

SOFc ceramic materials processing

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SOFc Summerschool 2011: SOFC ceramic materials processing

⇒ Aim of the lecture

➤ Traditional and high tech ceramics

➤ Oxide type technical ceramics

➤ Non oxide technical ceramics

➤ Nanostructures in ceramics

➤ Nanopowders: Synthesis and Challenge

➤ Summary

⇒ Aim of the lecture

- get an impression of ceramics and nano activities at Empa's lab for high performance ceramics
- understand, how differences in microstructures and composition lead to different properties for traditional and high tech ceramics
- see differences in production of oxide and nonoxide ceramics
- learn how high tech ceramic materials are synthesized and processed using well established and new processes
- show some potential future trends for nanopowders in ceramics

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Laboratory for High Performance Ceramics

10 scientists; 4 technicians, 8 PhD students; 5-10 diploma/master students



- Ceramic based composites
- Ceramics for energy research
- Functional and nano materials

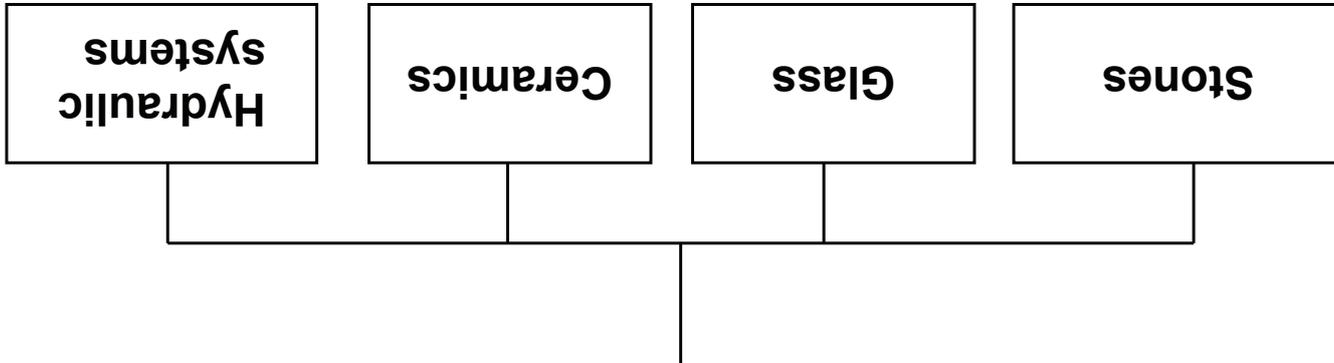
Main working field:

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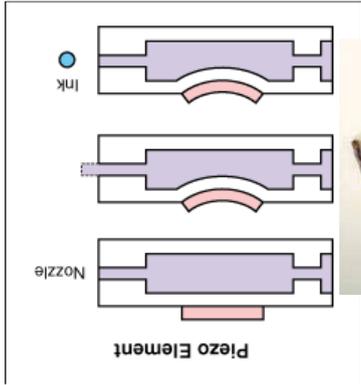
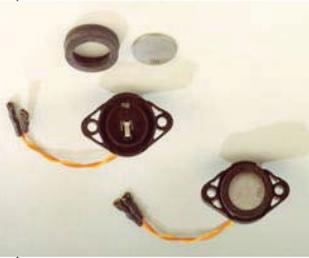
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Ceramics

Nonmetallic inorganic materials



Traditional and high performance ceramics



Fabrication of traditional and high performance ceramics

<p>High Tech Ceramics</p> <p>natural raw materials chemical powder synthesis powder preparation powder modification shaping thermal treatment/sintering metallisation magnetisation/polarisation bonding mech. treatment</p>	<p>raw mat.supplier chem.company ceramics factory "System" factory</p>
<p>Traditional</p> <p>natural raw materials integrated production firing decoration</p>	<p>liquid phase sintering</p>

Compositions in High Tech Ceramics

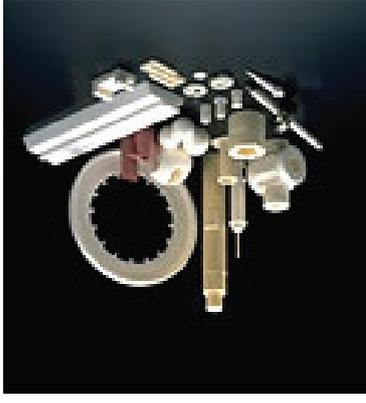
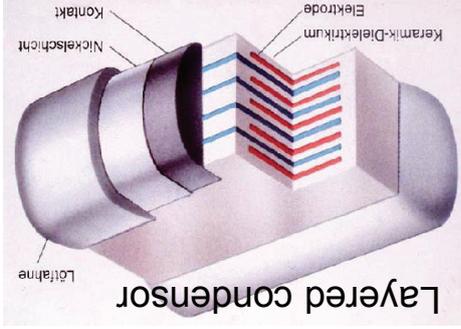
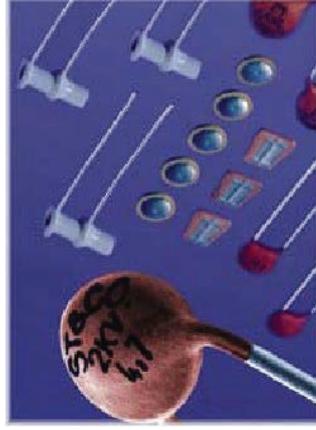
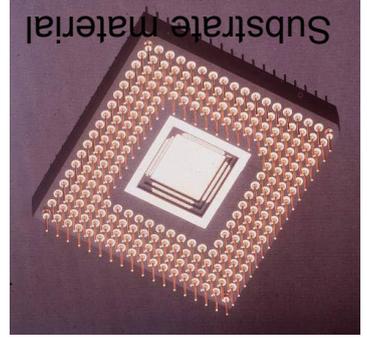
Func-tion	Materials
electrical or magnetic	Al ₂ O ₃ AlN BeO BaTiO ₃ PZT SIC ZnO-Bi ₂ O ₃ YBa ₂ Cu ₃ O ₇ TiO ₂ NiO ZrO ₂
thermal	SiO ₂ MgO Si ₃ N ₄ Fiber comp. SIC Mg ₂ SiO ₄ Mullite
optical	Al ₂ O ₃ MgO MgAl ₂ O ₄ PLZT
chemical/biological	Cordierite Al ₂ O ₃ ZrO ₂ MgO Titanates TiO ₂
mechanical	SIC B4C BN Al ₂ O ₃ ZrO ₂ Si ₃ N ₄

Large variety of oxides, carbides, nitrides

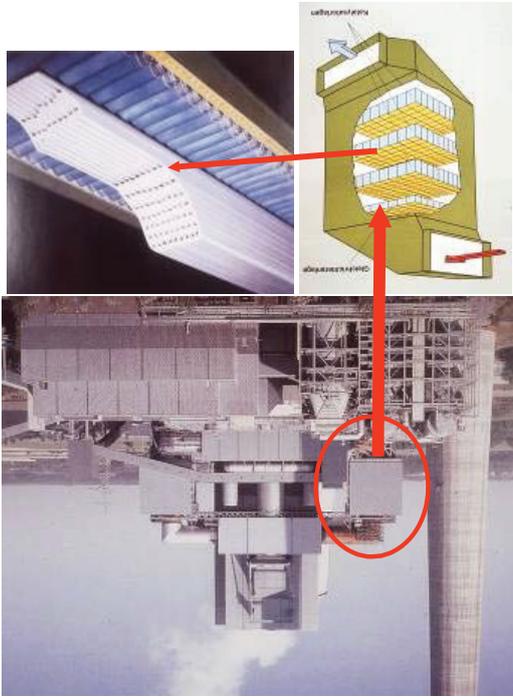
Technical applications of ceramic oxides

Oxide	Applications	Metal like	Piezo-ceramics	Pyro-ceramics	PTC cold conductor	NTC hot conductor	Ion conductor
	electrodes , conduction bands in electronics	ReO ₃ , Ferrites(LSF), Li ₂ TiO ₃	Pb (Zr,Ti) O ₃	(Pb,La)(Zr,Ti) O ₃	BaTiO ₃ doped	Fe ₂ O ₃ , NiO, FeCr ₂ O ₄	ZrO ₂ (Y ₂ O ₃), Al ₂ O ₃
	sensors, actuators			sensors	Heating elements	Temperature sensors	batteries, O ₂ sensors, fuel cells

Application area of high performance ceramics

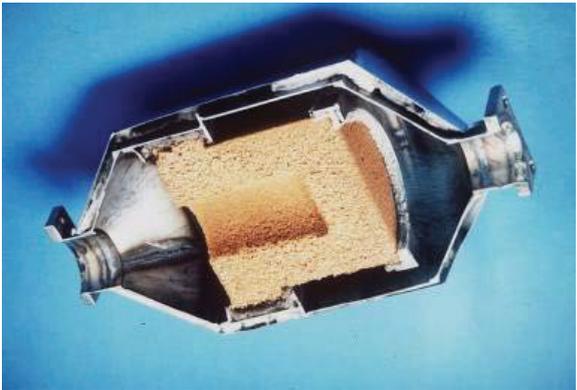
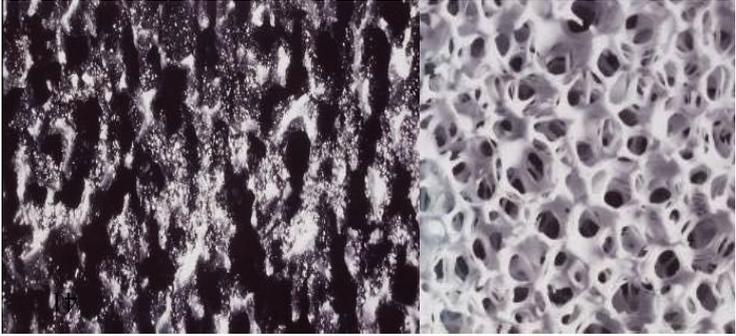


High performance ceramics for catalysts and filters



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clean loaded



Development of Biomaterials

REMOVAL

REPLACEMENT

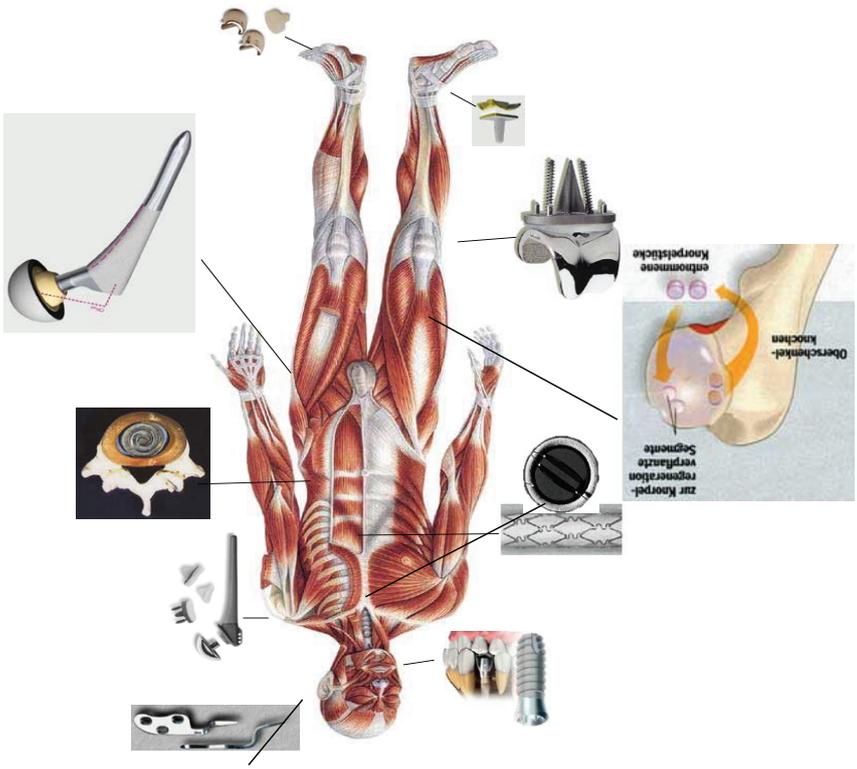
Allograft, Autograft, T!Al6V4

Bioinert,

Bioactive materials

REGENERATION of Tissues

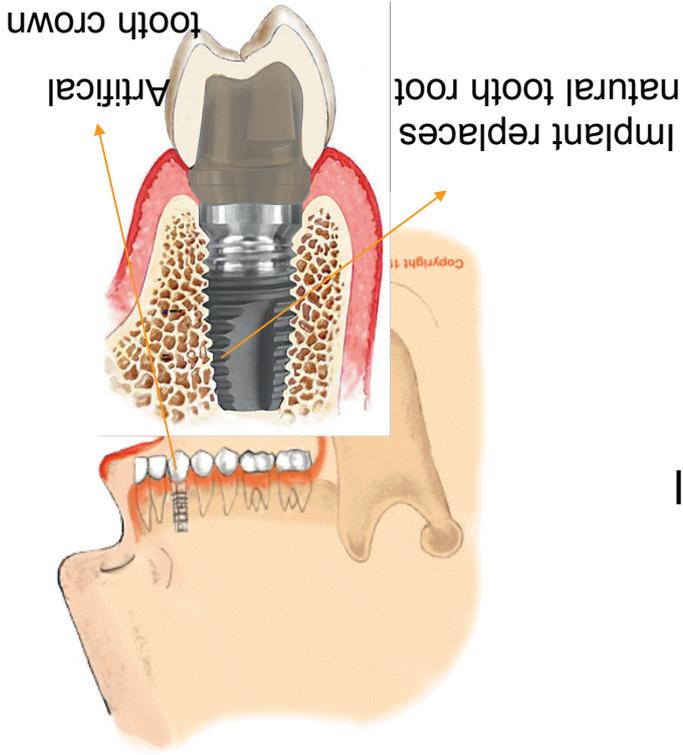
“Tissue engineering”



Ceramic Biomaterials BIOCERAMICS

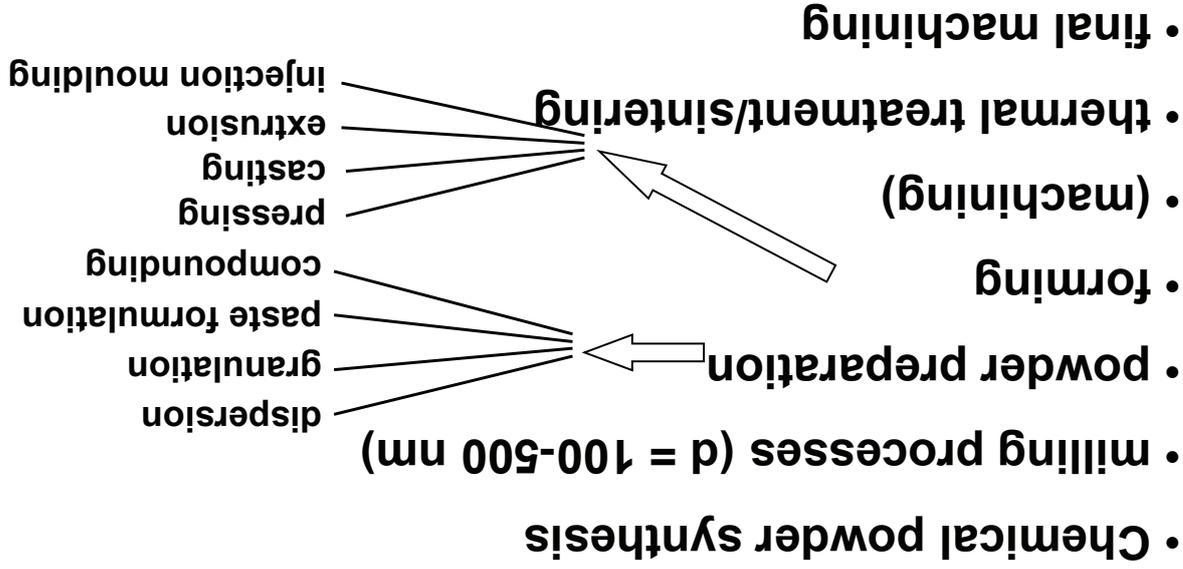
- Bioactive
- Biocompatible
- Degradation in physiological environments
- Brittle
- Poor tensile strength

Applications:
Orthopaedics
Dentistry



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Production of High Performance Ceramics



- special processes
- synthesis of ceramic metal composites
- synthesis of ceramic matrix composites (matrix: ceramics or polymer)

➤ **Synthesis** of ceramic based micron and submicron **powders**

- Solid state reactions
- Melt processes
- Precipitation from solutions
- Gas phase synthesis (of nanopowders)

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

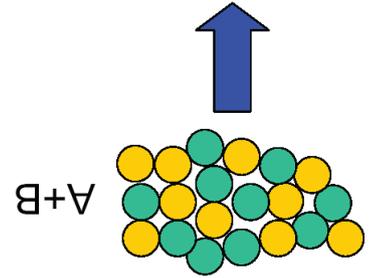
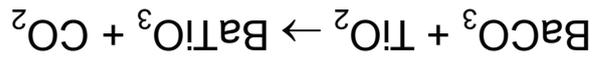
Impact on finished part	Properties	Remarks
microstructure homogeneity	particle size distribution	particle size < 1 μm narrow ± 10 % uniform
microstructure - composition	low impurity level in powder particles	low ppm range defined
crack formation/crack propagation	absence of large size secondary phases absence of agglomerates/aggregates	up to now not defined sufficiently
Processing properties	surface properties e.g. of colloid surface	

Solid state reactions

⇒ Solid state reactions

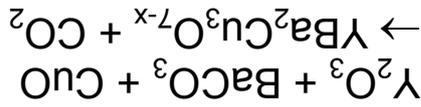
Example 1:

Bariumtitanate (very important for capacitors and piezoelectric ceramics)



Example 2:

Synthesis of a high temperature superconductor (but also fully stabilized zirconia Y-FSZ "Unitec")



Conclusions for solid state synthesis

⇒ Solid state reactions

Advantages

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

Disadvantages

1. Wide particle-size distribution
2. Coarse particle size ($\geq 1 \mu\text{m}$; typically not for nanopowder synth.)
3. Contamination during mixing and milling
4. High temperatures required for reaction (especially when the particle size is large or when the mixing is insufficient)
5. Compositional fluctuation due to incomplete reactions
6. Difficult to control the particle shape

► Precipitation from solutions

- precipitation
- sol gel processes
- coprecipitation

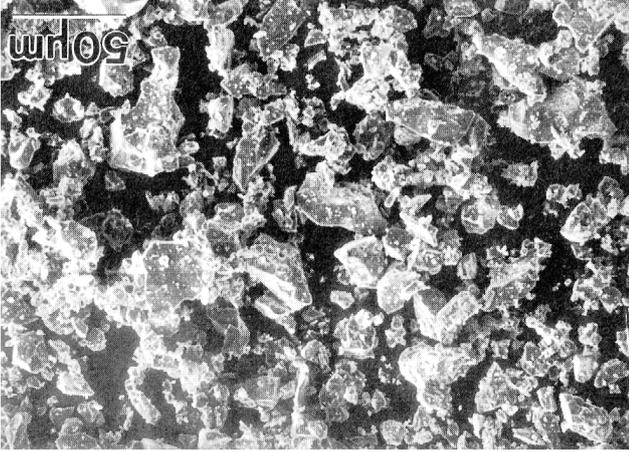
⇒ Precipitation

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SEM of corundum

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- Advantages:**
- low cost; purification during process (e.g. corundum: separation of SiO_2 impurities as slag)
- Disadvantages:**
- irregular shape; demixing possible (e.g. fully stab. ZrO_2)

- fine milling to less than 1 μm oxide, spinell
- important for synthesis of corundum, high quality corundum, zirconium abrasive paper fabrication (> 25 μm)
- broad application in refractory industry and for grinding disk and and milling
- small particle sizes by shock cooling of melt; subsequently crushing

⇒ melt process

► Melt processes

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Precipitation from solutions

⇒ Precipitation

- 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 for Al_2O_3)
- process often used for TiO_2 , BeO , ZrO_2 , Al_2O_3

process step	reaction
Mineral	Bauxite ($\text{AlOOH} \cdot x\text{Fe}_2\text{O}_3 \cdot y\text{SiO}_2$)
Dissolution	Bauxite + 2 NaOH + 3 H_2O → $2\text{Na}(\text{Al}(\text{OH})_4) + \text{Fe}_2\text{O}_3 + \text{SiO}_2$
Precipitation	$2\text{Na}(\text{Al}(\text{OH})_4) \rightarrow 2\text{Al}(\text{OH})_3 + 2\text{NaOH}$
Filtration	$2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
Calcination	
Milling	
Synthetic raw material	α -Aluminiumoxide

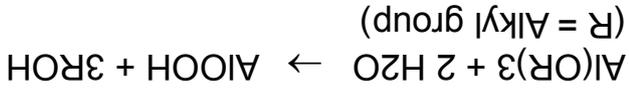
Synthesis of aluminium oxide (alumina) from minerals (Bayer process)

Composition of Bauxite:
Al-oxid hydrates
+ Fe-hydroxides
+ silicates

Sol gel processes

⇒ sol gel

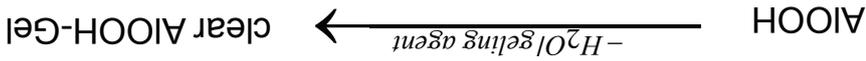
Hydrolysis of alkoxide



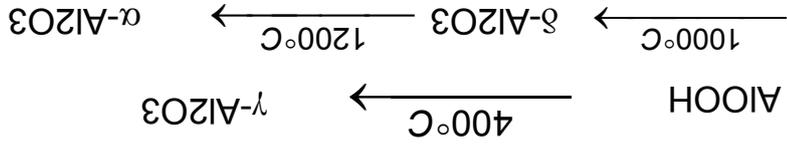
Peptisation (dispersion)



Gelation



Heat treatment



depending on reaction conditions formation of:

- submicron sized particles (spherical; monosized)

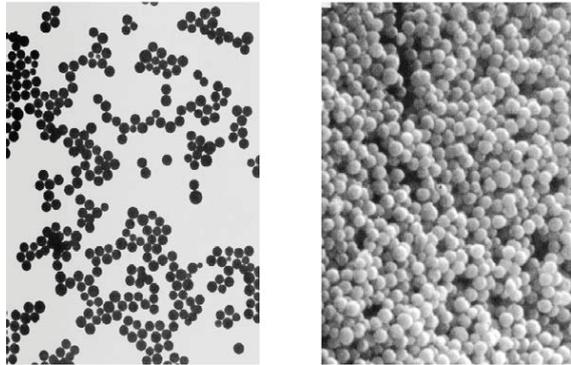
- fibres from gels

- layers or monolithic parts

Characteristics of sol gel processes

⇨ sol gel

monomodal powders by sol gel synthesis
 a) SEM image of BaTiO_3
 b) TEM image of $\text{Pb}^{2+}\text{Nb}^{2+}\text{O}_7$



Advantages: a) very fine powders, extremely pure and homogeneous starting materials
 narrow particle size distributions
 low sintering temperature till complete densification; high sintered densities

Disadvantages: high raw materials and process costs (expensive precursors, organic solvents)
 high shrinkage rates (monolithic structures difficult to achieve)
 formation of oxides or even hydroxides → no high temperature materials

⇨ Coprecipitation

⇨ precipitation

Synthesis of ferrites, titanates and stabilised zirconium oxide
 $\text{Ba} + \text{Ti-salts} + \text{H}_2(\text{C}_2\text{O}_4) + \text{H}_2\text{O} \rightarrow \text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$

drying (200°C) → $\text{BaTiO}(\text{C}_2\text{O}_4)_2$

calcination in O_2 (400°C) → $\text{BaCO}_3 + \text{TiO}_2$ (finely distributed)

calcination (700°C) → BaTiO_3 (extremely fine)

Advantages:

well defined chemical compositions; high phase purity
 achieved by dissolution of e.g. soluble nitrates; precipitation as carbonates or oxalates and subsequent heat treatment
 coprecipitation also possible by temperature; pressure or pH change
 Limitations: Calcination → grain growth → milling necessary

➤ Gas phase synthesis

- Spray pyrolysis (separate file)
- Flame spray synthesis
- Plasma processes

➤ Gas phase synthesis (of nanopowders)

Advantages:

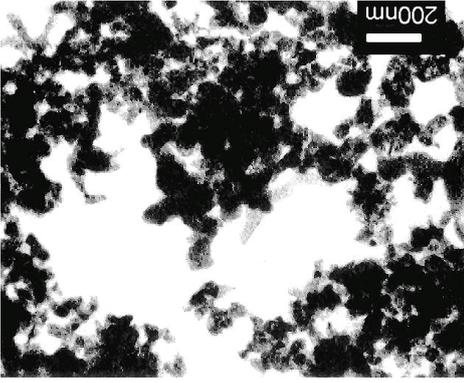
- submicron or even nanosized particles
- high specific surface area (up to several 100 m²/g)
- frequently spherical particles
- low impurity content (especially metal contamination)
- homogeneous distribution of sintering additives

most important

- high temperature flow reactors
- plasma reactors

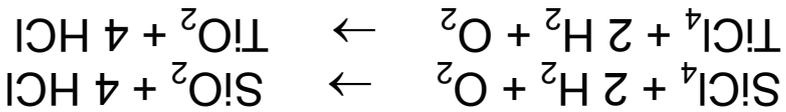
High temperature flow reactor

synthesis of silicon carbide from methylsilane
 $\text{CH}_3\text{SiH}_3 \rightarrow \text{SiC} + 3 \text{H}_2$ (1500 – 1800 °C)

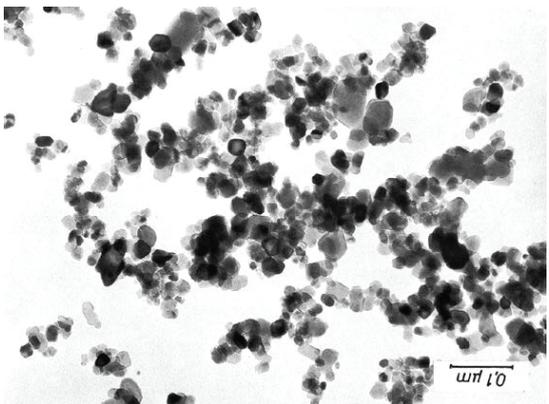
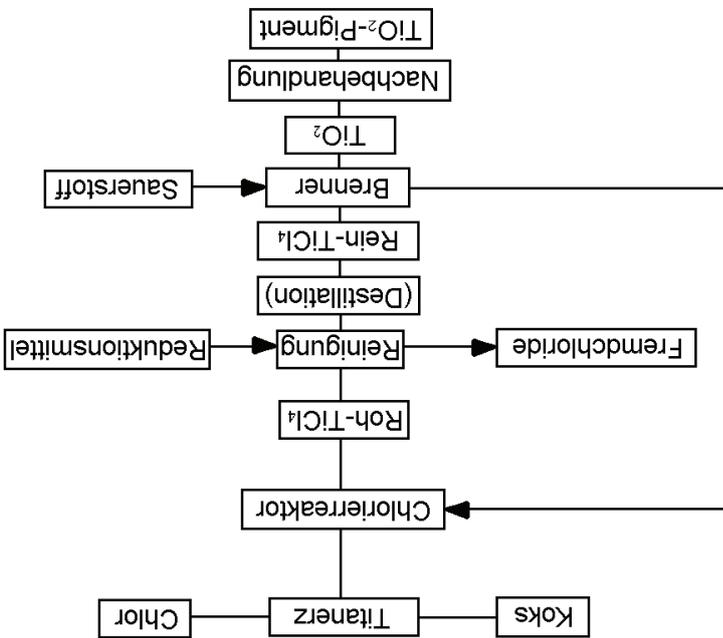


⇒ gas phase synthesis

Widely used industrial process (Degussa; Cabot): **millions of tons/year**



(Aerosil)
(Titanweiss)



TEM image of TiO₂

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⇨ Commintion processes for ceramic powders (not for nanopowder synthesis)

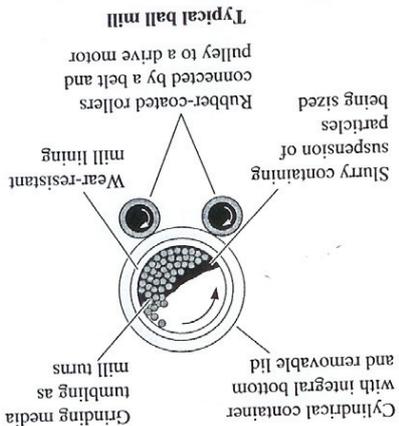
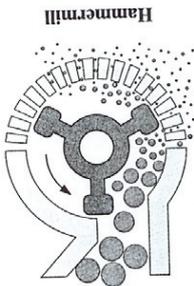
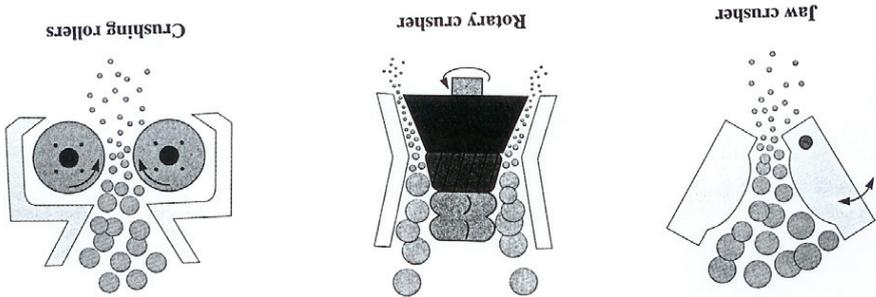
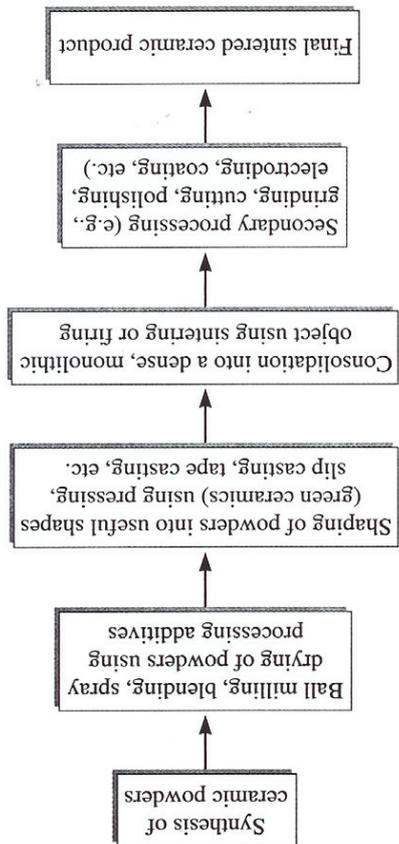
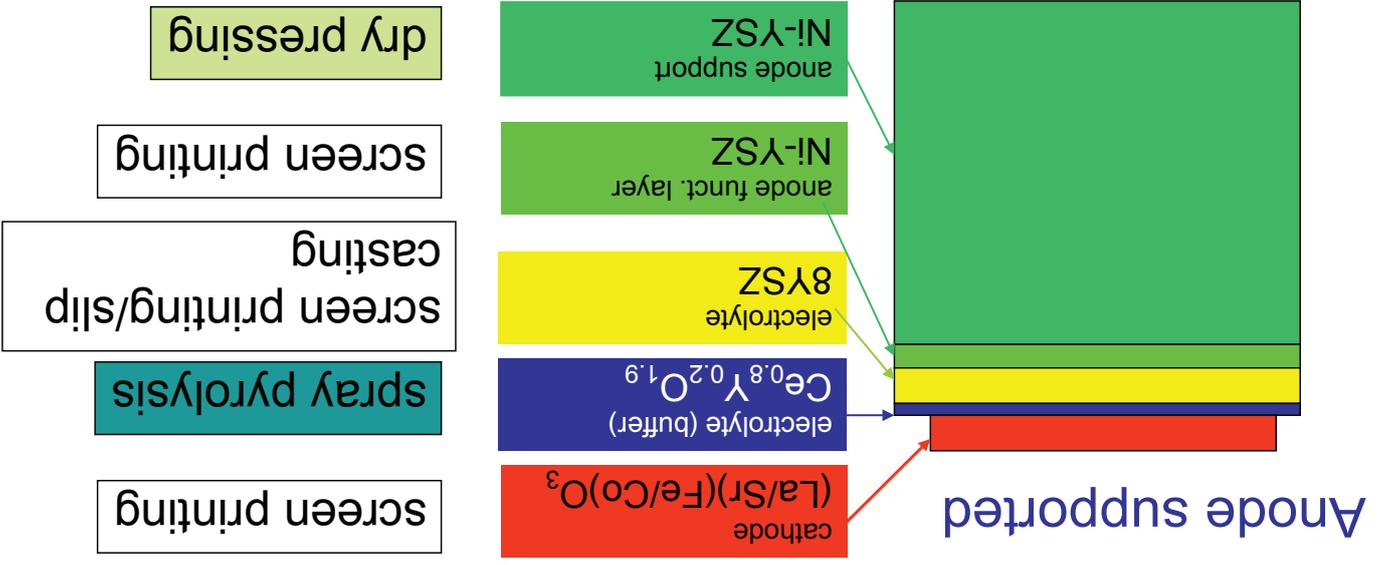


Figure 14-2 Schematic of the jaw, rotary, crushing rollers, and hammermill crushing

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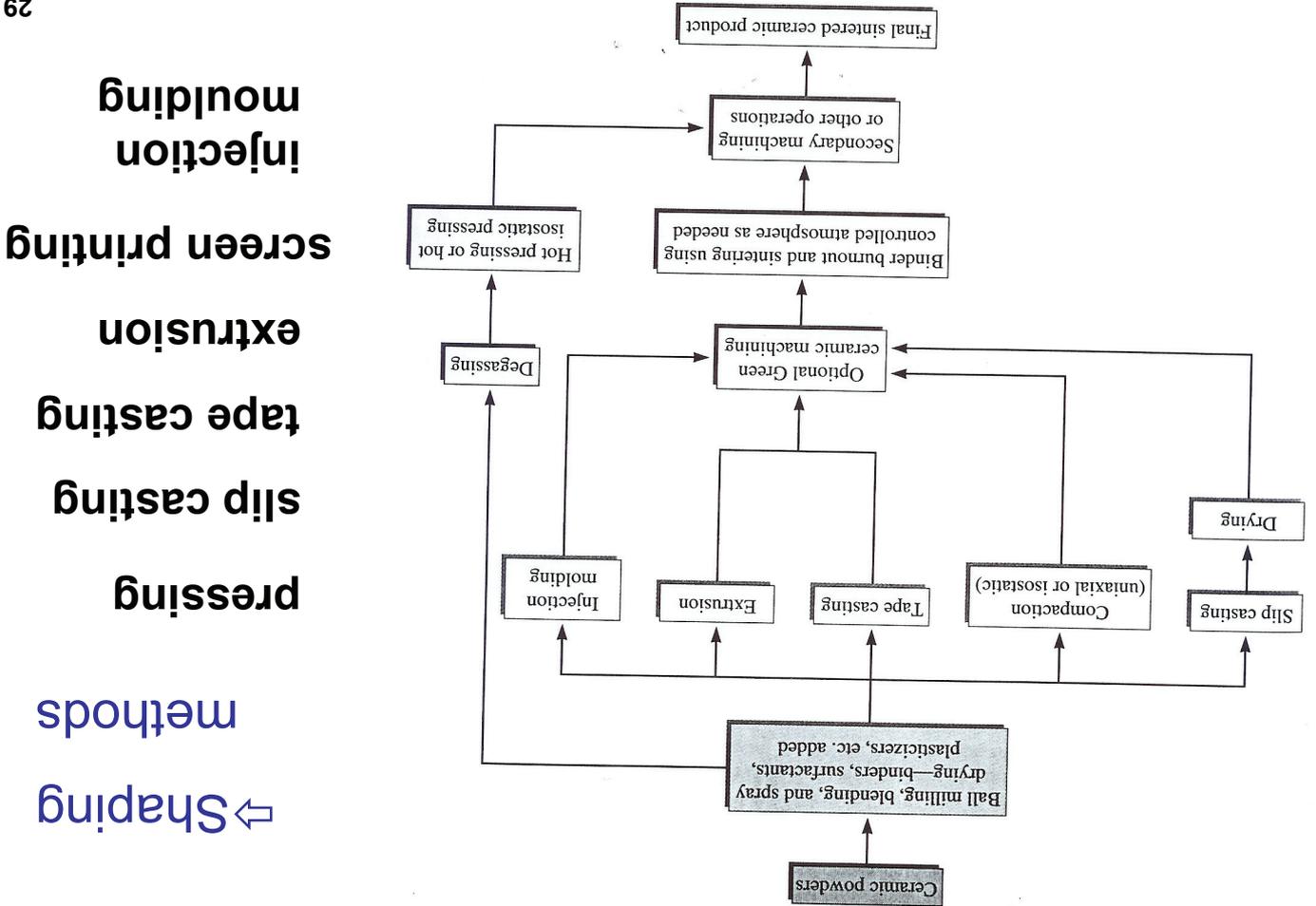
Electrolyte supported: tape casting



Examples for shaping of SOFC elements

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Figure 14-3 Different techniques for processing of advanced ceramics.

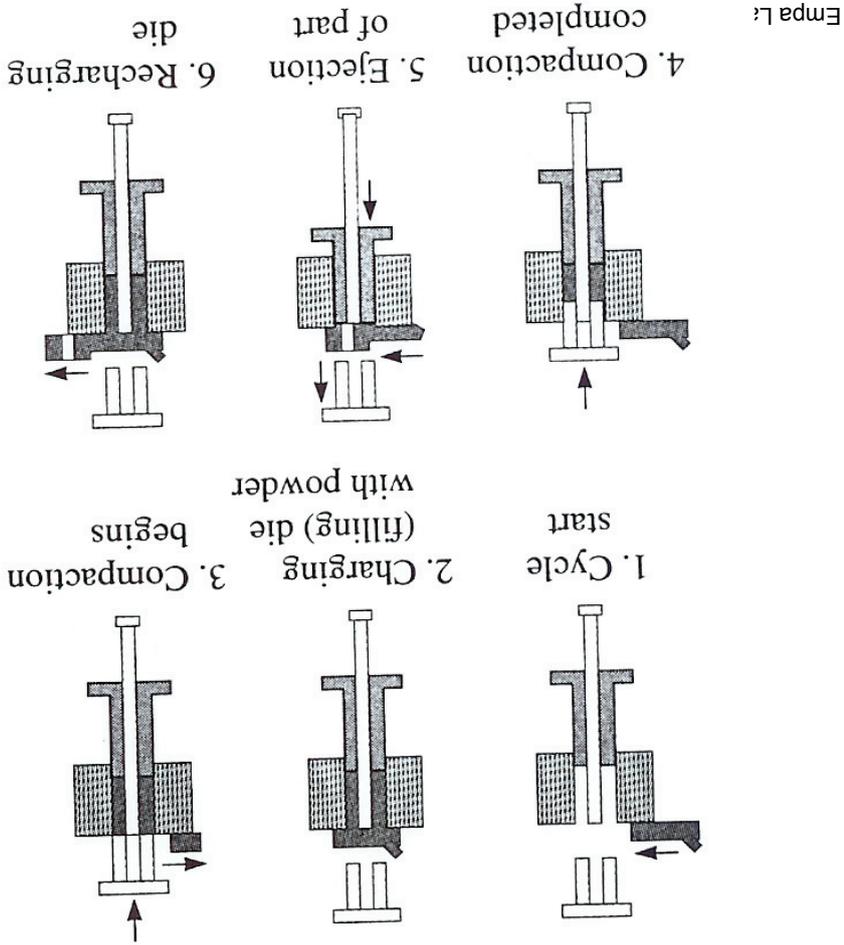


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⇐ shaping techniques; overview

method	product- geometrie	mass- consistency	tool costs	product examples
dry pressing axial	simple - complex	granules	high	ferrites piezoceramics
iso pressing	simple	granules	medium	tubes, spark plugs, rams
tape casting	tape	slurry	very low	condensers substrates
extrusion	simple	plastic mass	low	tubes, rods
pressure slip casting	simple	slurry	low	sanitary ceramics
slip casting	complex	slip/slurry	low	sanitary ceramics
injection moulding	complex	plastic mass	high	thread liner turbine blades

Uniaxial pressing:
most popular
and cost
effective
forming
method for
ceramic parts



⇨ Shaping of sheets by tape casting

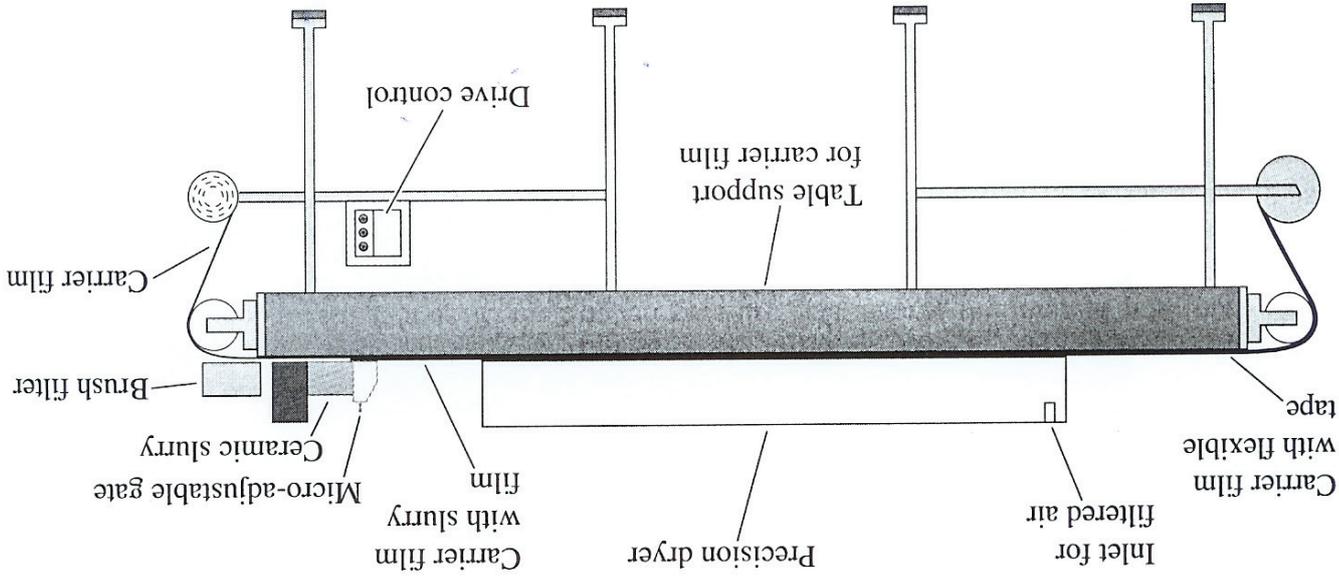


Figure 14-5 Schematic of a tape casting machine. (Source: From Principles of Ceramics Processing, Second Edition, by J.S. Reed, p. 532, Fig. 26-6. Copyright © 1995 John Wiley & Sons, Inc. Reprinted by permission.)

Challenge: Preparation of low viscous dispersions/pastes with high solids loading

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⇨ Forming by Slip Casting and pressure slip casting

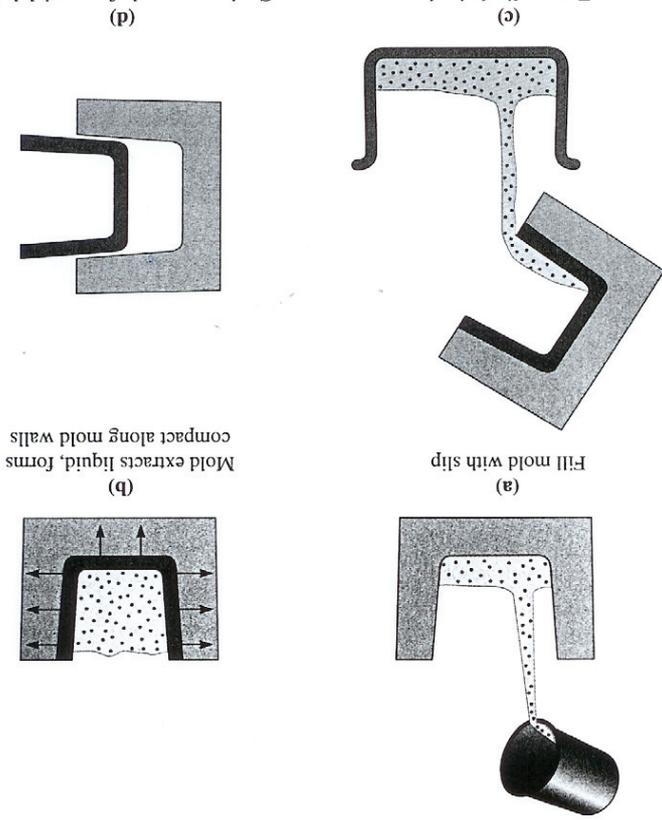


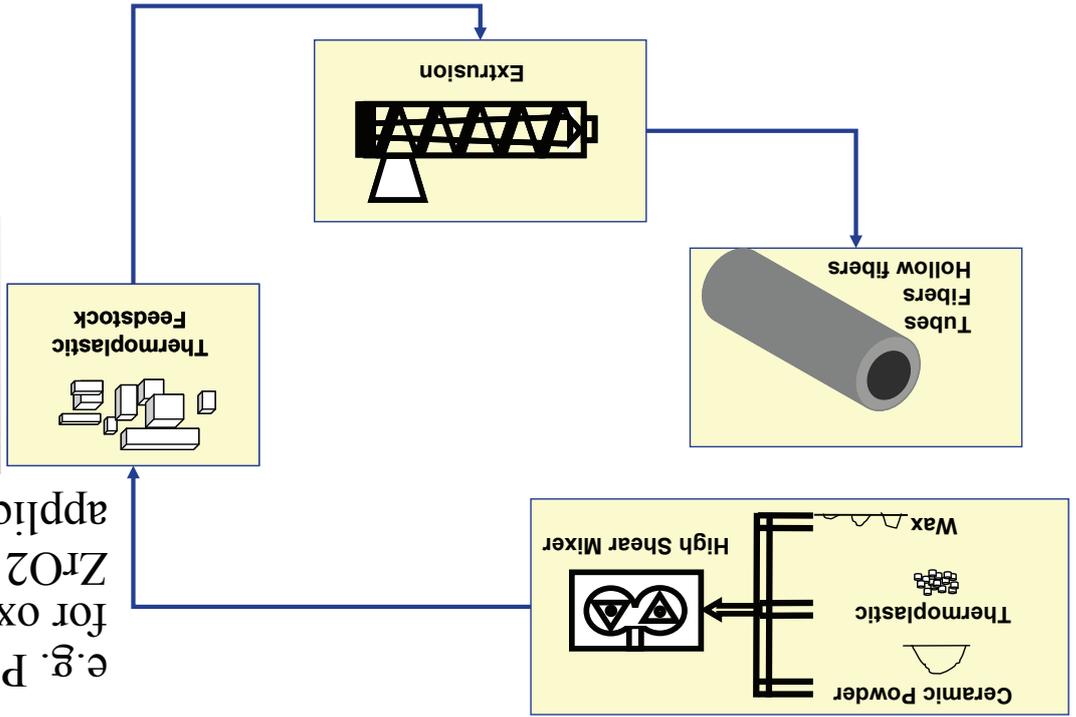
Figure 14-6 Steps in slip casting of ceramics. (Source: From Modern Ceramic Engineering, by D.W. Richerson, p. 462, Fig. 10-34. Copyright © 1992 Marcel Dekker. Reprinted by permission.)

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Extrusion Technology

e.g. Perovskite tubes for oxygen separation
 ZrO₂ tubes for SOFC application

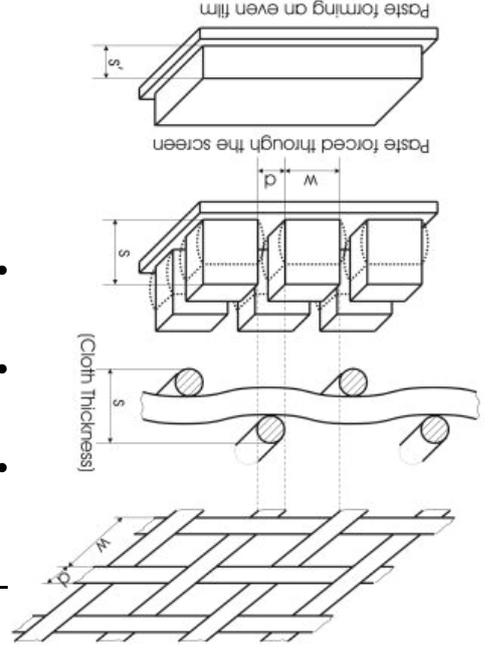


e.g. Silica quartz fibers by extrusion of thermoplast based feedstocks with extremely high amount of nanosilica OX 50 (up to 58 vol. % in PE-wax-mixture)

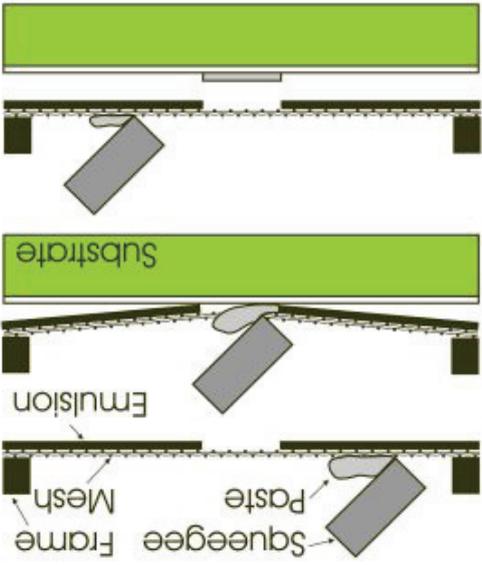
Screenprinting - a tool for coating of fuel cell anodes

Three steps:

- Application of paste on screen
- Pressing through screen
- Formation of film on substrate



Rheological requirement of paste:
Shear thinning



- understand, how differences in microstructures and composition lead to different properties for traditional and high tech ceramics
 - see differences in production of oxide and nonoxide ceramics
 - learn how nanostructured ceramics are synthesized using well established and new processes
- Aim of this lecture part

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- traditional ceramics (brick, porcelain)
 - aluminium oxide
 - zirconium oxide (TZP; PSZ, FSZ)
 - silicon nitride (sintered, reaction bonded)
 - silicon carbide (sintered, Si infiltrated, recrystallized)
 - functional ceramics
- Examples for traditional and technical ceramics

⇨ Traditional and technical ceramics

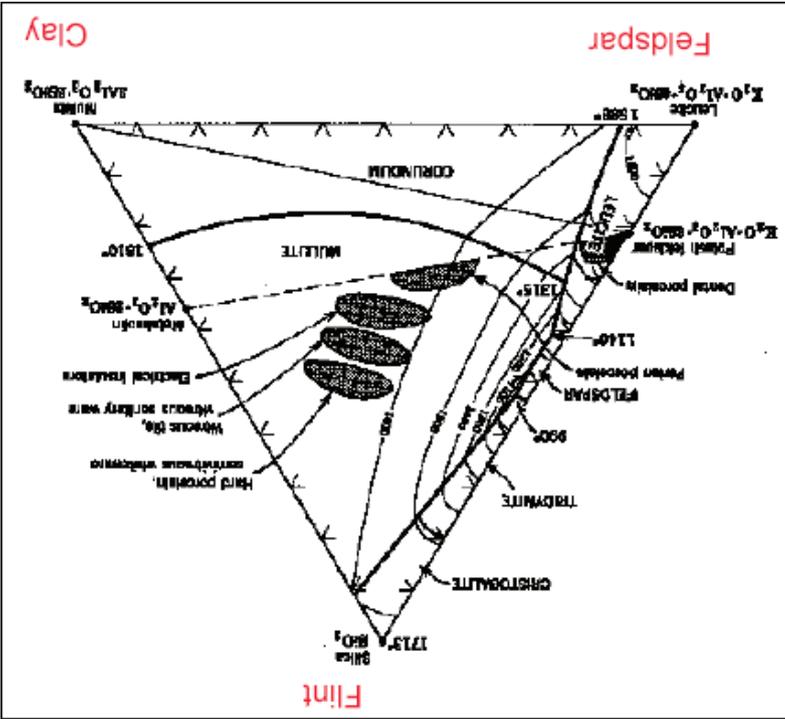
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- Dental porcelains need good translucency - high feldspar and low clay
 - Low glass content ceramics (high clay) are harder and more resistant to chemical attack
 - China clays have large particles and give white products; ball clays have very fine particles but impurities give dark product. Ball clays make easier formed green bodies but give inferior product-
- Whitewares: Applications

➤ Traditional and high tech ceramics

⇒ Traditional ceramics

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- Different compositions are used for different applications
- **Liquid phase** sintering with liquid content controlled by **feldspar content**
- High feldspar content gives lower firing temperature and high translucency
- High clay content is easier to form into green bodies (higher plasticity especially in comparison with high perf. ceramics)

➤ Traditional ceramics

⇒ Traditional ceramics

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Typical alumina properties

- Young's modulus: 380 - 400 GPa
- Hardness: 16 - 18 GPa
- Fracture Toughness: $3.5 - 4.5 \text{ MPa m}^{1/2}$
- Bending Strength: 300 - 500 MPa
- Grain sizes: 1-2 μm (Hot pressed) 3 - 25 μm (Sintered)
- Thermal expansion co-eff: $9 \times 10^{-6} \text{ K}^{-1}$
- Thermal conductivity: $8 \text{ W m}^{-1} \text{ K}^{-1}$

(low)

⇒ Aluminium oxide

Zirconia

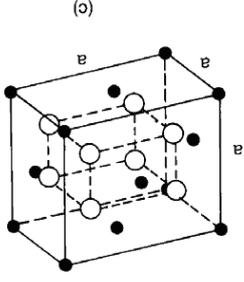
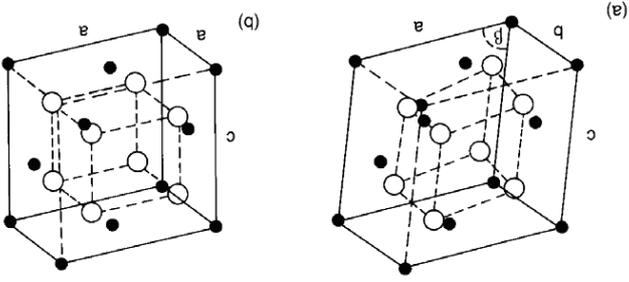
⇒ Zirconium oxide

Zirconia exists in 3 different crystal structures based on the fluorite structure

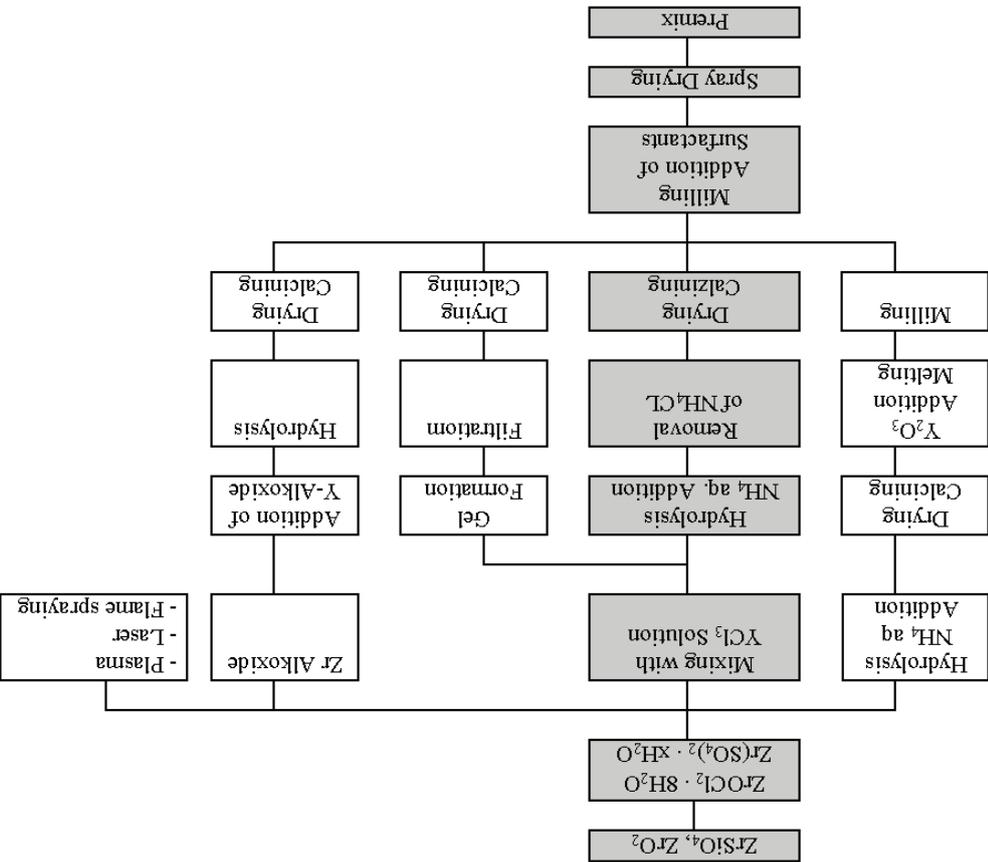
- a) monoclinic at low temperature ($< 1170^\circ\text{C}$)
- b) tetragonal at intermediate temperature
- c) cubic at high temperature

Cubic tetragonal transformation is diffusion controlled

Tetragonal monoclinic transformation is martensitic with a volume increase of 6%



Synthesis of zirconia powder



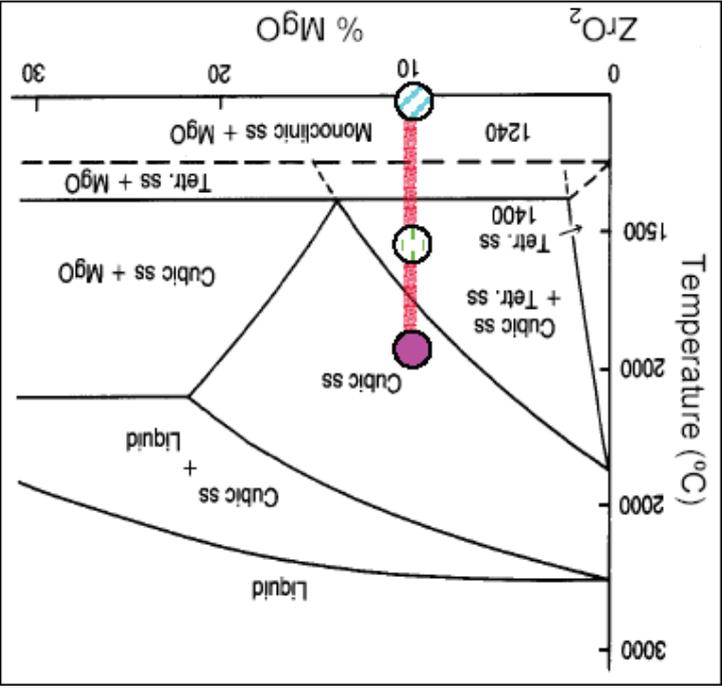
Zirconia:

⇔ Zirconium oxide

Partially stabilized zirconia (for structural applications)

A number of dopants can be used to stabilise the cubic phase to lower temperatures. Most important dopants are CaO, MgO, Y₂O₃ and CeO₂.

Example: Add about 10% MgO. Since the material in the cubic phase Lower temperature and heat treat (age) to nucleate small precipitates of t-phase. These are grown to below the critical size for t-m transformation. Cool to room temperature. Remaining c-phase does not get time to transform.



Partially stabilized zirconia

Mg-PSZ Microstructures

Age at 1400°C.

After 4-5 hours tetragonal precipitates

form and grow by conventional

diffusional processes as coherent

spheroids along {001} cube planes.

- Below a well defined critical size of

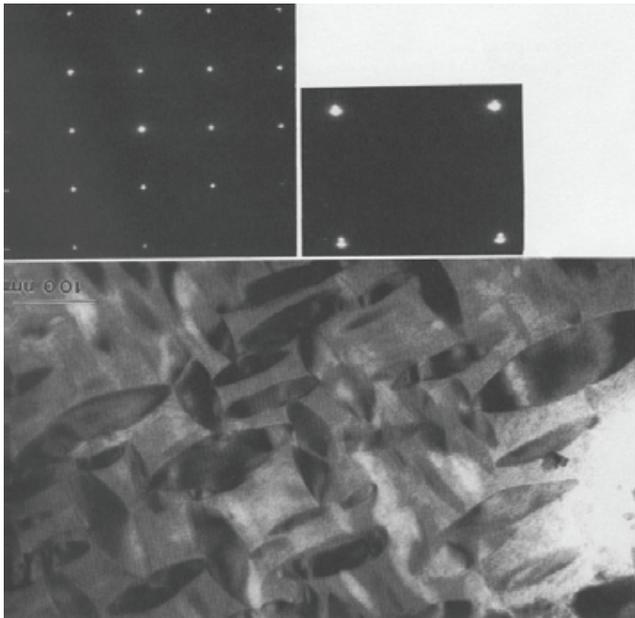
about 200 nm the t-particles are retained

on cooling to room temp.

- Optimum microstructures contain about

25% - 30% by volume of tetragonal

phase.

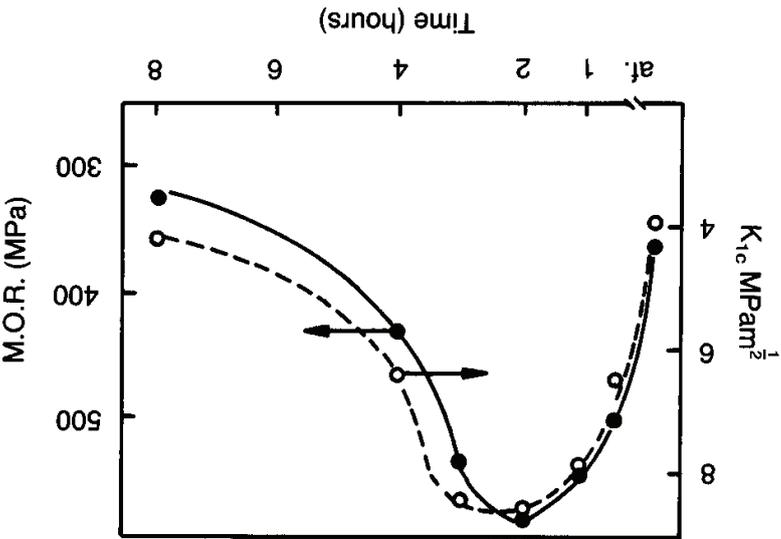


⇒ Zirconium oxide

Partially stabilized zirconia (PSZ)

⇒ Zirconium oxide

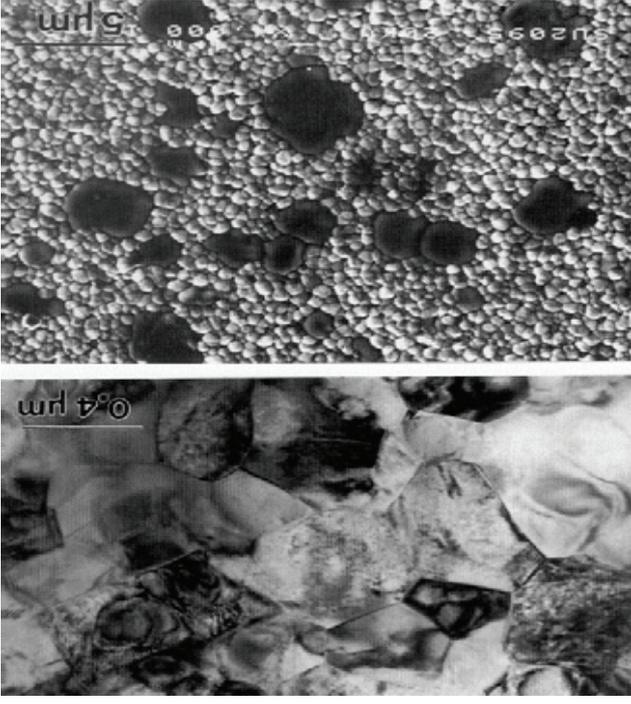
Toughness / Aging Time Relation



Peak toughness in PSZ microstructure is obtained when optimum mean precipitate size is achieved.

Optimum size is just below that for spontaneous transformation.

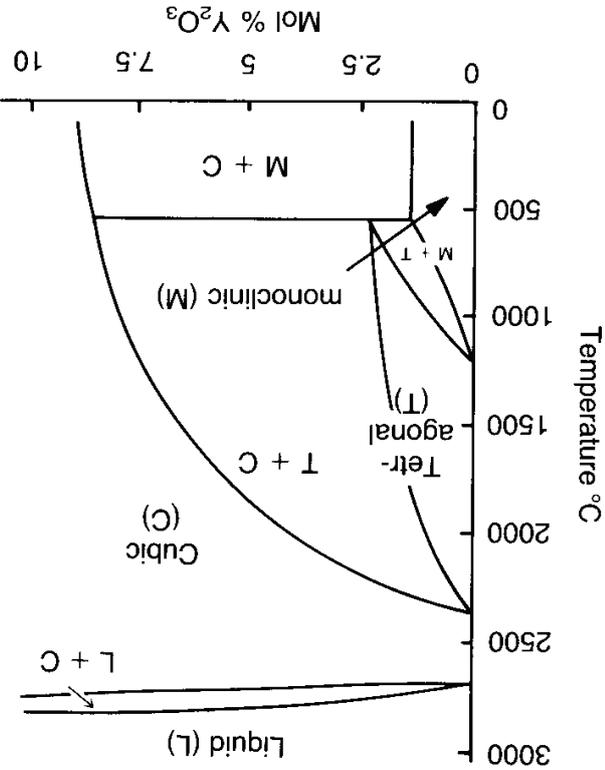
However, in the overaged state *microcrack toughening* is possible and so toughness falls away more slowly than expected



TZP Microstructure
 Sinter at 1400- 1550°C,
 much lower than 1800°C
 for PSZ
 Potentially 100% of the
 microstructure is
 transformable giving
 tougher ceramics
 Powders often contain
 small inclusions of cubic
 material

Tetragonal Zirconia Polycrystals (TZP)

⇒ Zirconium oxide



Toughness
 Addition of 2.5% Y₂O₃
 results in a considerable
 tetragonal phase field
 Similar behaviour seen
 with CeO₂ additions
 Phase stability influenced
 by impurities

Tetragonal Zirconia Polycrystals (TZP)

⇒ Zirconium oxide



$\beta\text{-Si}_3\text{N}_4$ stable at high temperatures above 1420°C
 Both phases can be stabilised by impurities - notably oxygen impurities stabilise

α and β forms are distinguished by the stacking sequence of Si-N layers
 α phase is harder than β
 2 crystal structures α and β are known; both are hexagonal
 Bonding is intermediate ionic-covalent - about 70% covalent
 N corners are shared by 3 tetrahedra
 Si atom is surrounded by 4 N to form SiN_4 tetrahedra similar in size to SiO_4 tetrahedra in silicates

Si₃N₄ Crystal Structure and Stability

Si₃N₄: sintered, hot pressed, reaction bonded,

⇒ Silicon nitride

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	Y-TZP	Ce-TZP
wt.% Stabiliser	2 - 3	12 - 15
Hardness (GPa)	10 - 12	7 - 10
Young's Modulus (GPa)	140 - 200	200 - 220
Bending Strength (MPa)	800 - 1300	500 - 800
Fracture Toughness (MPa m ^{1/2})	6 - 15	6 - 30

Fracture toughness in Y-TZP can be very high
 Critical grain size for transformation is a function of Ytria content

Tetragonal Zirconia Polycrystals (TZP): Properties

⇒ Zirconium oxide

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Usually add 2-3% of a metal oxide e.g. MgO, Al₂O₃, La₂O₃ or Y₂O₃. These combine with a surface SiO₂ layer on the Si₃N₄ powder. This forms a low melting point oxynitride glass which aids liquid phase sintering and solidifies to a grain boundary glass. Sintering is usually in range 1550-1800°C so starting α-Si₃N₄ powder transforms to β-Si₃N₄.

Sintering Aids

Covalent nature of Si₃N₄ hinders sintering. If we use very high temperatures to promote sintering tend to get thermal decomposition

$$\text{Si}_3\text{N}_4 \rightarrow 3\text{Si} + 2\text{N}_2$$
 Densification is usually achieved by Hot-Pressing in a N₂ atmosphere

Hot Pressed/Sintered Silicon Nitride

⇒ Silicon nitride

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- Use reaction $3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$
 - React solid Si with N₂ gas - endothermic reaction: energy expensive
 - Forms porous ceramic: pores needed to ensure N₂ transport
 - Forms very pure Si₃N₄ with no glassy phases at grain boundaries
 - Slow process: may take 2 - 10 days to form component
 - Most commercial Si₃N₄ **powder** is made by grinding RBSN
- Volatile oxide SiO is formed in reducing conditions
- SiO transports Si to gas phase reacts with N₂ to deposit Si₃N₄
 - Both α and β phases formed depending on temperature (α if T > 1410°C)

Reaction Bonded Si₃N₄

⇒ Silicon nitride

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α - β Transformation \rightarrow high toughness

\Rightarrow Silicon nitride

Starting α powder has SiO_2

coating

Reacts with metal oxide

additive to form sintering

liquid

At sintering temperature β -

phase precipitates out of the

melt as α phase dissolves -

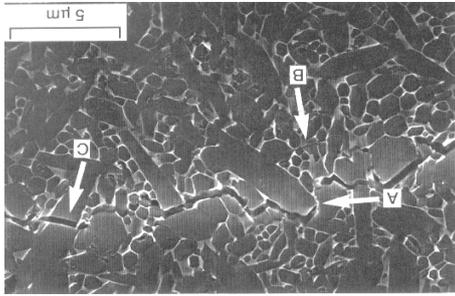
dissolution reprecipitation

Final microstructure has

elongated β -grains in glassy

matrix

Elongated grains deflect cracks and increase toughness by generating R-curve behaviour



Si_3N_4 : Properties

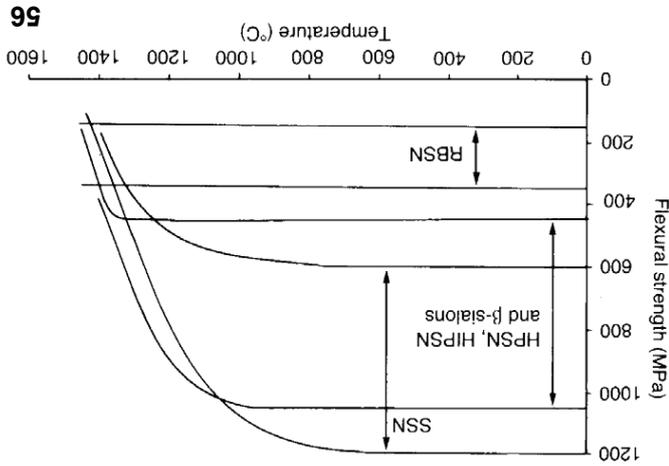
	SSN	RBSN
Density (gcm^{-3})	3.2-3.9	2.2-3.2
Hardness (GPa)	14-18	4-7
Toughness ($\text{MPa}\sqrt{\text{m}}$)	3.4-8.2	1.5-3.6
Modulus (GPa)	280-320	100-220
Bending Strength (MPa)	400-1000	190-400

\Rightarrow Silicon nitride

Hard and strong ceramic; also excellent thermal shock resistance

High Temperature Properties

Generally good properties up to 1000°C
 Degradation increased if lots of grain boundary glass present
 RBSN properties retained to higher temperatures because there is no grain boundary glass phase



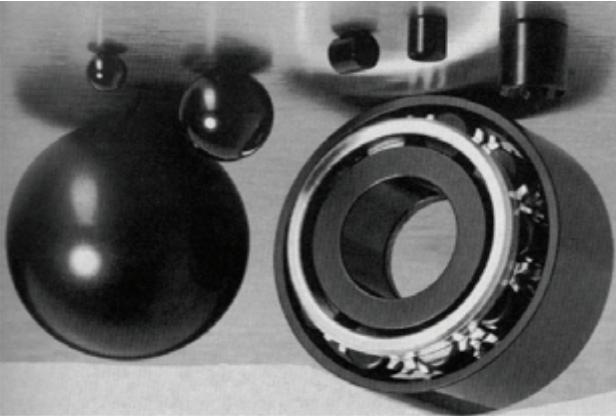
Most widely used non-oxide ceramic
 Mostly used as an abrasive
 Very high melting point and almost completely covalent structure;
 very difficult to sinter > 2000 °C
 Sintering aids: B, C and Al
 Closely related to diamond and silicon.
 Both C and Si atoms are in sp^3 hybridisation

Silicon Carbide

⇒ Silicon carbide

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Cutting tools, grinding media, grit blasting nozzles, turbocharger rotors, crucibles, ball bearings



Applications of Silicon Nitride & Sialon

⇒ Silicon nitride

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The covalent nature of SiC makes it very difficult to sinter. Sintering occurs at very high temperatures near to 2000°C or higher. Must use very fine, sub-micron powders. C has low solubility in oxide glasses so liquid phase sintering is not favoured. Sintering aids are B, C or Al. Role of sintering aids is unclear - all are very strong reducing agents and possibly have a role in reducing the SiO₂ coating on the powder. Single doping of Al or B leads to grain growth - doping with both Al and B simultaneously leads to equiaxed fine grained structures. Fine β-SiC powders sintered in the presence of Al, B, C or BeO can transform to α-SiC and grow elongated grains analogous to Si₃N₄ transformation. But: R-curve generating microstructures cannot be routinely fabricated.

Sintered SiC

⇒ Silicon carbide

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SiC can be fabricated at lower temperatures using more finely divided SiO₂ and CO gas or carbon black to give β-SiC. Other routes include direct reaction of Si and C or pyrolysis of SiO₂ containing vegetable matter (e.g. rice hulls).

Highly endothermic, requires very cheap energy resource. Reaction occurs at 2200°C and produces α-SiC.



Most SiC is made for abrasive applications – not for ceramics. Acheson process - carbothermal reduction of sand by coke.

SiC Powder Synthesis

⇒ Silicon carbide

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⇒ Silicon carbide

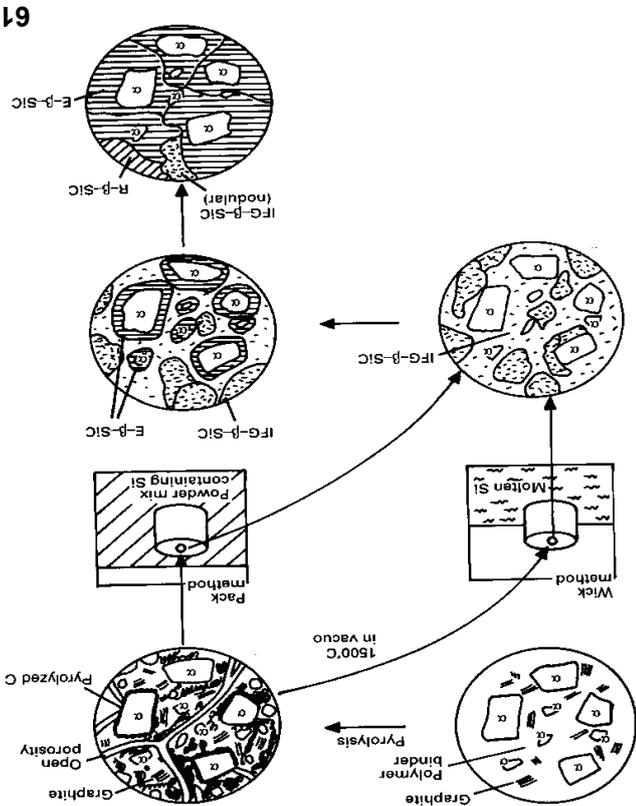
Reaction Bonded SiC (RBSC)

Direct reaction between Si and C can be exploited



- Two commercial reaction bonding processes:

- a) Infiltrate SiC & C compact with liquid Si ("REFEL")
- b) Form SiC compact bonded with phenolic resin and carbonise before infiltration.



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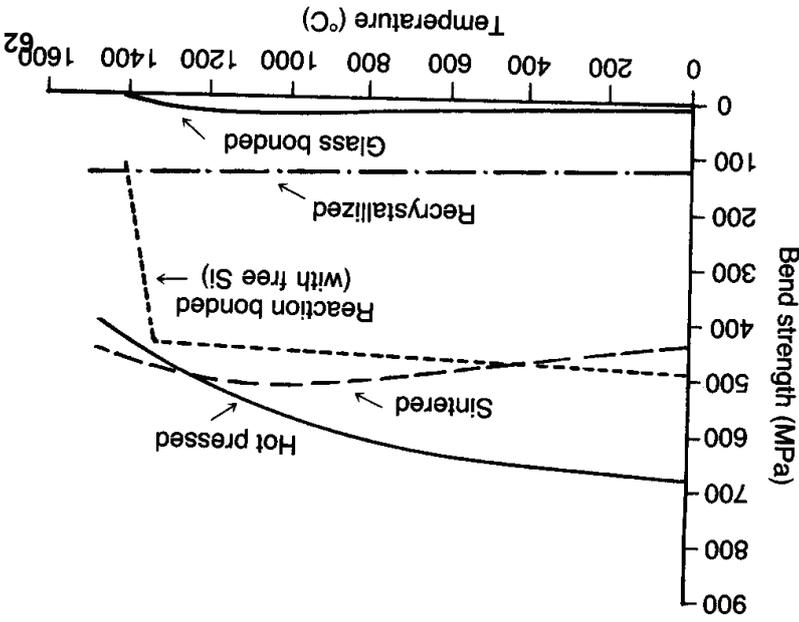
⇒ Silicon carbide

Reaction bonded SiC properties

Density (gcm⁻³)
 Hardness (GPa)
 Modulus (GPa)
 Bending Strength (MPa)
 Toughness (MPa√m)

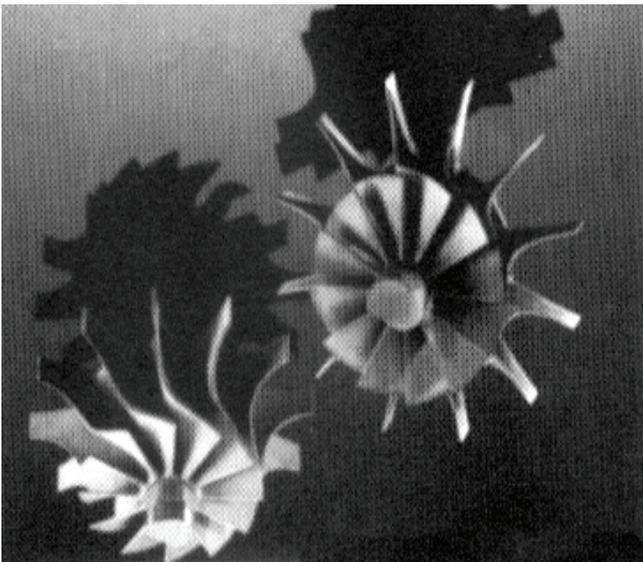
Material	Density (gcm ⁻³)	Hardness (GPa)	Modulus (GPa)	Bending Strength (MPa)	Toughness (MPa√m)
RBSC	3.15 - 3.25	18 - 22	280 - 390	350 - 540	4 - 5
SSC	3.1 - 3.15	21 - 25	410	430	3 - 5
HPSC	3.20	23 - 30	450	640	5 - 6

At elevated temperatures SiC shows less degradation than Si₃N₄
 RBSC retains good properties at high T
 - but only up to melting point of Si!



Applications of SiC

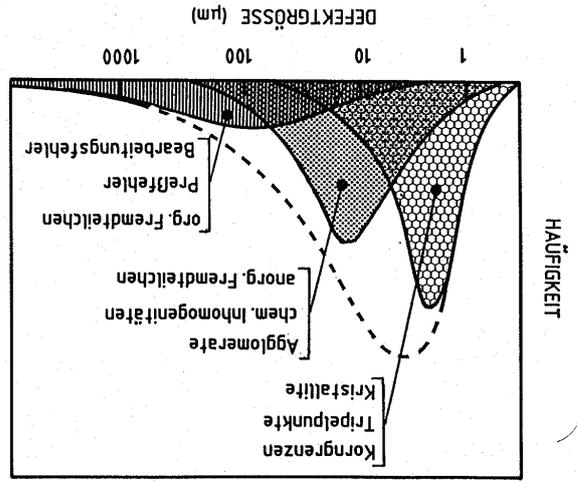
- Abrasives are (by far) most important application
- More temperature stable than Si_3N_4
- often used for "BRENNHILFSMITTEL"
- Not as tough as Si_3N_4
- High thermal conductivity (2-3 x higher than steel)
- Very wear resistant
- Not good as a cutting tool because of C reactivity with metals



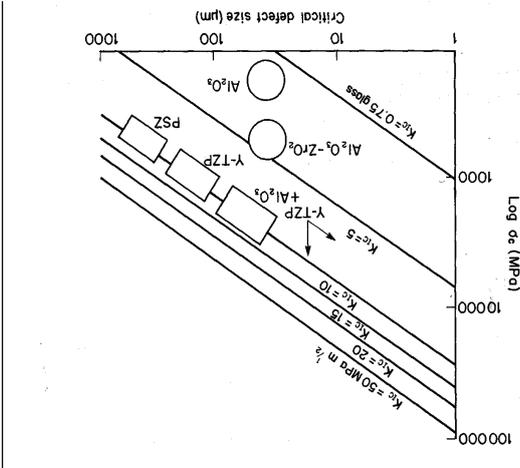
SiC turbocharger rotors

Future potential of nanoceramics

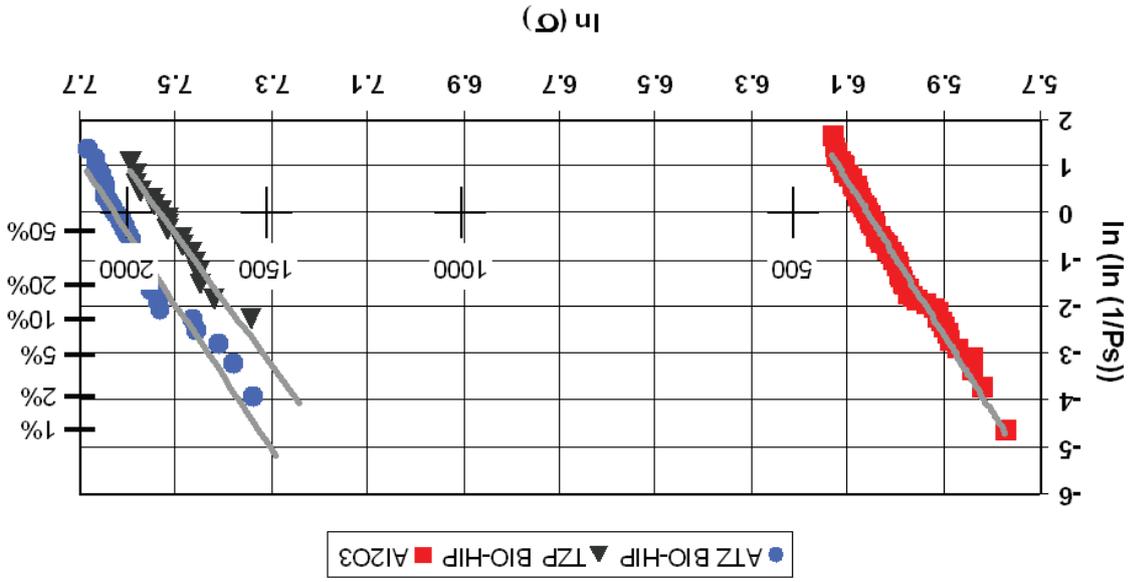
➔ reduced size of defects (in ultimate case: grain size) leads to increased strength of brittle ceramic materials (according to Griffith)



characteristic distribution of flaws in high tech ceramics



correlation of strength, toughness and critical defect size

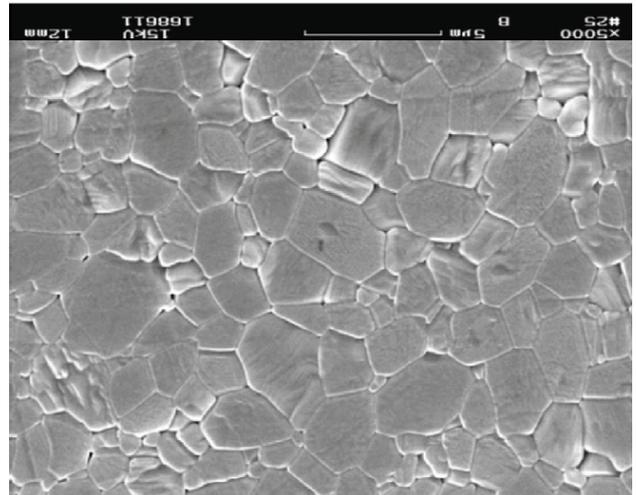
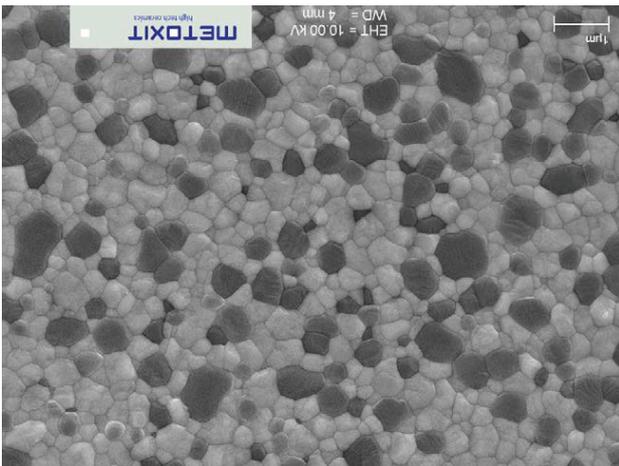


↪ bending strength as high as 2000 MPa achieved
 ↪ from microstructured to nanostructured ceramics

Future potential of nanoceramics

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Empa Lab: High Performance Ceramics



↪ microstructure decreasing from 1 µm to 0.3 µm using nanopowders
 as starting material

Future potential of nanoceramics

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Ceramics and nanoparticle technology

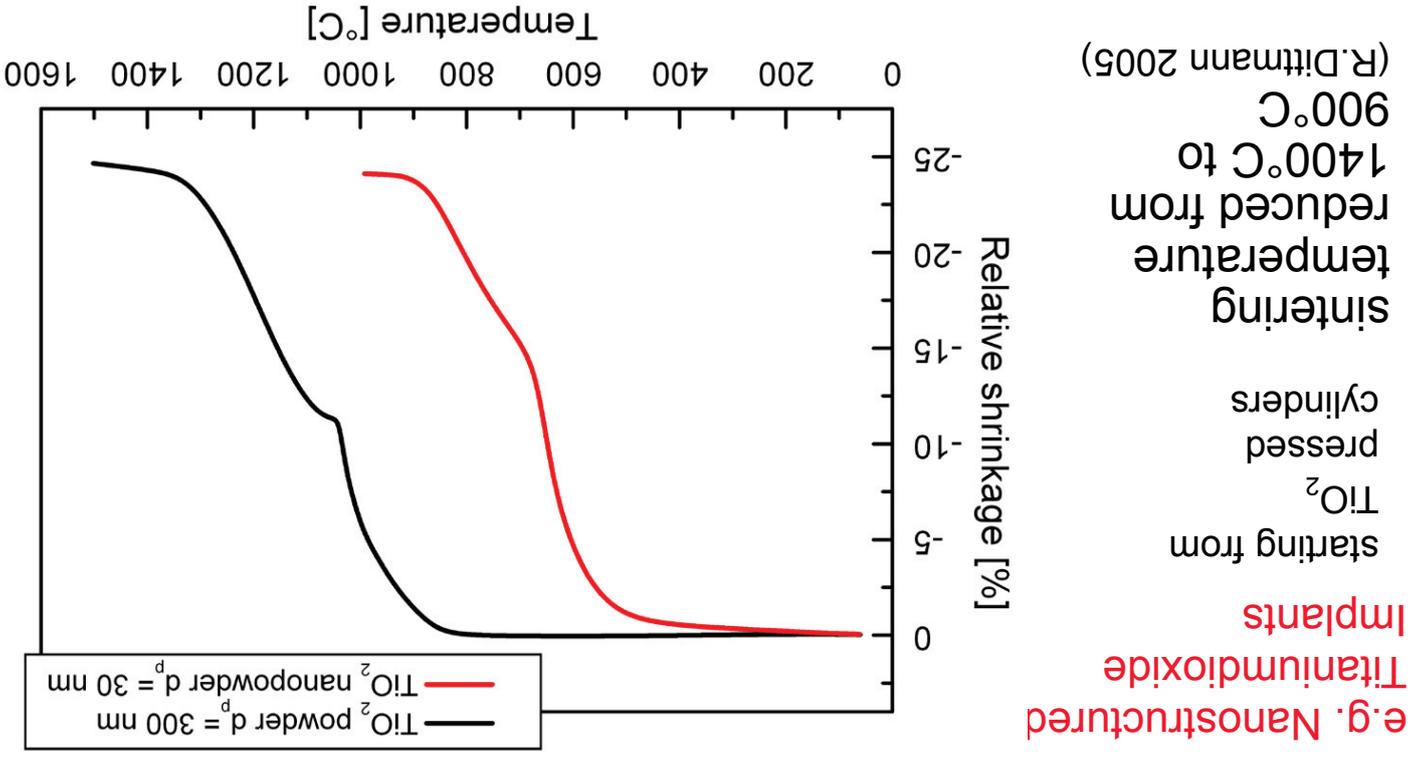
Potential of nanoparticles in ceramics and related fields

- monolithic nanostructured high strength ceramics
- polymer ceramic nanocomposites for medical implants and scratch resistant clear lacquers
- nanopowders for photocatalytically active coatings
- in energy production (SOFC) and storage
- in nanofiltration technology

Motivation for nanopowders in ceramics

⇒ Nanopowders

↪ lower sintering temperature; smaller grain size



Nano particle synthesis

• Nano milling

• Aerosol

• Sol-Gel

• Hot-Wall Reactor, Furnace

• Electron Beam

• Laser

• Plasma

• Flame Aerosol

+ simple process, rather cheap
- limited to > 100 nm

+ low temperature

+ controlled particle size

+ in-situ coating

- aqueous dispersions

- soft particles

+ dry powder

+ high production rate

+ oxide/non-oxide particles

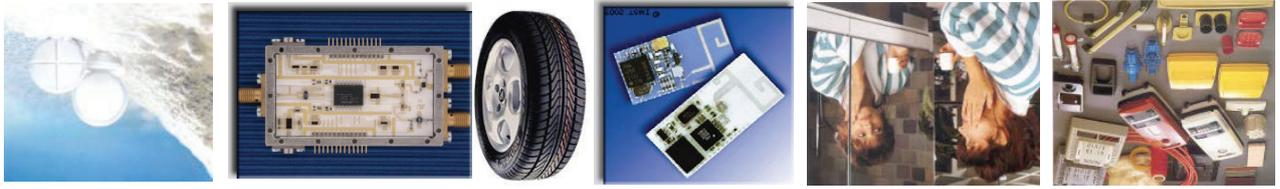
- energy input

- particle aggregation

Routes

Nanoparticles in everyday life

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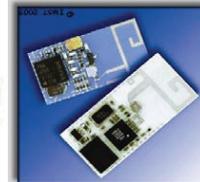
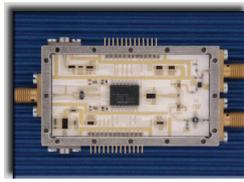
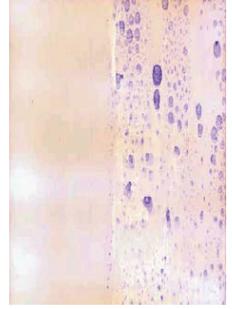
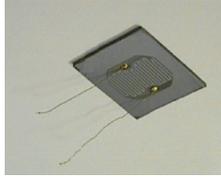


thickener / binding agent

reinforcement

catalyst / sensor

electronic components



But:

⇒ Nanopowders

Nanoparticles - dwarfs with a giant's force

- dry nanoparticles agglomerate strongly (low powder packing density)
- well dispersed nanoparticles are invisible (no visible light scattering, if < 50 nm)
- nanoparticles form reversible networks (thixotropy/ shear thinning in ketchup or paints)
- nanoparticles may chemically aggregate to form stable structures (sol-gel-processes)
- nanoparticles may form thermolabile gels (curiosity)

↪ Demand for non aggregated and even non-agglomerated nanopowders

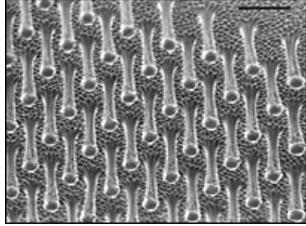
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Why strong agglomeration ⇔ Van der Waals forces between particles

Why not be SPIDERMAN???



Synthetic hairs

Juvenile Tokay Gecko (Gekko gekko)
Photo by: Greg Christenson ©2002



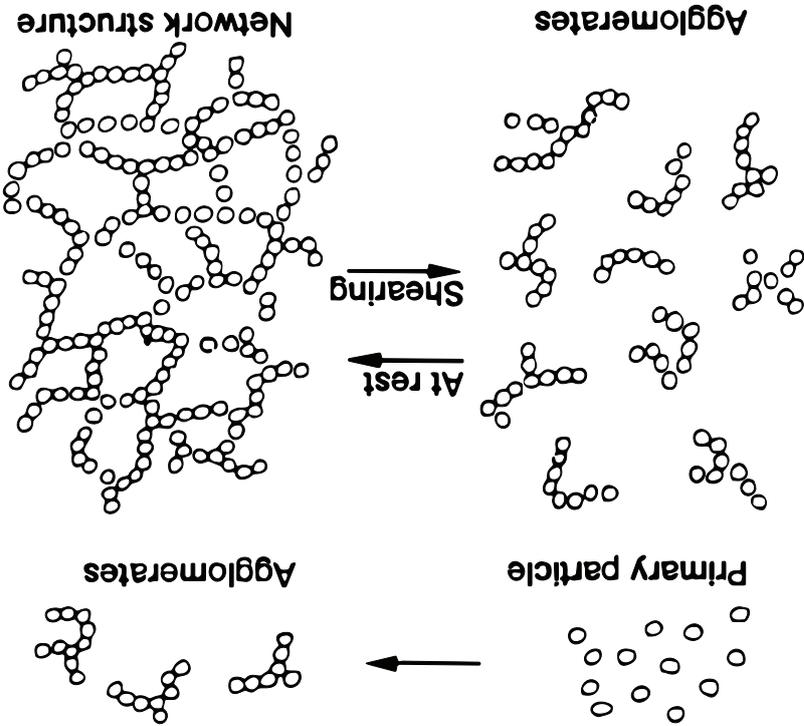
The trick of the gecko:
increase area of close contact
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Spiderman weighs
40 grams

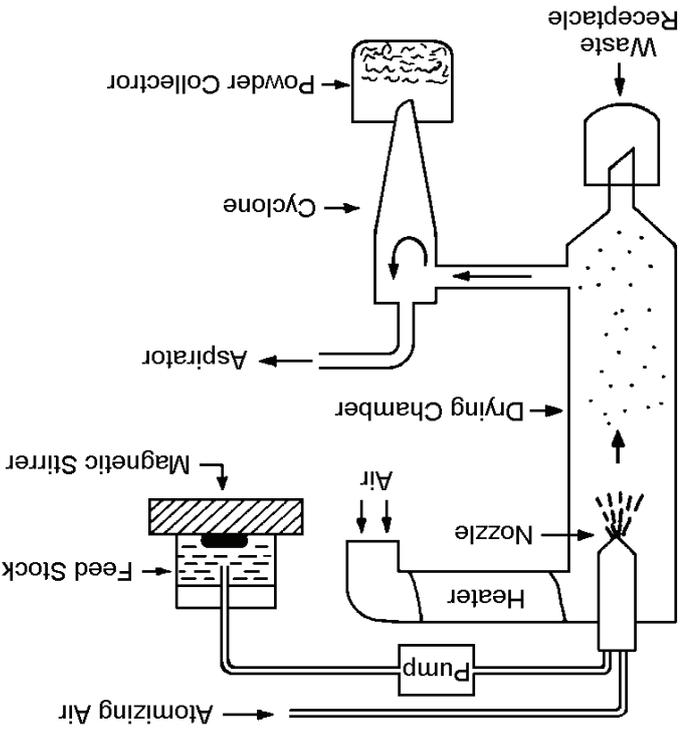
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Handling of nanopowders: Thixotropy and gelation ==> network formation of nanoparticles in dispersion



Processing steps for spray granule preparation

- dispersion of ceramic starting powder in water (typ. 30 vol.%)
- addition of required additives e.g. stabilisers and binders and homogenisation of dispersion
- dewatering and granulation of dispersion in a spray dryer
- ↳ - storage/transportation of pressing granules (conditioning; humidity!!!)



lab size spray dryer

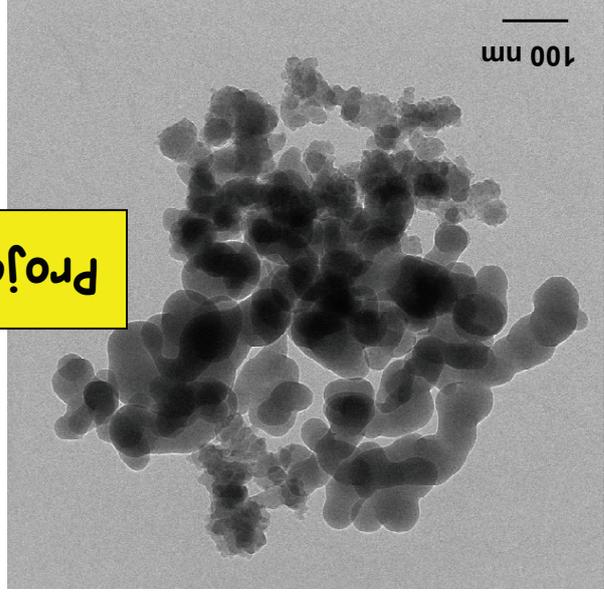
Additives for spray granulation

- dispersant/difloculant for deagglomeration
- binder to increase green strength; handling / machinability of green parts
- plasticizer for modification of binder properties
- anti foaming agent to avoid gas bubble formation during spray drying (← uniform granules)
- lubricant for reduced friction between granules and pressing mould
- preservatives to prevent biological degradation of organic additives in granules

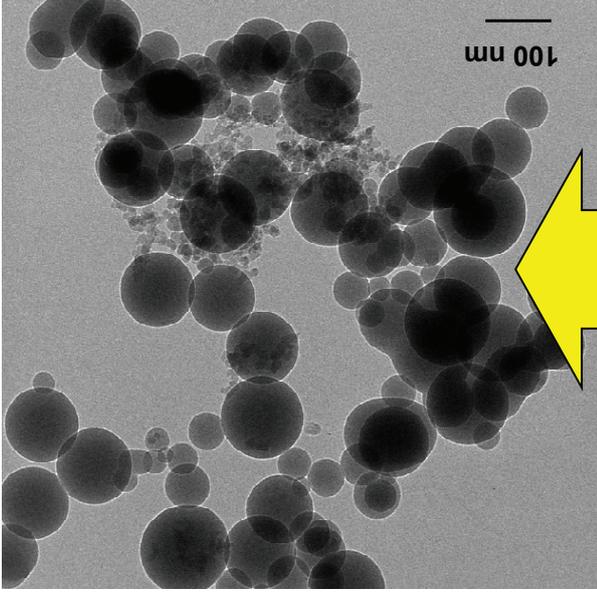
Objective

Non-aggregated silica; preparation and surface modification

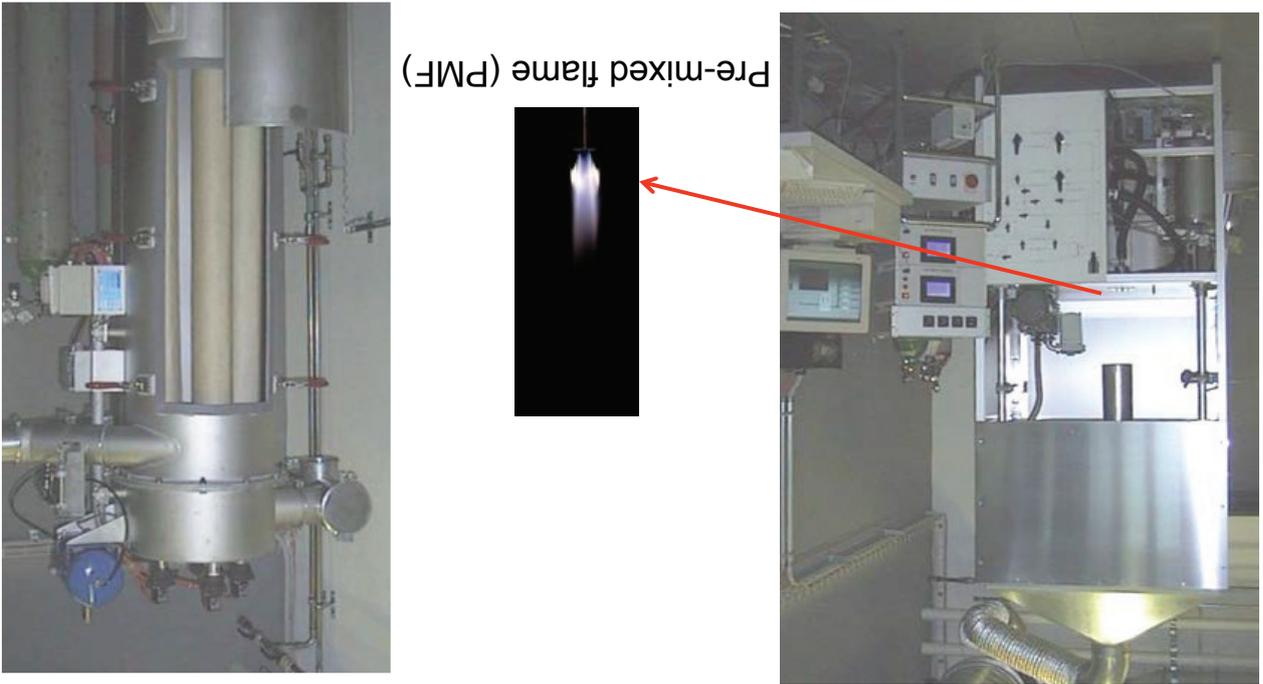
Aggregated SiO_2
 e.g. Aerosil OX50, $50\text{m}^2/\text{g}$, $d_{\text{equiv}}=55\text{nm}$



Non-aggregated SiO_2
 $37\text{m}^2/\text{g}$, $d_{\text{equiv}}=74\text{nm}$

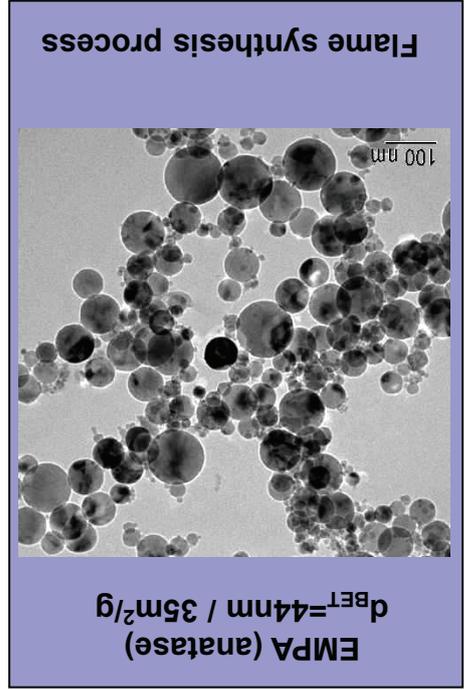


Synthesis of nanosized metal oxide powders

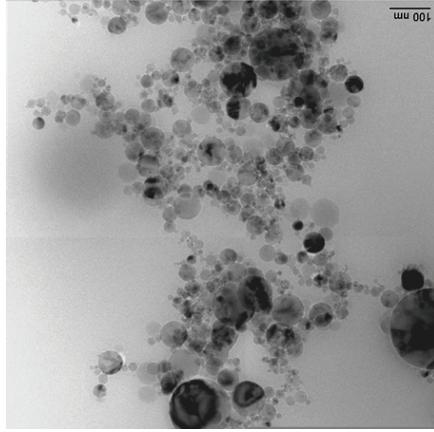


TiO₂ nanoparticles

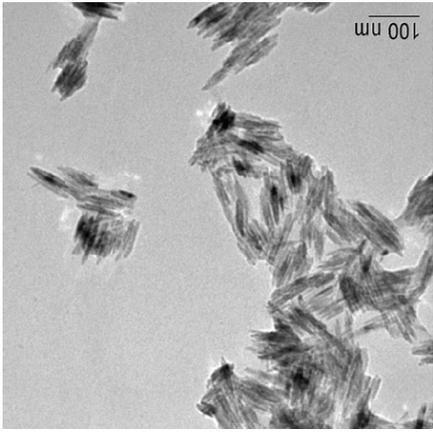
- Comparison



Commercial available anatase
d_{BET}=32nm / 45m²/g

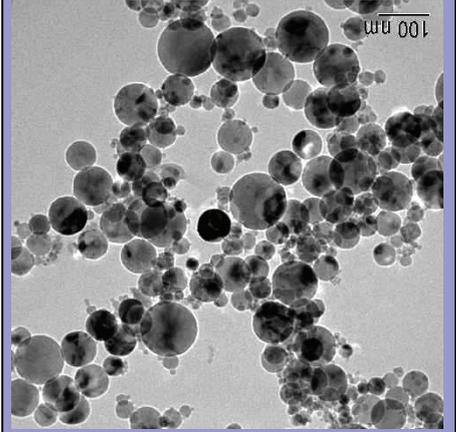


Alfa Aesar



Hombitec RM 400 LP

Flame synthesis process



Traditional ceramics produced from various, not well defined starting materials; densification by liquid phase sintering

Technical ceramics based on different oxide, nitrides and carbides with high purity; solid state sintering

Most important technical ceramics:
 alumina, zirconia (TZP, PSZ, FSZ), alumina-zirconia nanocomposites, barium titanate, silicon carbide, silicon nitride

Technical ceramics both for structural and functional applications (e.g. piezoelectric or ion conductive materials → SOFC)

Sintering mainly by solid phase; depending on dopants different phase compositions with tailor made microstructures

Summary ⇐

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powder production - functionalisation - composites - characterisation

- **Demand: from powders to solutions**
- **By flame spray synthesis more materials options e.g. ZrO_2 , CeO_2 , Al_2O_3 ; mixed oxides, perovskites, catalysts**
- **Production of metal oxide nanoparticles in a laboratory and pilot scale by flame gas synthesis**

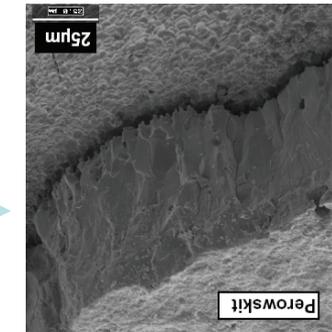
SiO_2 : 7 - 2600g/h TiO_2 : 3 - 1000g/h

Nanopowder production line at EMPA

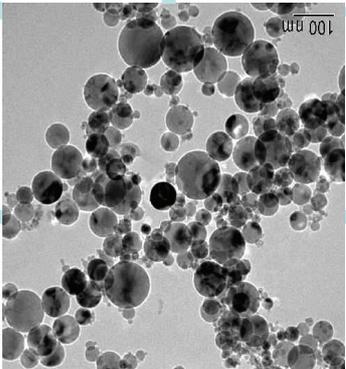
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Exploitation Potential for surface modified nanopowders

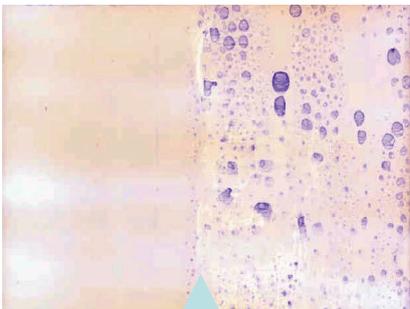
propellants



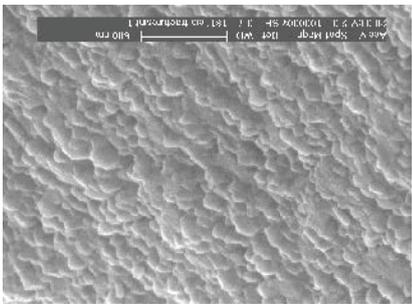
functional coatings



self-cleaning, anti-bacterial surfaces



nanostuctured
bulk ceramics



biocomposites for medicine