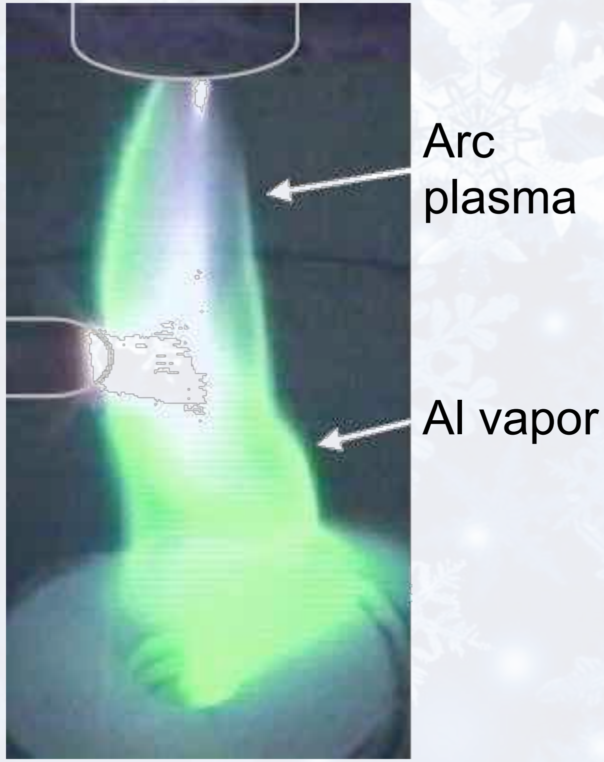


Plasma synthesis of AlN: 2 Al + N_2 ➔ 2 AlN

[*Watanabe, Proc. Int. Powder Metall. Conf., Düsseldorf 1986*]

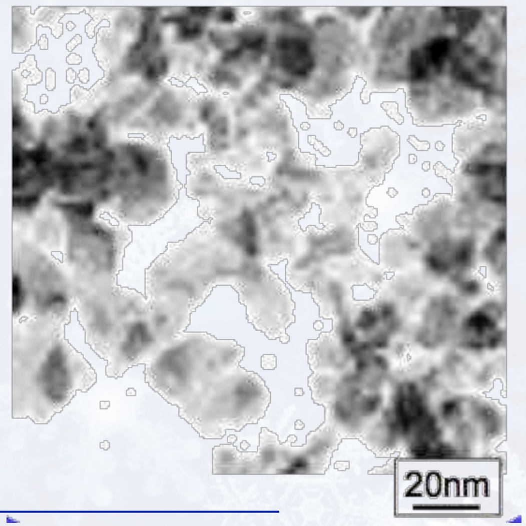
➢ Gas Phase Reactions: Plasma Process

- Plasma generated by arc discharge burner or inductively heated burner
- Ionised gas with temperatures up to 15000°C
- Substances with high volatilization temperature easily transferred to liquid or gas
- Precursor metals vaporized in plasma react with oxygen or nitrogen



Powders that are produced via the Plasma Process

Oxides: Al_2O_3, SiO_2
Nitrides: AlN, Si_3N_4
Carbides: WC, SiC
Borides: TiB_2



Depending on processing conditions particles with 10 - 100 nm are produced with an output of 1,5 kg/h.

➢ Summary Gas Phase Reactions

Advantages

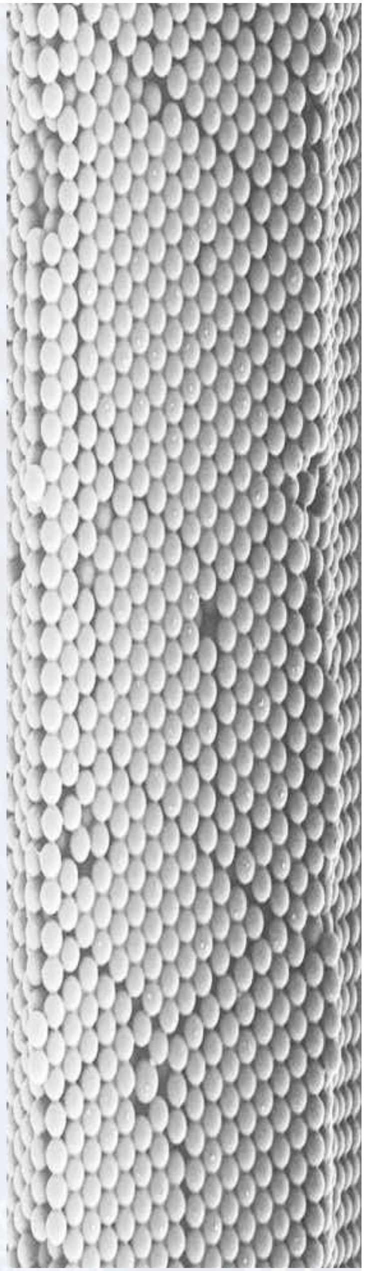
- Submicron or even nanosized particles
- High specific surface area (up to several 100 m^2/g)
- Frequently spherical particles
- Low impurity content (especially metal contamination)
- Homogeneous distribution of sintering additives

Disadvantages

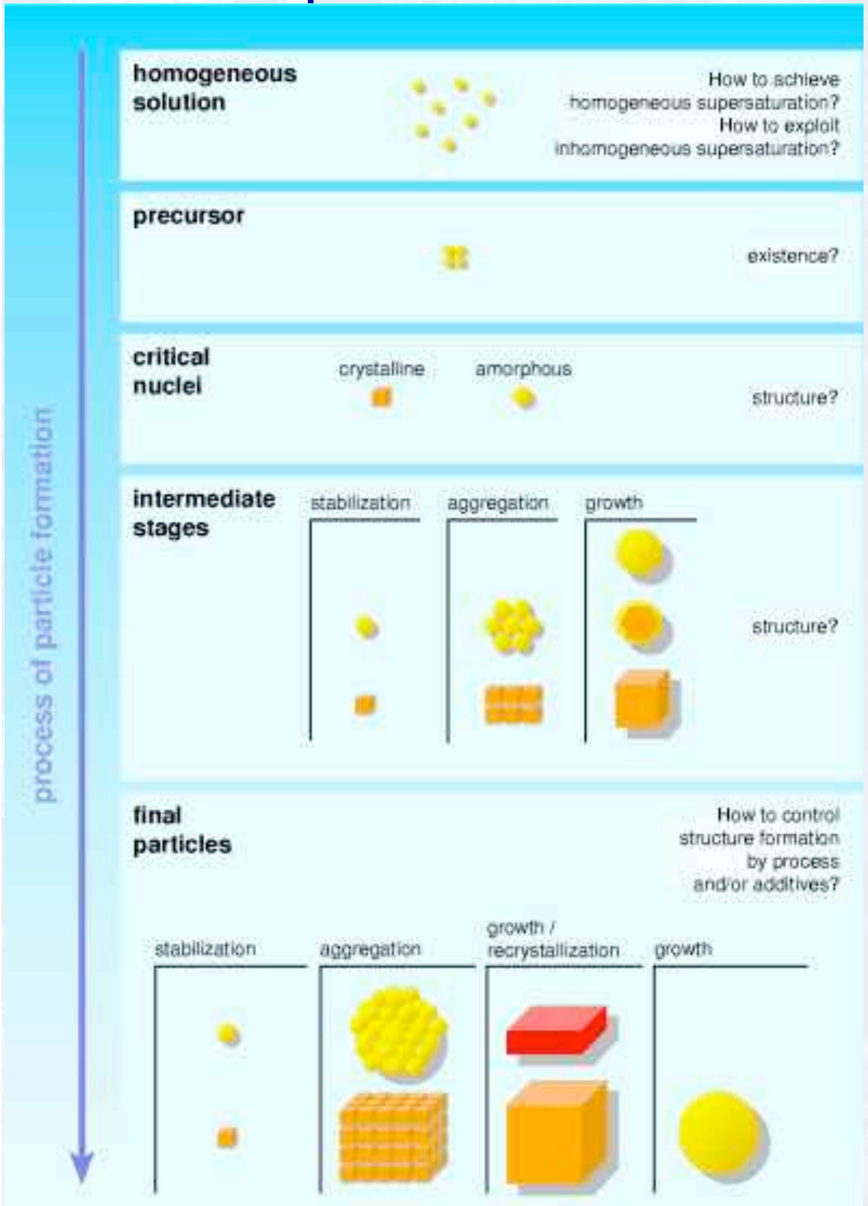
- High energy consumption
- Bad post-processability of powders due to high specific surface area
- Precursors can be expensive
- In general a very expensive production process

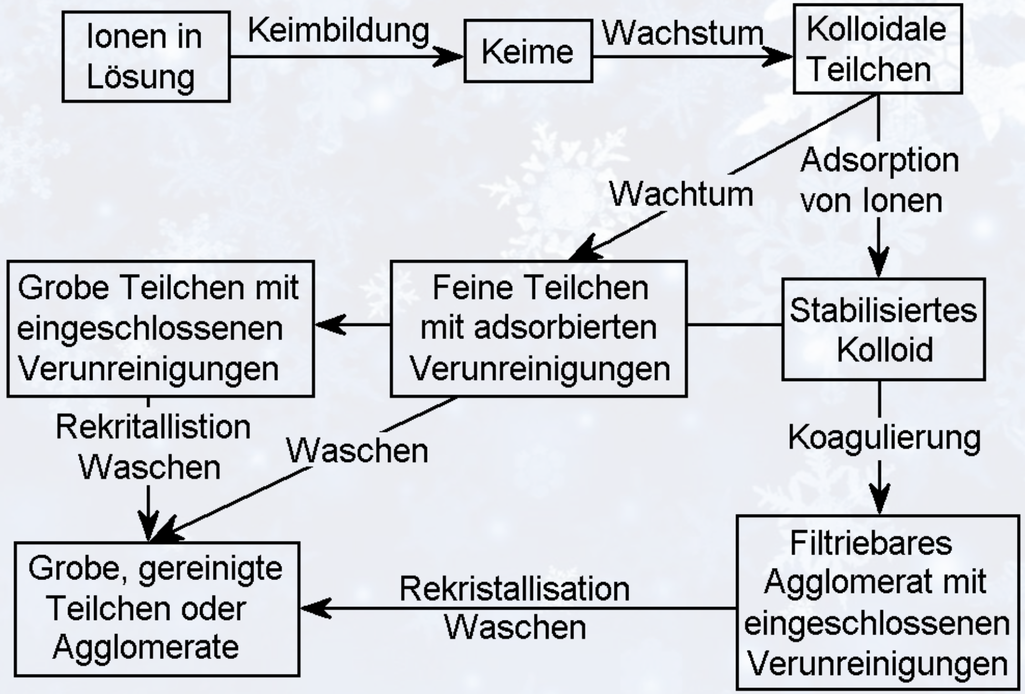
➢ Course Outline

- **Physical/Mechanical Preparation Methods**
- **Solid State Reactions**
- **Gas-Solid Reactions**
- **Gas Phase Reactions**
- **Precipitation from Solutions**
    - **Surfactant Systems**
    - **Precipitation**
    - **Coprecipitation**



➢ Precipitation from solutions: Principle





Horn, D., Rieger, J. Angewandte Chemie International Edition, 2001, 40, 23, 4330–4361

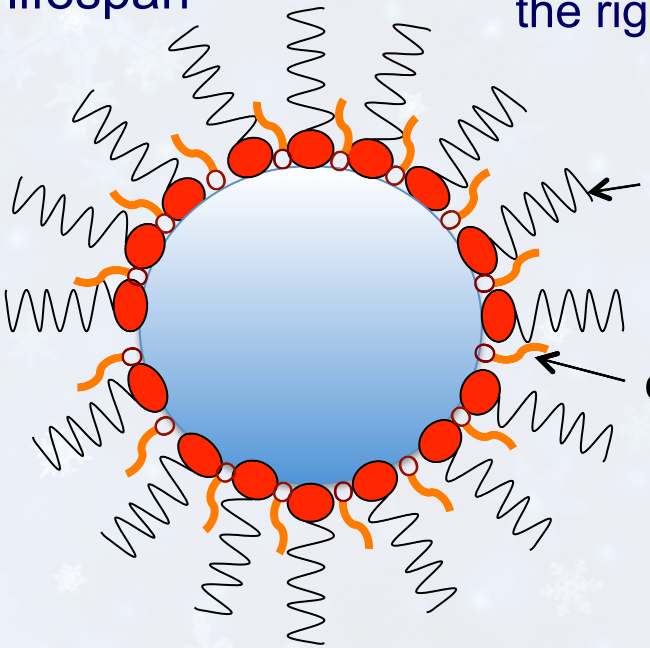
➢ Microemulsions

Properties

- Droplet diameter: 1 nm – 0.1 µm
- extremely small surface tension
- thermodynamically stable
- spontaneous formation
- short individual droplet lifespan
- translucent

Fabrication

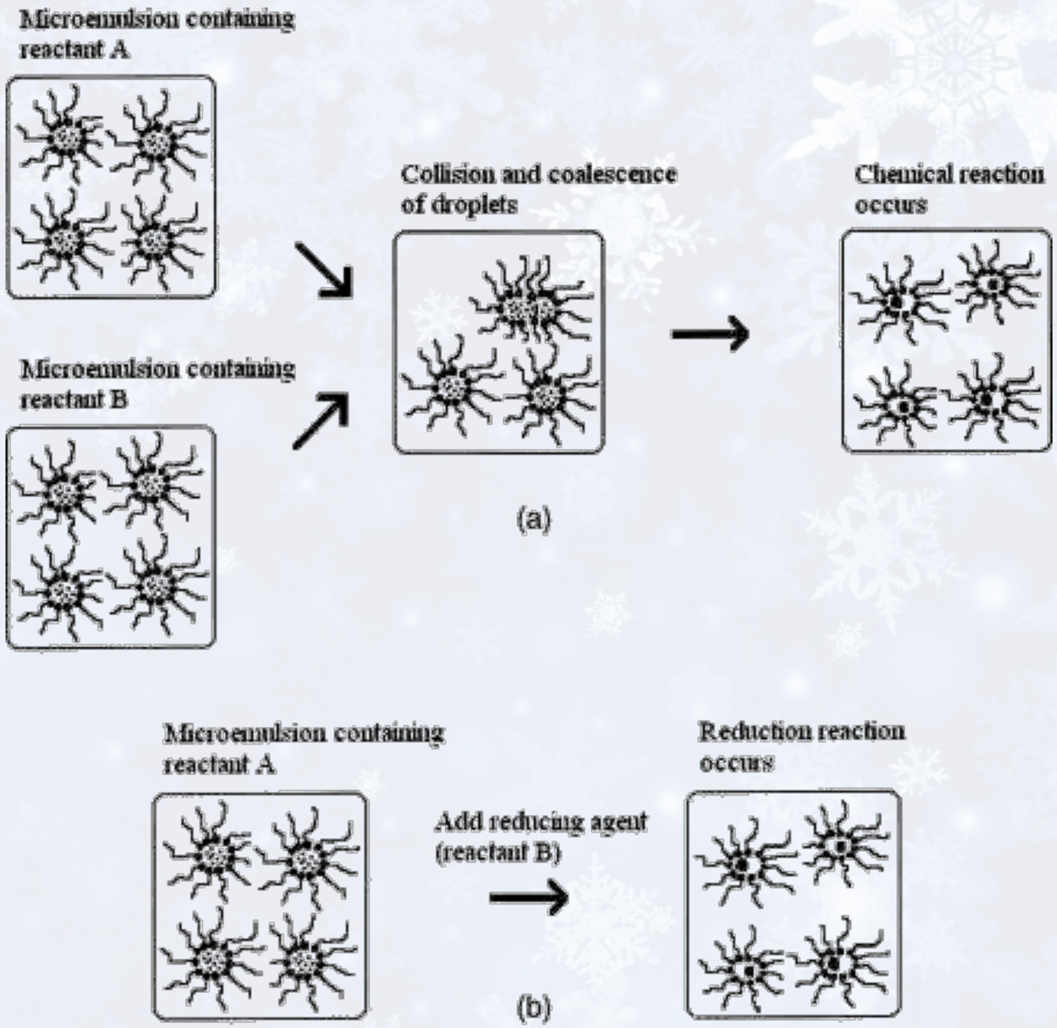
- combination of hydrophilic surfactant (high HLB) and co-surfactant (low HLB)
- some double-chain lipids
- some non-ionic surfactants at the right temperature



Microemulsion ≠ Emulsion with small droplets (Miniemulsion)

➢ Emulsions: Examples

Nanoparticle synthesis

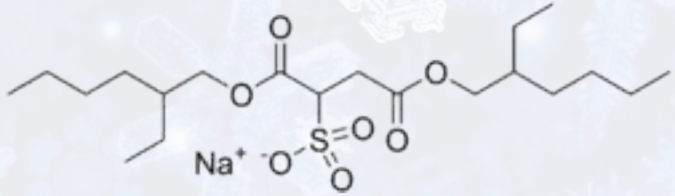


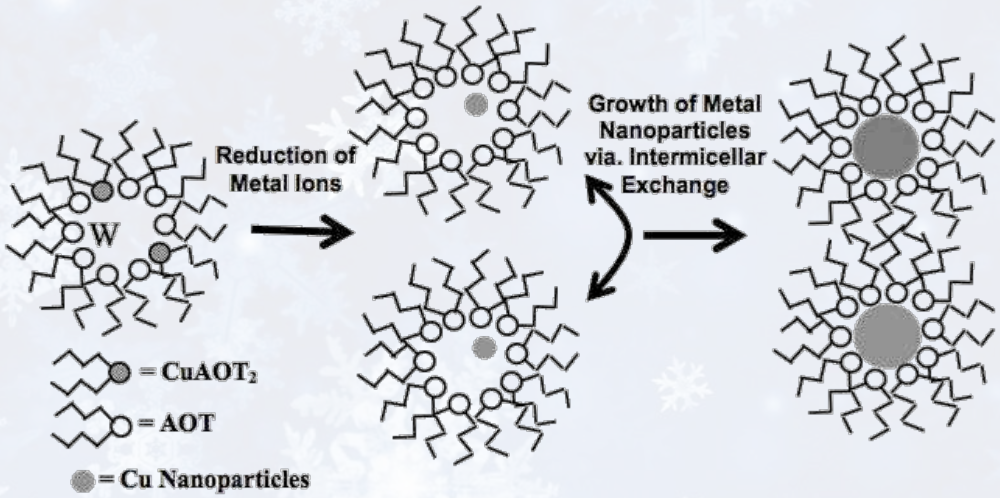
Other technical examples:
- Heterogeneous catalysis
- Oil recovery

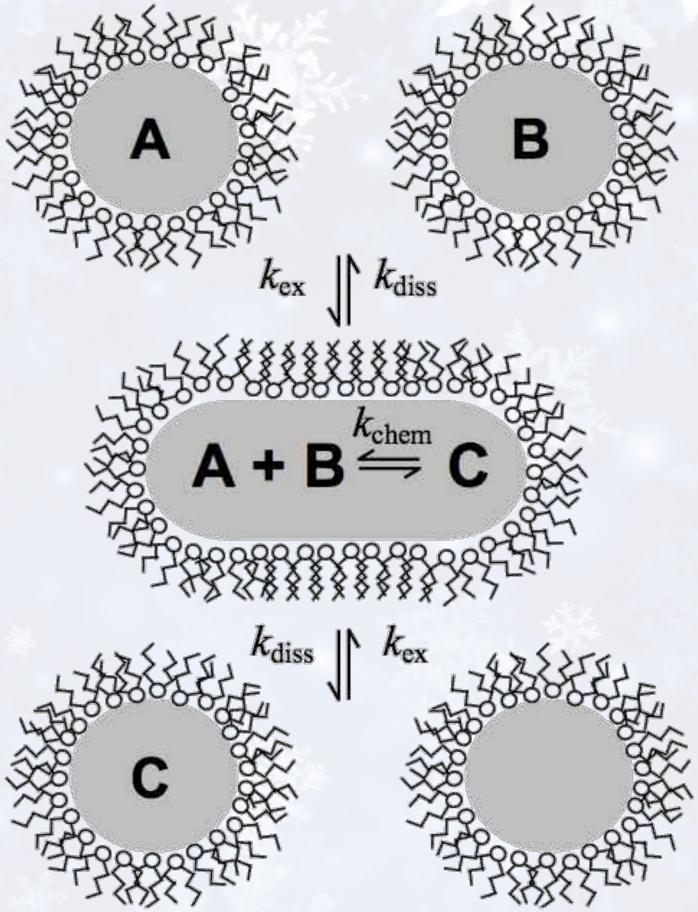
Eriksson, S.; Nylén, U.; Rojas, S.; Boutonnet, M. Applied Catalysis A: General 2004, 265, 207-219.

➢ Inverse Micelles for Nanoparticle Synthesis

Surfactant: AOT







C. Kitchens, Dissertation 2004

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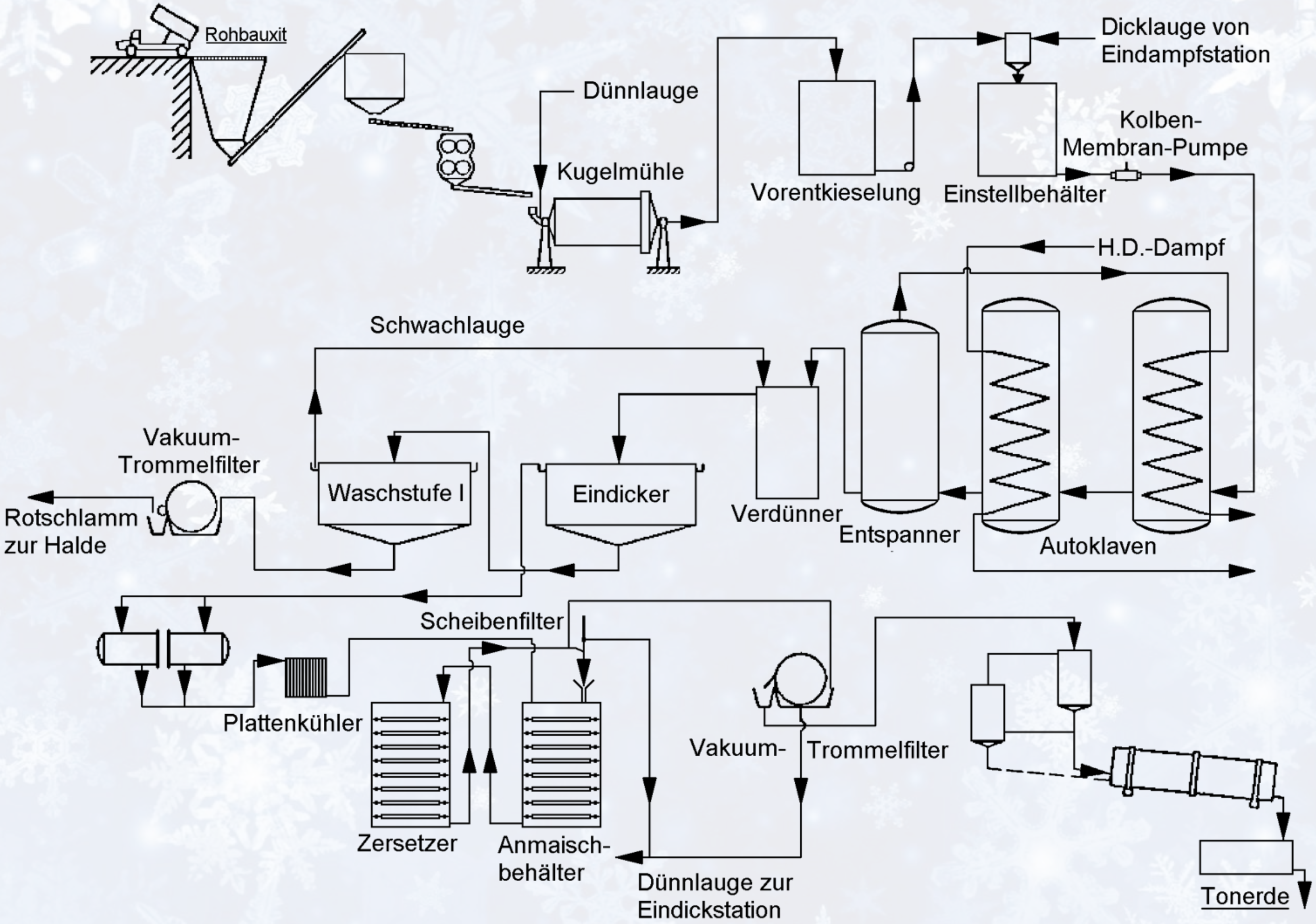
➢ Precipitation from solutions: The Bayer Process

Process Step	**Reaction**
Mineral	Bauxite ($AlOOH \cdot xFe_2O_3 \cdot ySiO_2$)
Dissolution	Bauxite + 2 NaOH + 3 H_2O → $2Na(Al(OH)_4) + Fe_2O_3 + SiO_2$
Precipitation	$2\ Na(Al(OH)_4) \rightarrow 2Al(OH)_3 + 2NaOH$
Filtration Calcination	$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$
Milling	
Synthetic raw material	α-Aluminiumoxide

Bayer process
Synthesis of Al_2O_3 (alumina) from the Mineral Bauxite

- Precipitation from solutions due to change in solubility (pH shift; temperature or pressure change
- Separation of undesired impurities (e.g. SiO_2 or Fe_2O_3 in the case of Al_2O_3)
- Process often used for TiO_2, BeO, ZrO_2, Al_2O_3

➢ Bayer Process on the Industrial Scale



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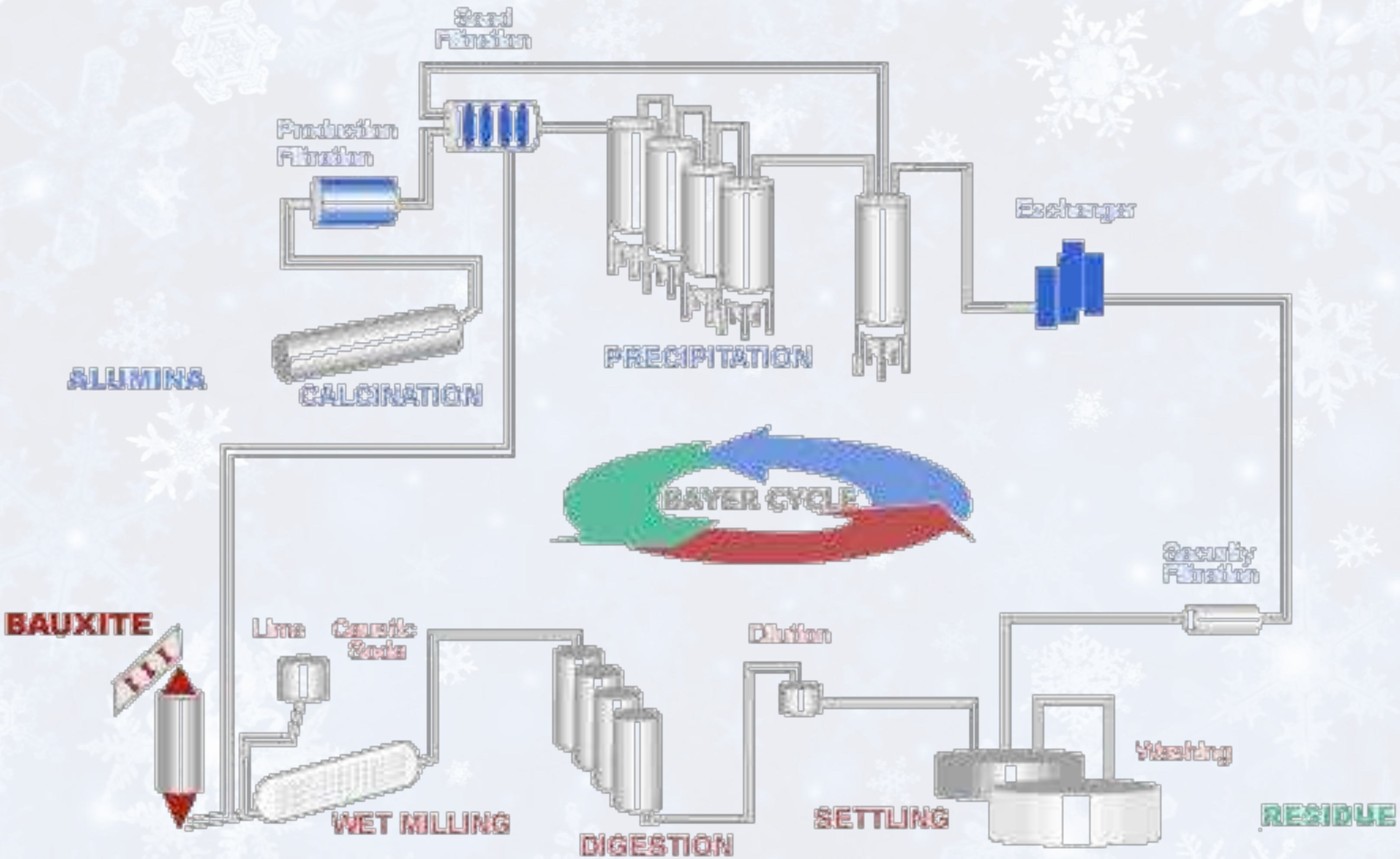
➢ Bayer Process on the Industrial Scale



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➢ Red Mud

Alcalic residue from alumina production
60 % iron oxides + silicates, titania,…

In October 2010, approximately one million cubic meters of red mud from an alumina plant near Kolontár in Hungary were accidentally released into the surrounding countryside in the Ajka alumina plant accident, killing nine people and contaminating a large area.

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Coprecipitation

Synthesis of ferrites, titanates and stabilised zirconium oxide

Ba- + Ti- salts + $H_2(C_2O_4)$ + H_2O (Oxalic Acid)	→	$BaTiO(C_2O_4)_2 \bullet 4\ H_2O$
Drying at 200°C	→	$BaTiO(C_2O_4)_2$
Calcination in O_2 (400°C)	→	$BaCO_3 + TiO_2$ (finely distributed)
Calcination at 700°C	→	$BaTiO_3$ (extremely fine)

Advantages

- well defined chemical compositions
- high phase purity achieved by dissolution of e.g. soluble nitrates
- mixing on atomic level, hence extremely homogeneous phases

Disadvantages

- Expensive and matching salt educts needed

➢ Melt processing

• small particle sizes by shock cooling of melt; subsequently crushing and milling

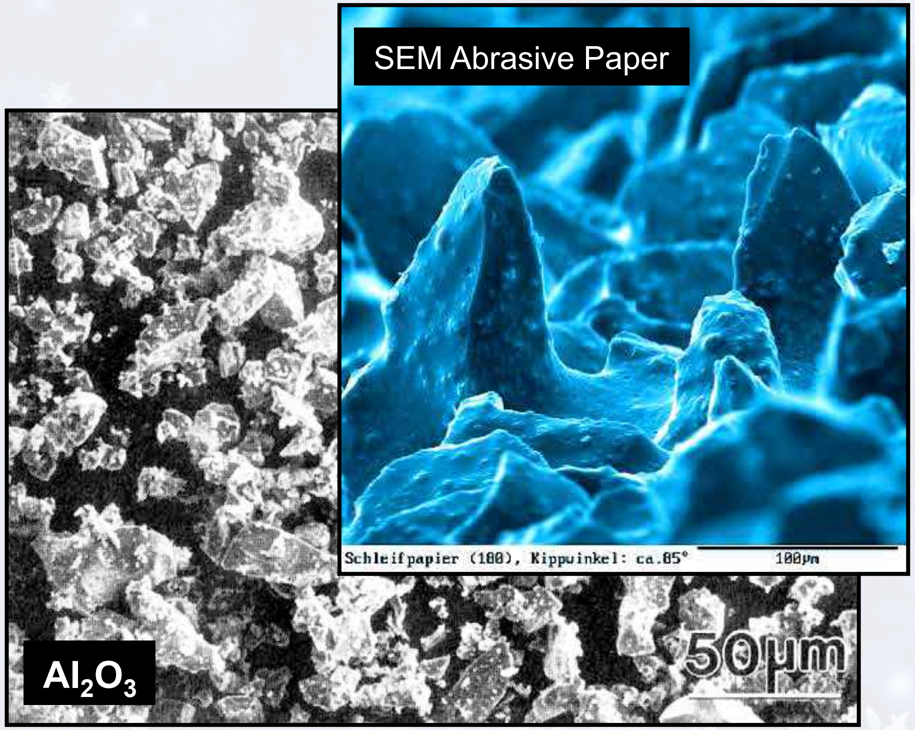
• broad application in refractory industry and for grinding disk and abrasive paper fabrication (> 25 μm)

• important for synthesis of corundum, high quality corundum, zirconium oxide, spinell

• fine milling to less than 1 μm

Advantages:
low cost
purification during process (e.g. corundum: separation of SiO_2 by evaporation)

Disadvantages:
irregular shape
demixing possible (e.g. fully stab. ZrO_2)



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➢ Overview Al_2O_3 Synthesis

Bayer-process
Bauxite + NaOH ↓
Digestion
↓
Precipitation
↓
$Al(OH)_3$
↓
Calcination
↓
α-Al_2O_3

Alum process
$Al(OH)_3 + H_2SO_4$ + $(NH_4)_2SO_4$ ↓
$NH_4Al(SO_4)_2 \cdot 12H_2O$
↓
Purification
↓
Decomposition
↓
α-Al_2O_3

Sol-Gel-Process
Al-Metal + C_3H_7OH ↓
$Al(OC_3H_7)_3$
↓
Hydrolysis
↓
Al_2O_3 -Gel
↓
Calcination
↓
α-Al_2O_3

Plasma-Process (“Iwatani Process”)
Al-Metal-Pellets + H_2O ↓
Arc Discharge
↓
$Al(OH)_3$
↓
Calcination
↓
α-Al_2O_3

➢ Class Outline „Ceramic Nanotechnology“

1. Introduction – Applications – Challenges
2. Fundamentals of Colloid and Interface Science
3. Particle Interactions in Colloidal Systems
4. Characterization of Nano- and Microparticles
5. Colloidal Dispersions
6. Rheology of Suspensions I
7. Rheology of Suspensions II
8. Biomineralization of Nanostructured Materials
9. Functional Ceramic Nanoparticles
10. Powder Synthesis and Conditioning
11. Sol – Gel Technology and Hybrid Materials
12. Shaping Ceramics I: Bulk Materials and Foams
13. Shaping Ceramics II: Thin Films
14. Summary


Merry Christmas and Happy New Year..