Summer School

Madrid 2015

Ceramic & Glass Science & Technology

Application to Bioceramics & Bioglasses

Processing: the industry point of view

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Common feature of technical ceramics ?

Materials of choice

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Image of ceramics ?

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Ceramic Processing

Clay Mining

Raw materials for porcelain

China clay Silica

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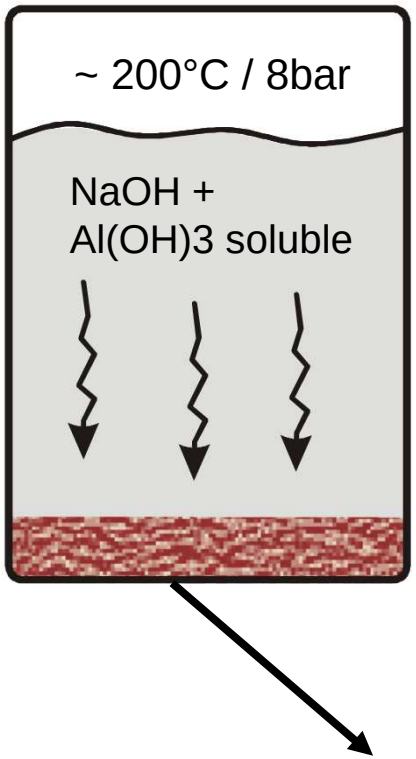
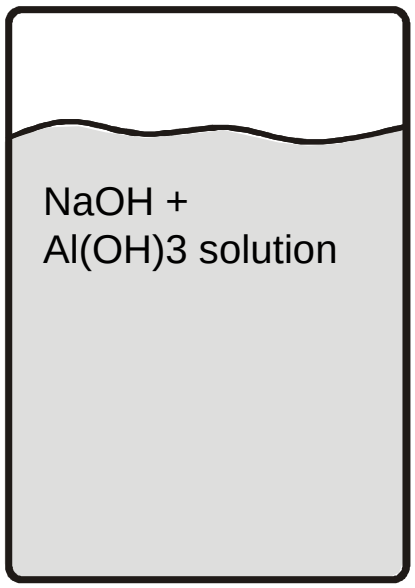
Bauxite Mining

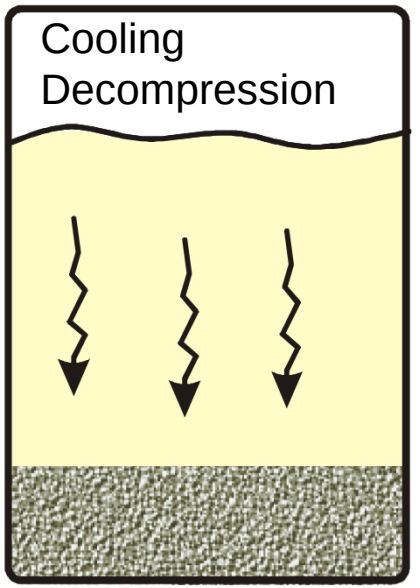
Purification of Alumina

Bauxite
= Aluminum hydroxide
+ Impurities
(Mainly Iron Oxide)



Red Mud
→ Waste





Aluminum hydroxide
precipitation

→ Calcination (furnace)

$$Al(OH)_3 \rightarrow Al_2O_3 + H_2O\uparrow$$

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Kolontar dam bursting

4. Oktober 2010, Kolontár, Hungary
Aluminum plant MAL AG

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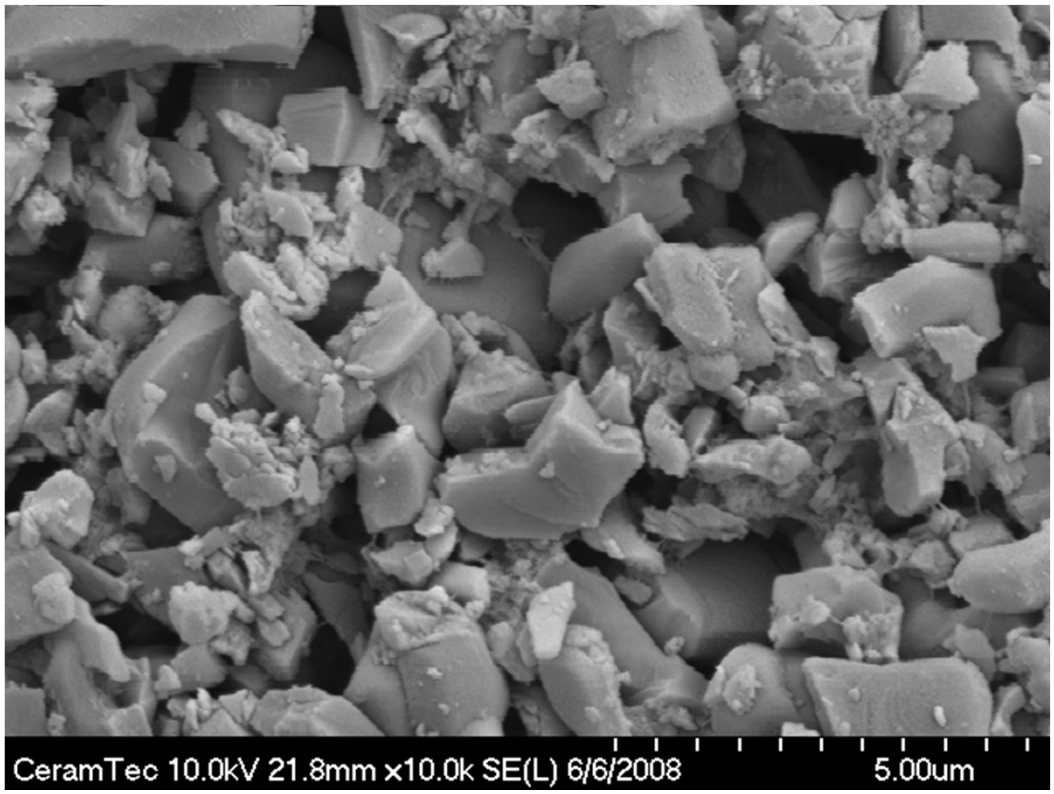
Low and High Performance Alumina Raw Materials



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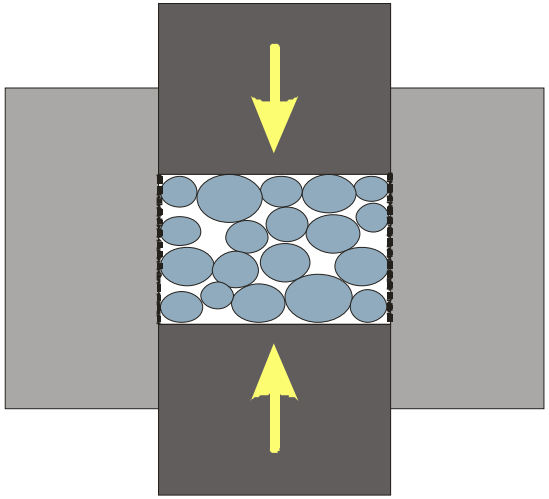
Conventional Ceramic processing

1. Raw Material

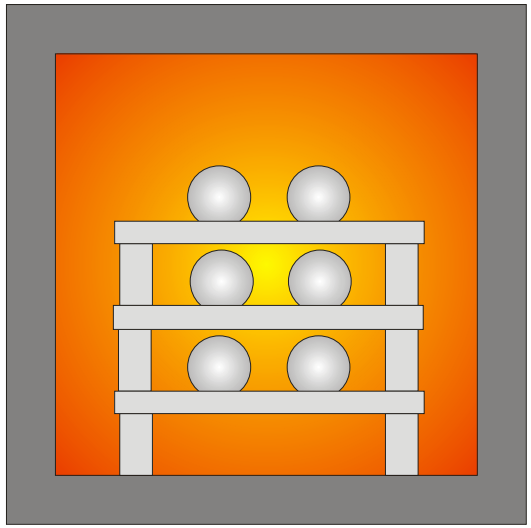
2. Ready to Press

3. Powder Pressing

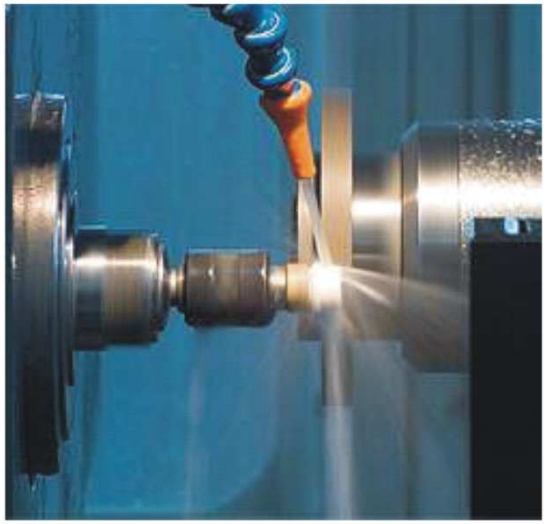


4. Green shaping

5. Sintering



6. Hard machining



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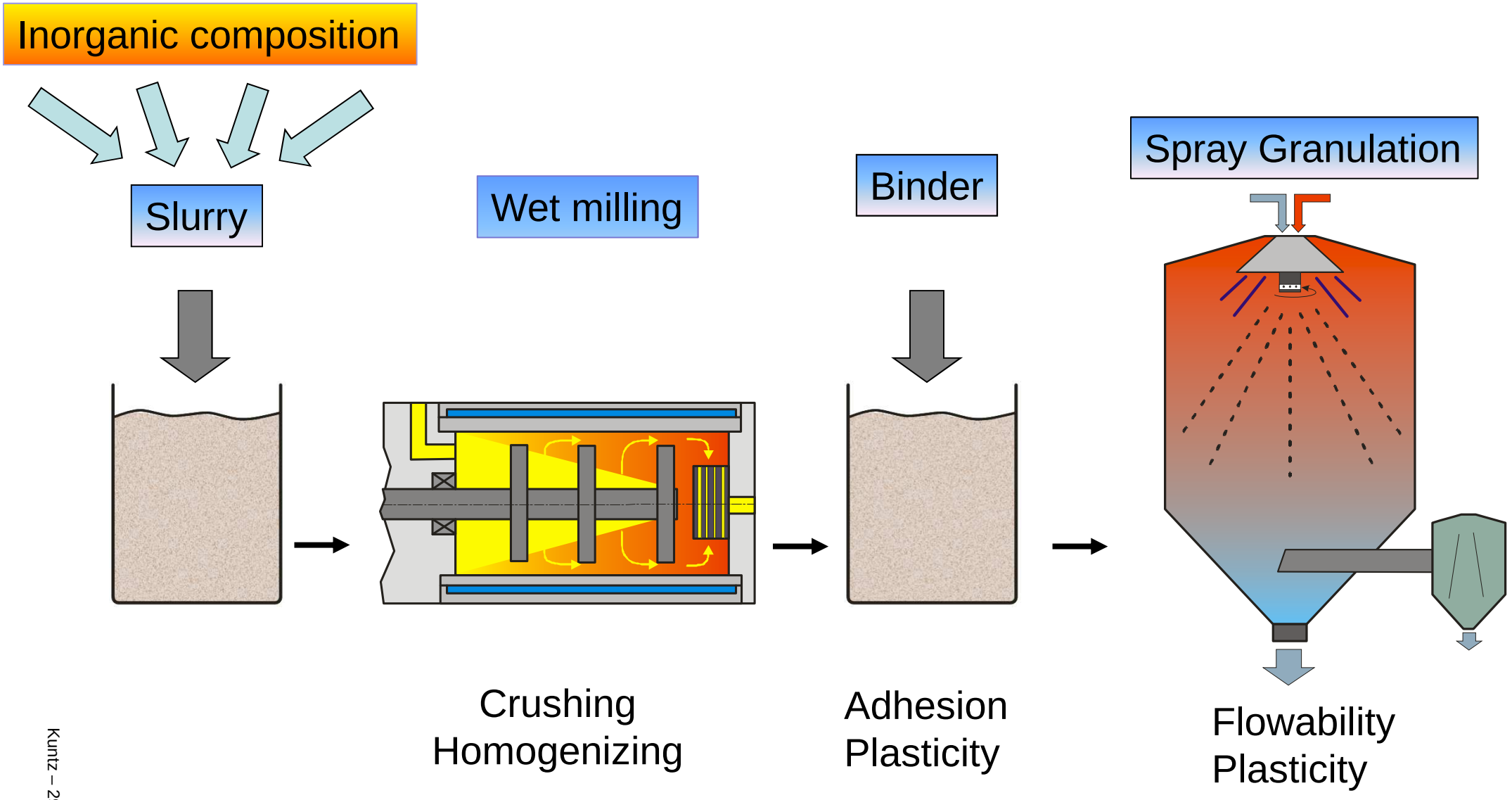
Preparation Ready-to-press powder



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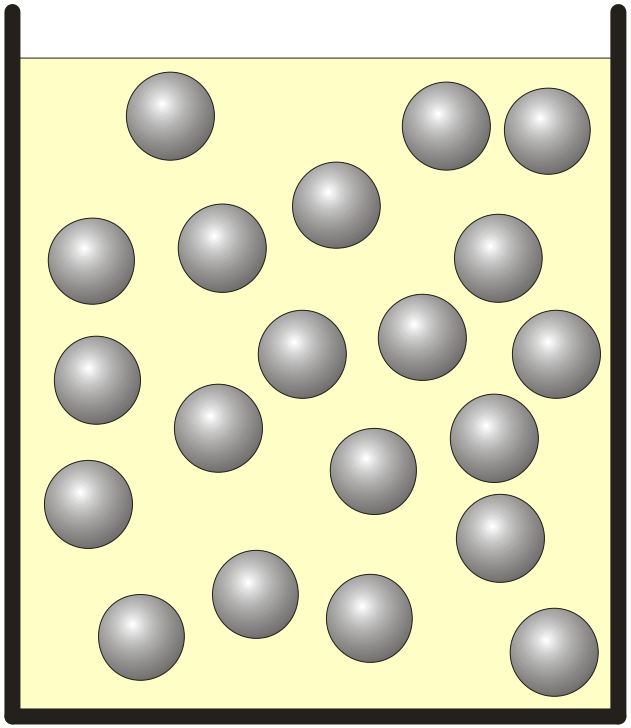
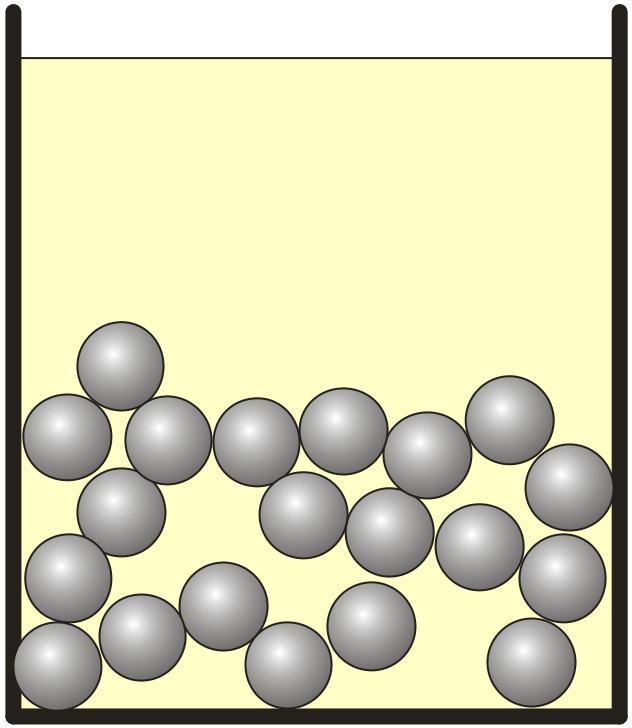
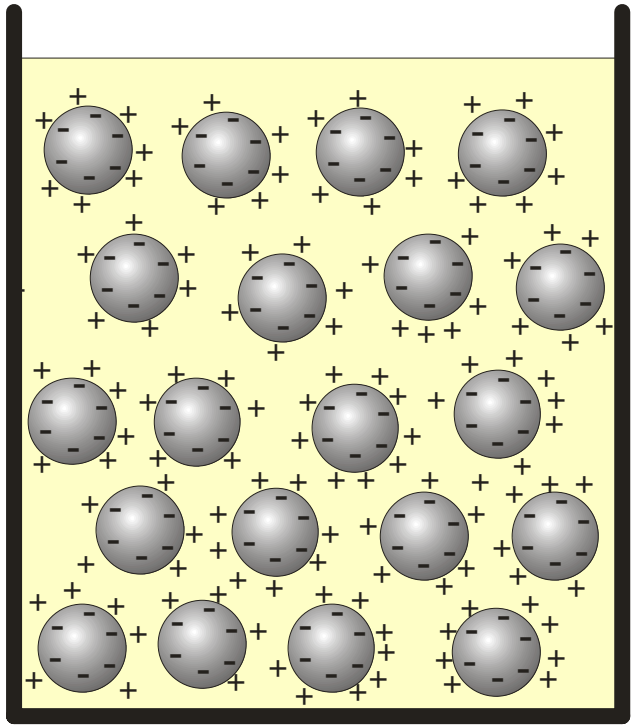
Slurry stabilization



Particles in water

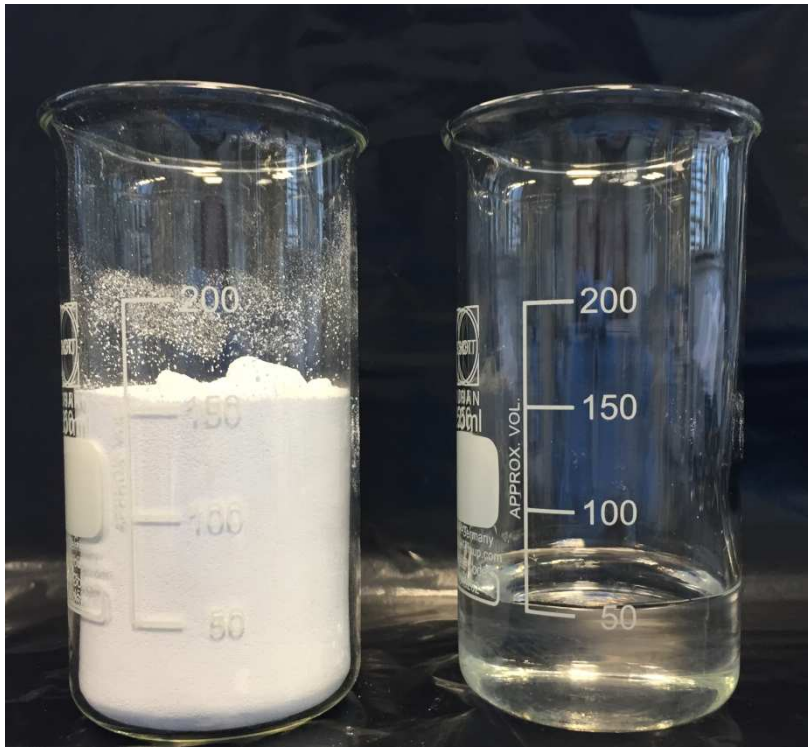


Sedimentation



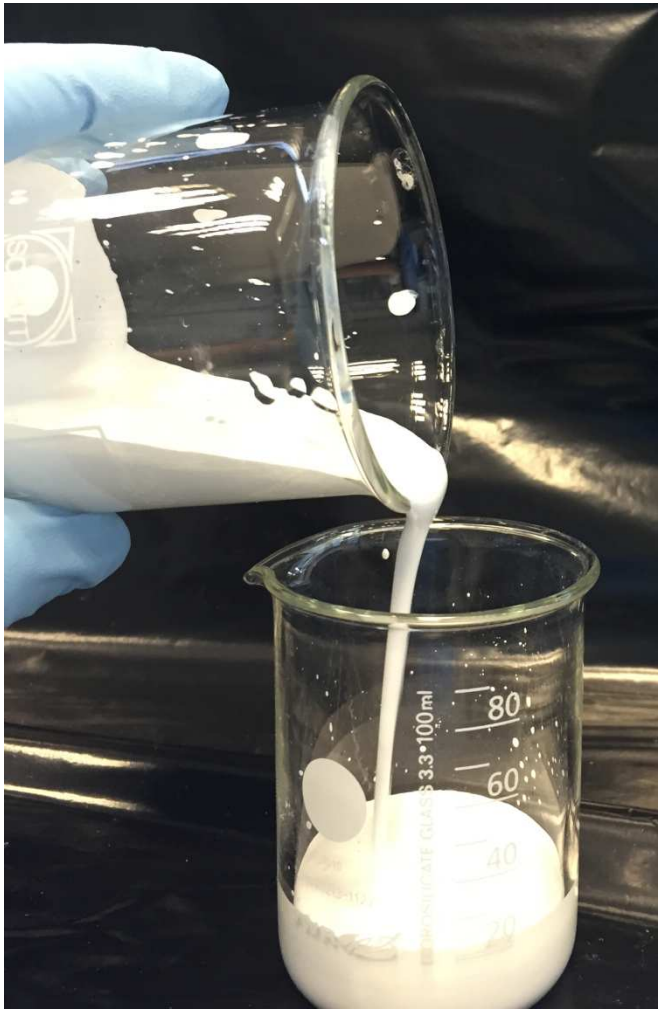
Electrostatic stabilization

Preparation of an alumina slurry



64 wt% alumina

Dispersant



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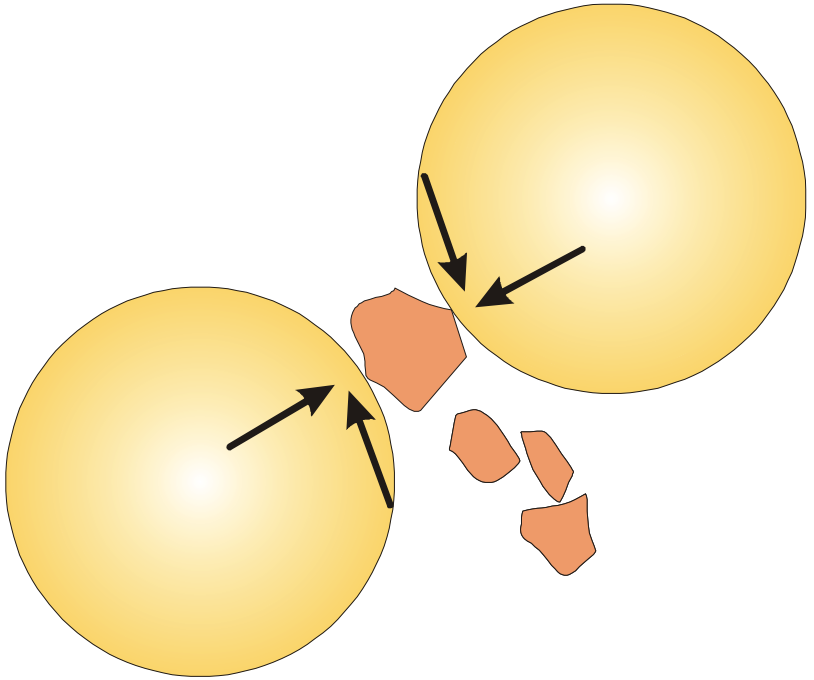
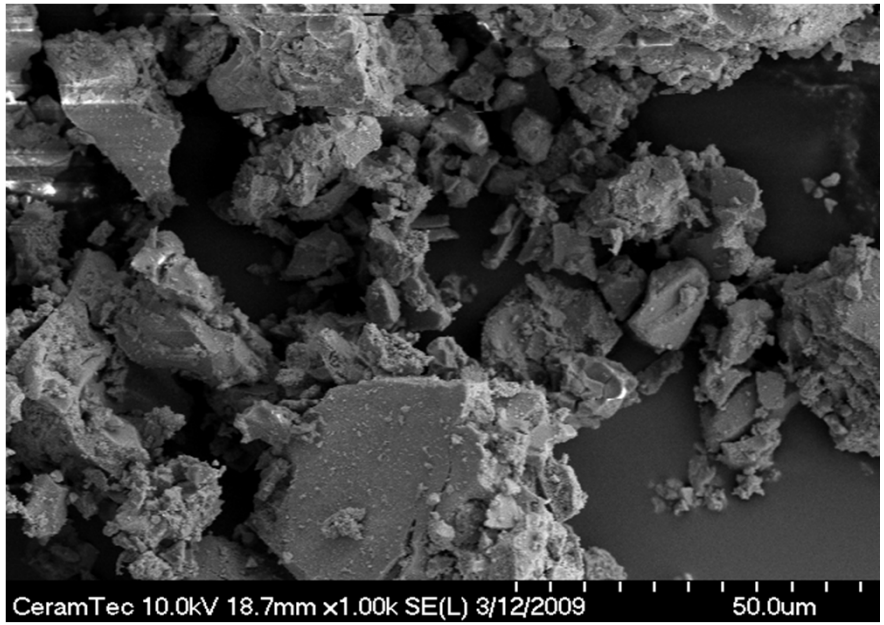
Milling

Milling balls diameter 50mm .. 0,05mm

Destroy Agglomerates and large crystals
Homogenize powder mixture
Mechanical activation





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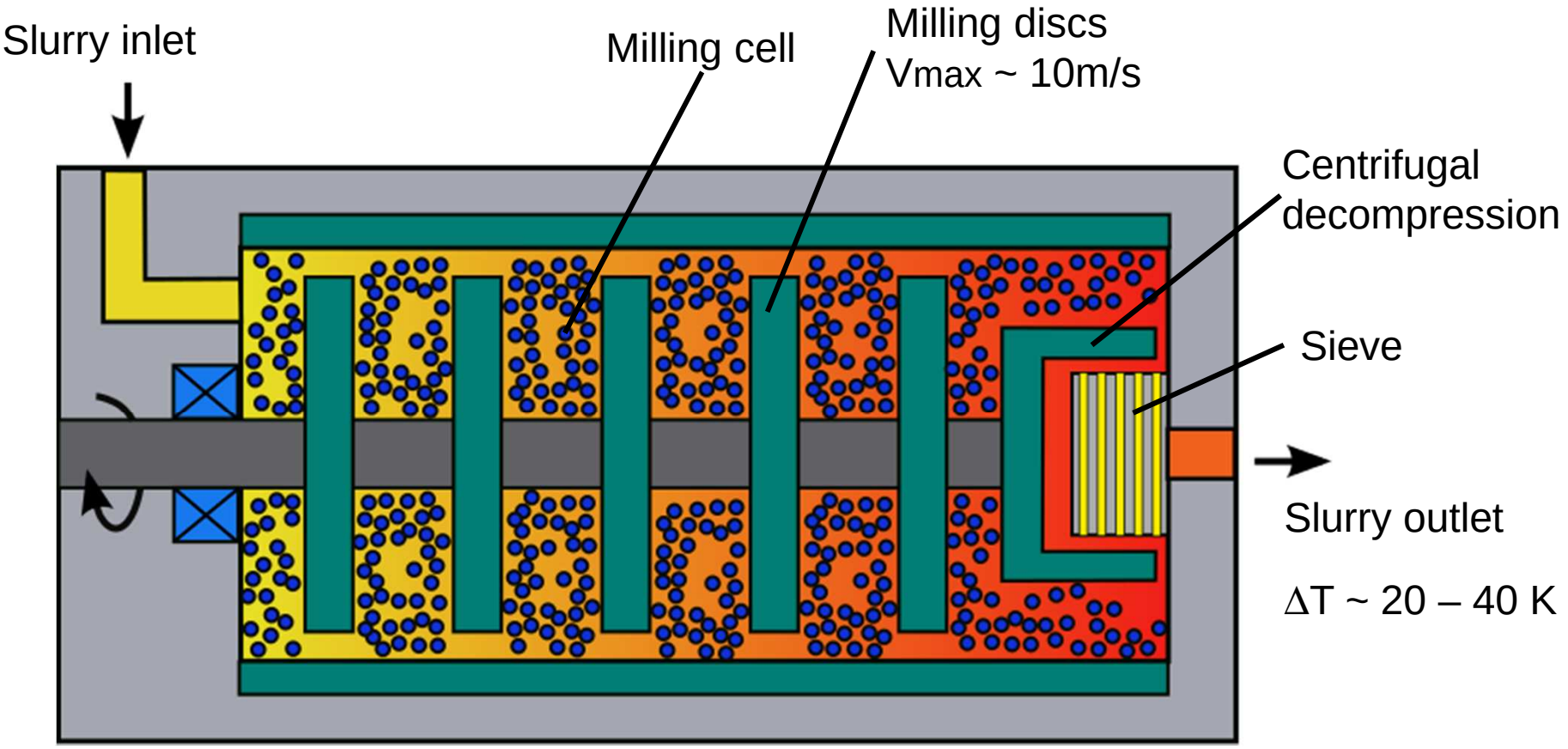
Wet milling



Specific energy up to 500 kWh / t

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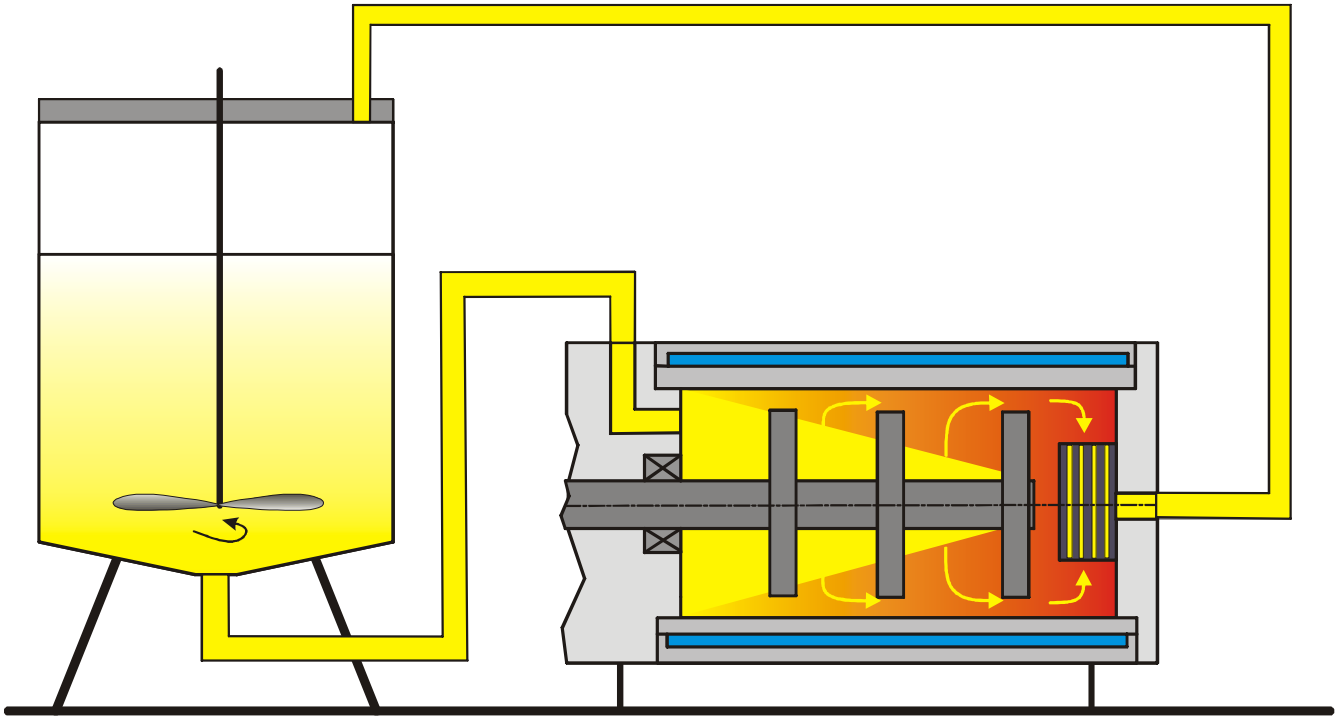
Wet milling
Circulation mode



Typical processing data:
Batch size 2000 kg
Milling energy 1000 kW h
Duration 5 days
Passages 20

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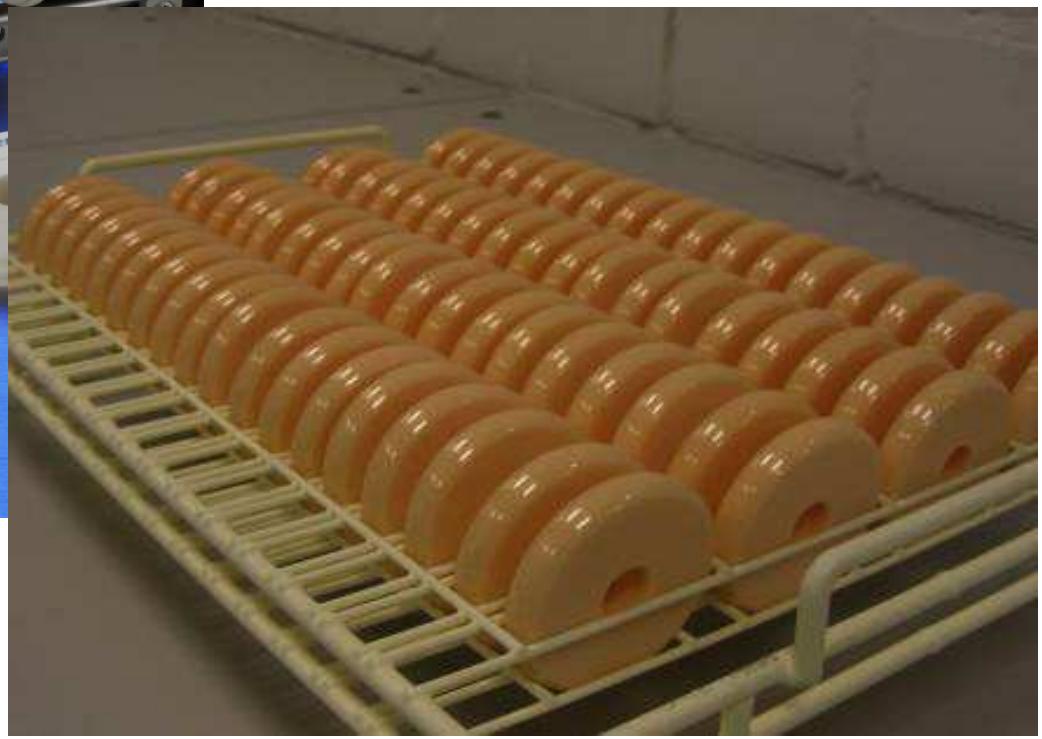
Example for milling parameter development: Textile ceramics



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Surface quality

Final density, grain size, machining

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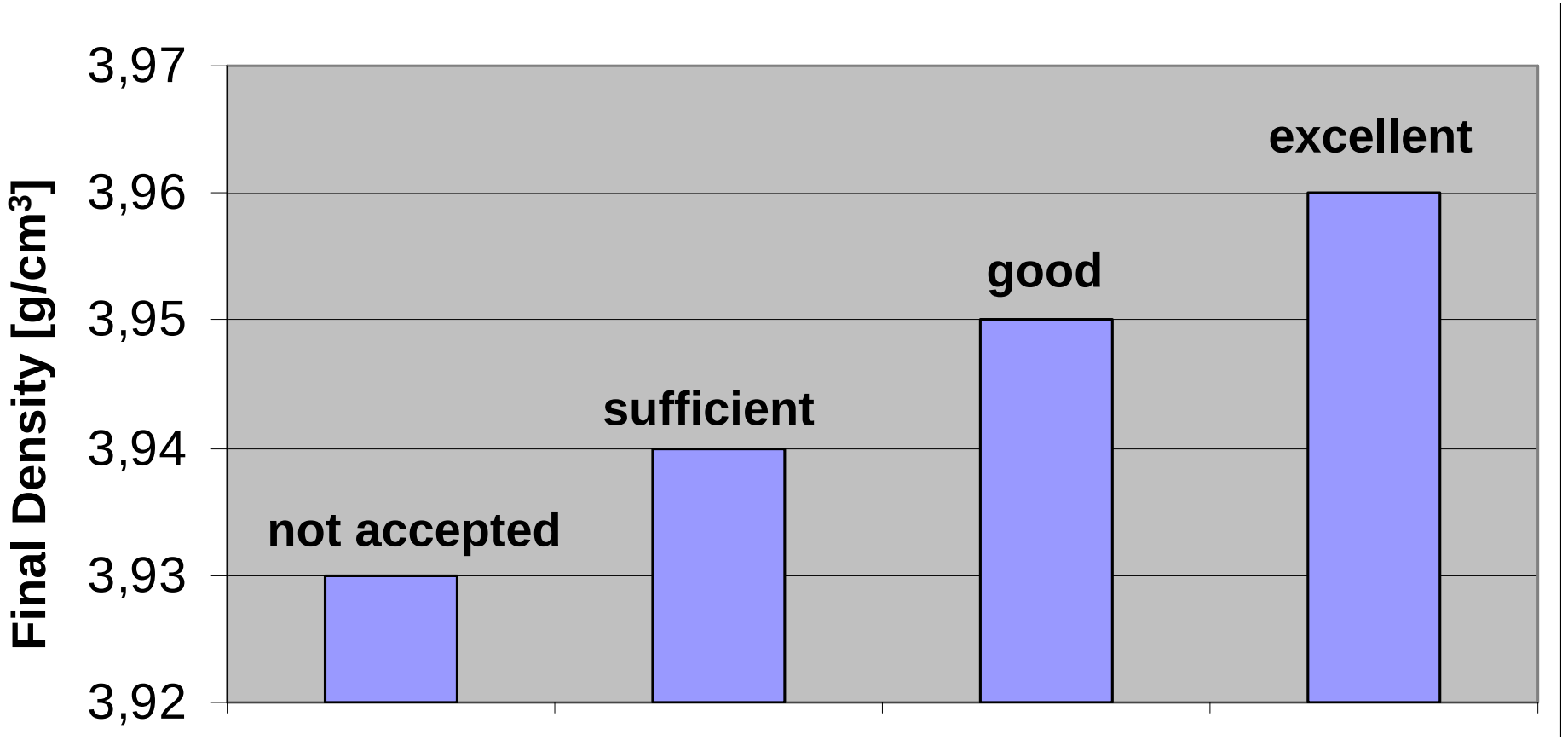
Assessment of „Final Density“



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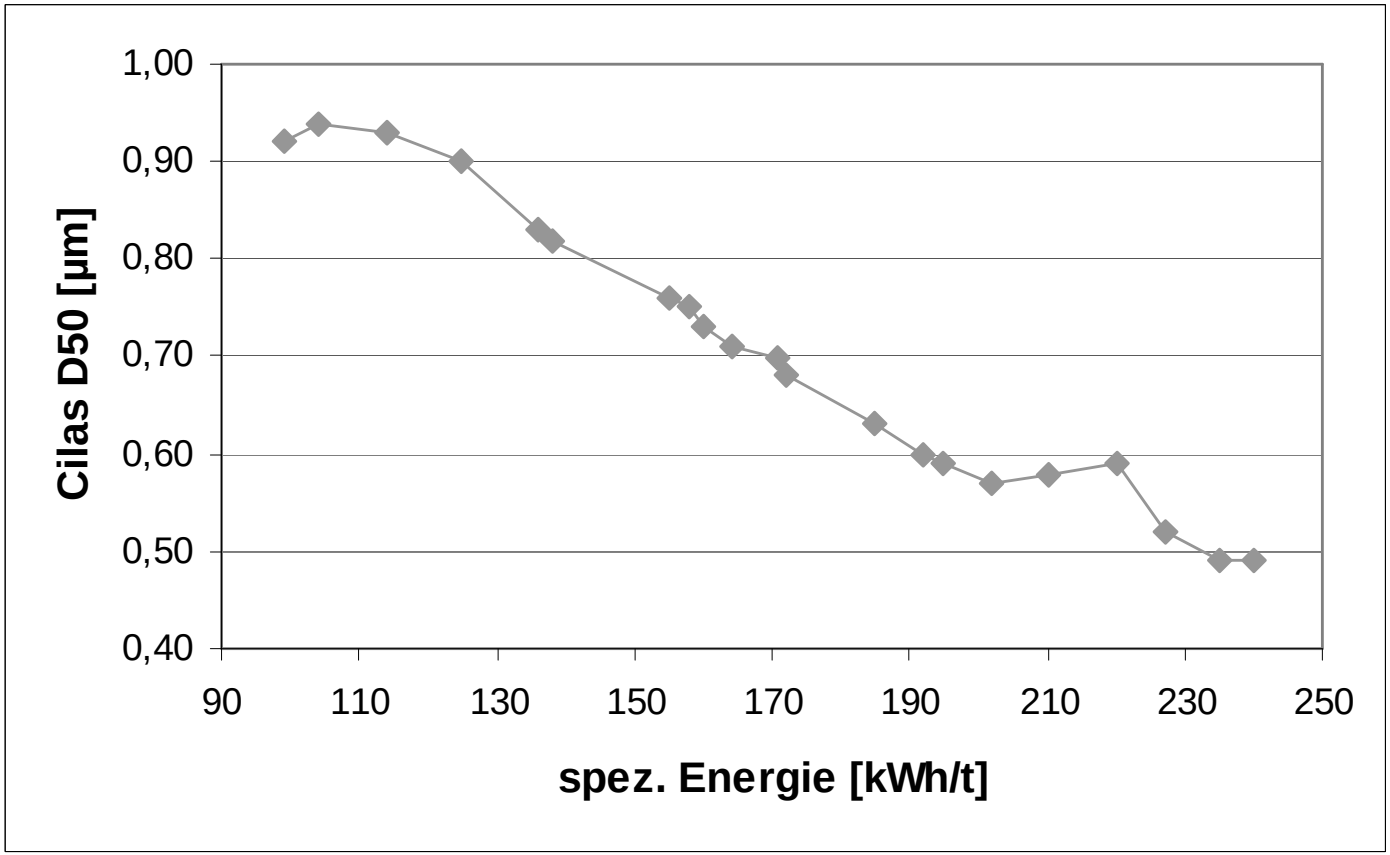
Particle size control at milling

Possible control parameters

1. Specific surface(BET)
2. Grain size
3. Milling energy



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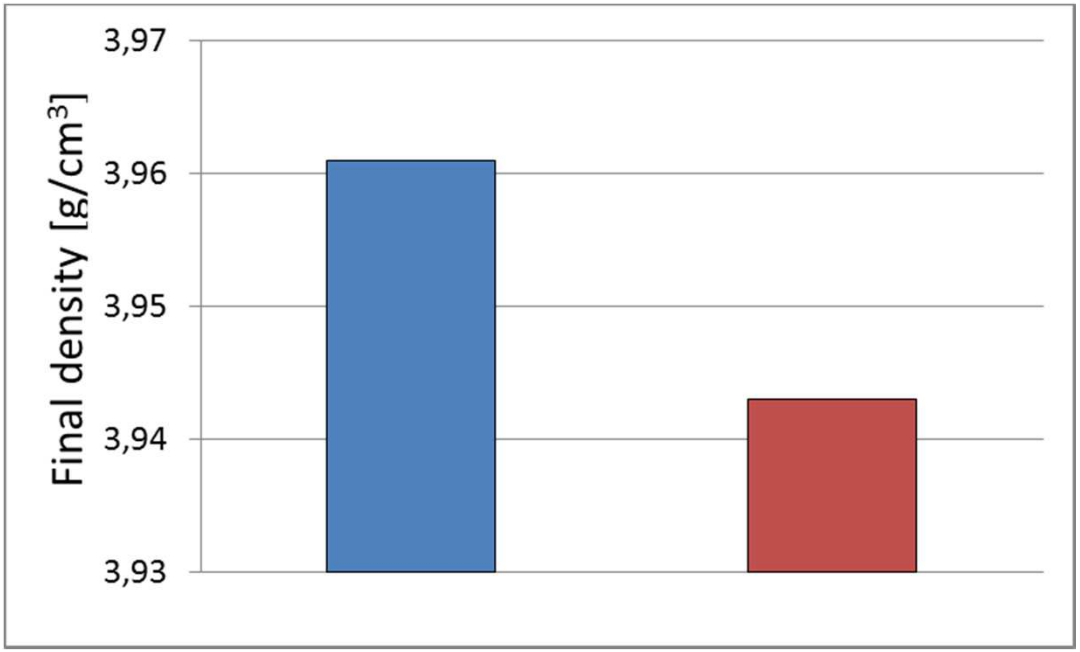
„Mechanical Activation“

Correlation of sintering density and milling parameters ?



D10 [µm]	0,14	0,12
D50 [µm]	0,48	0,46
D90 [µm]	1,03	1,02
BET [m^2/g]	9,4	12,3

Sintering acivity ≠ f(particle size)
→ technology / development

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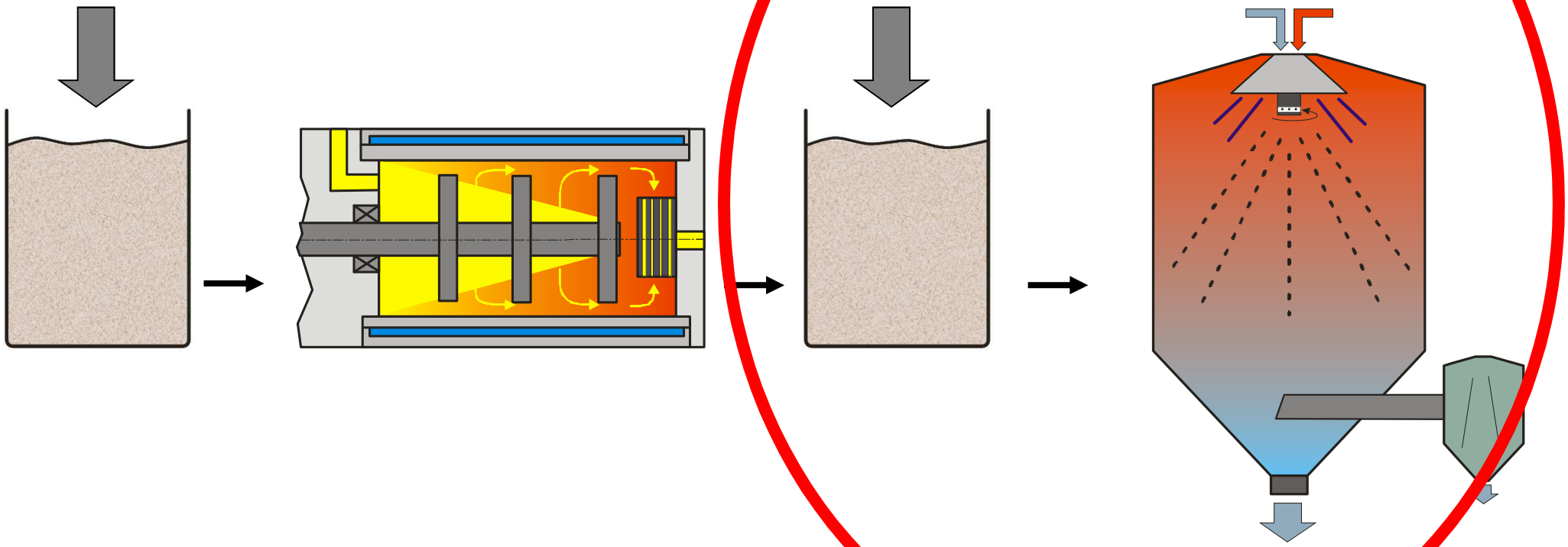
Preparation
Ready-to-press powder

Slurry

Wet milling

Binder

Spray Granulation



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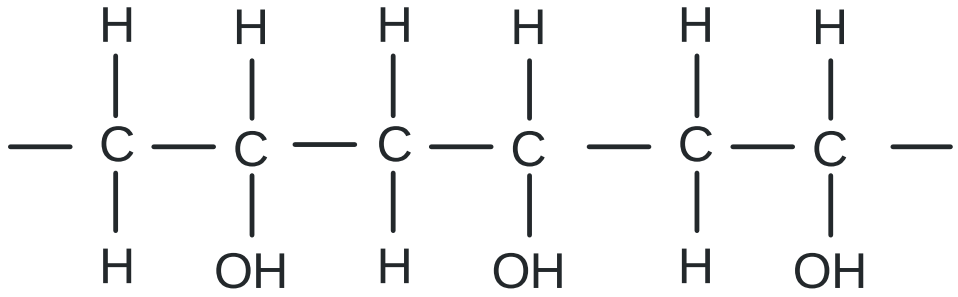
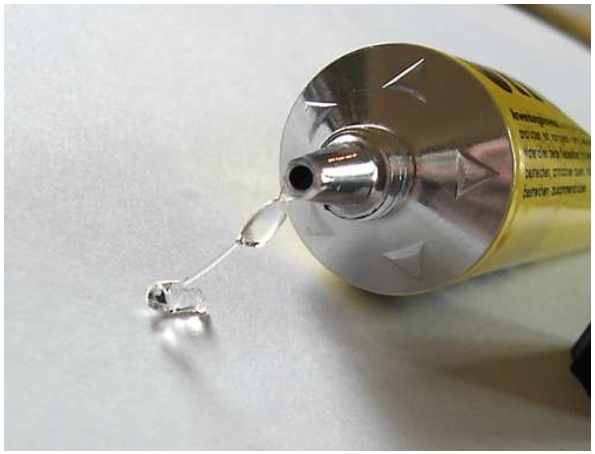
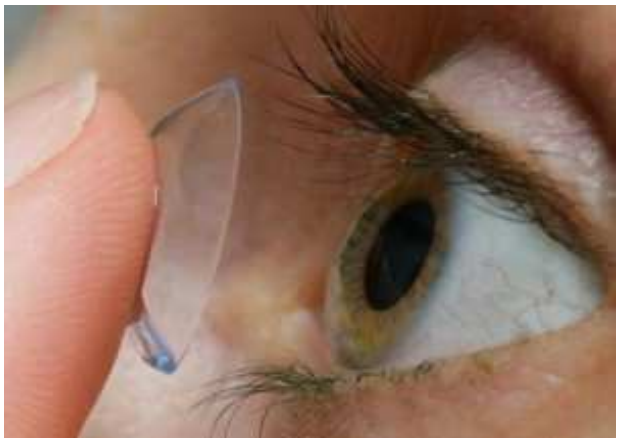
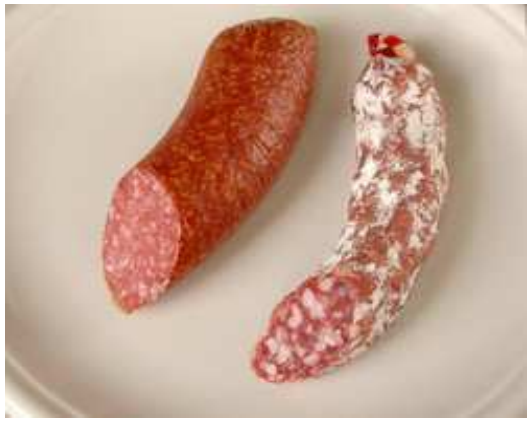
Example for binder: Polyvinyl alcohol

usw.  *usw.*







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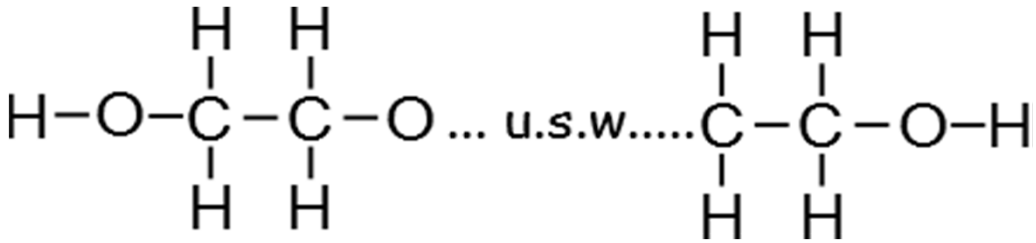
Polyethylene glykol



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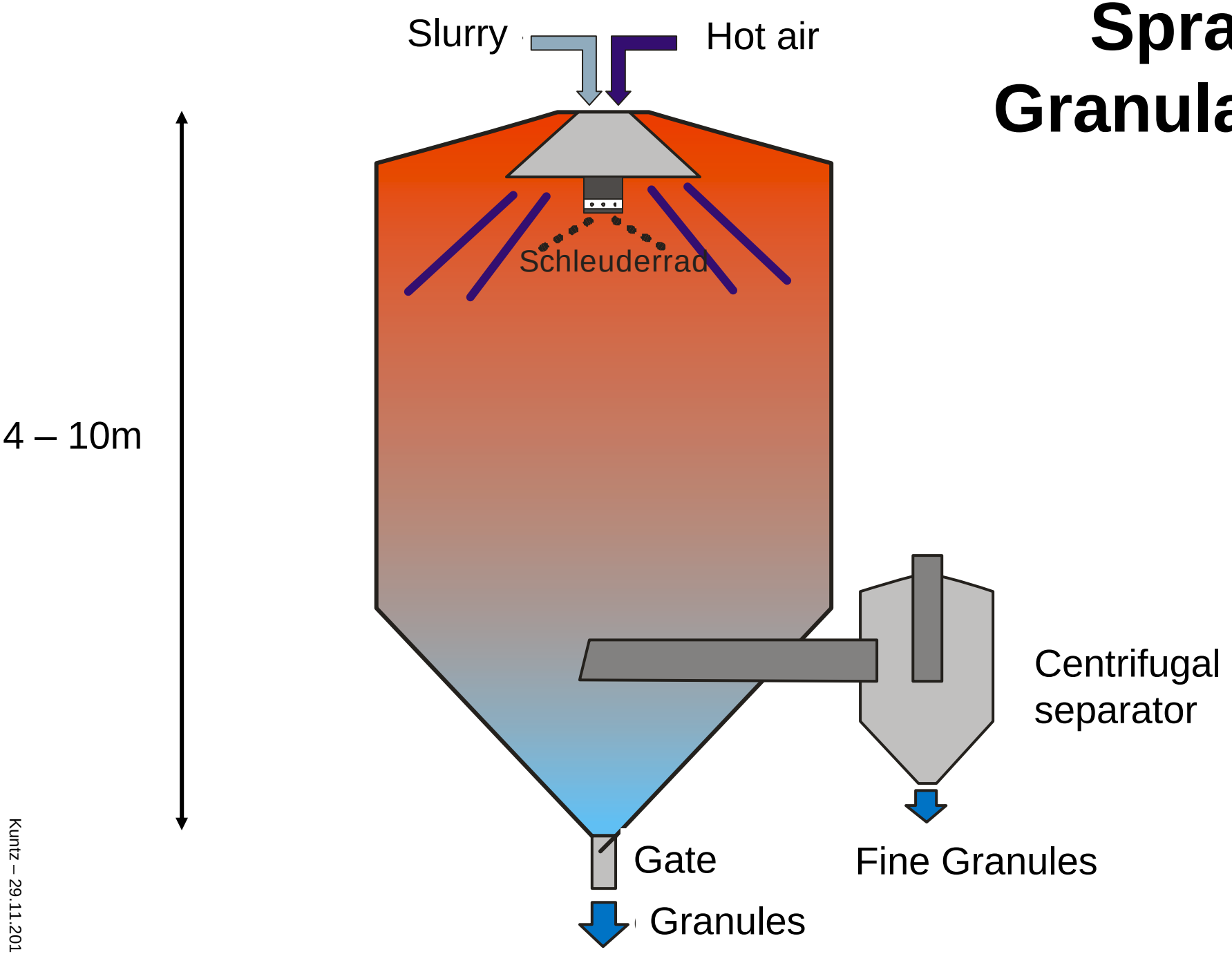
Spray Granulation



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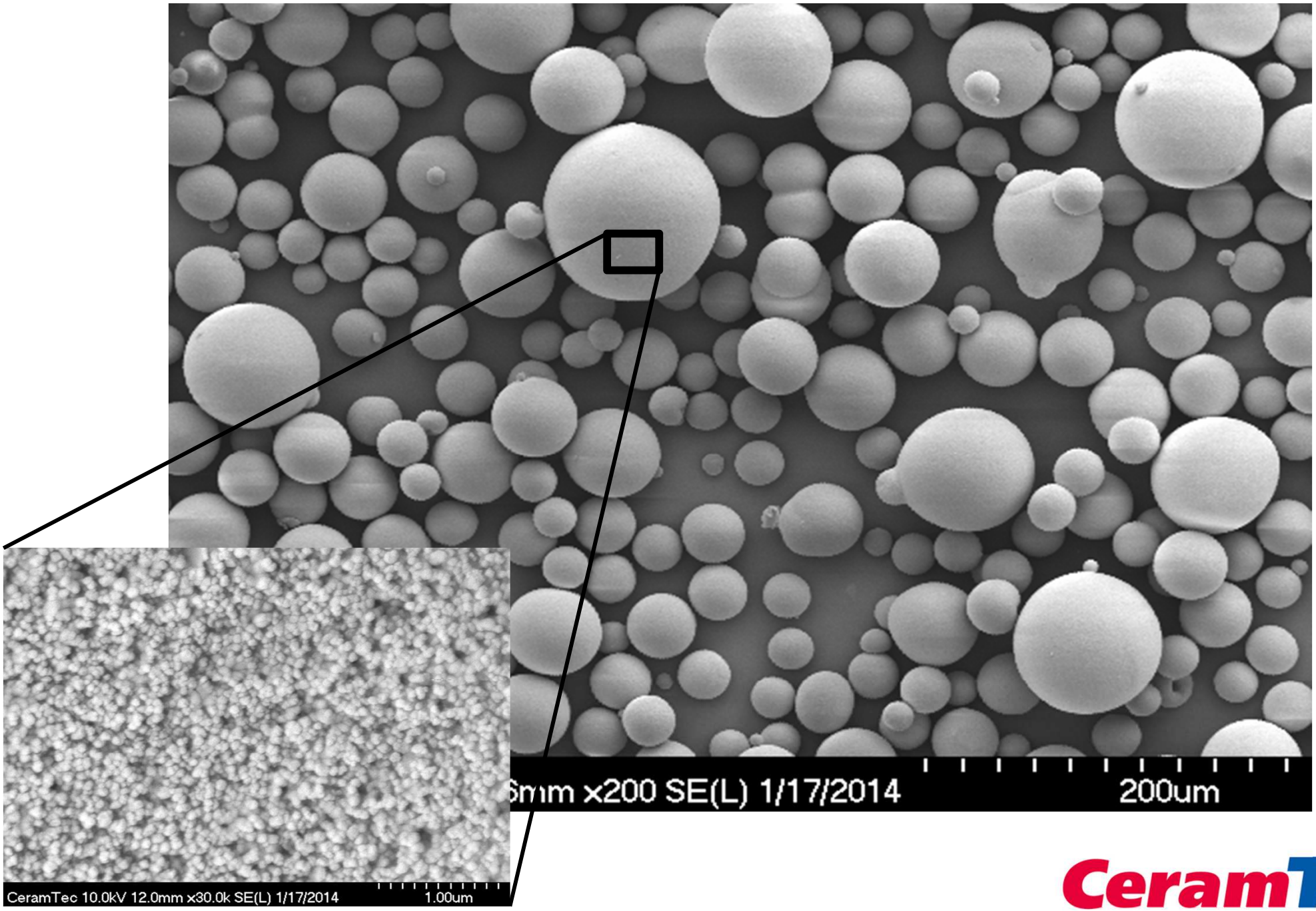
Granules



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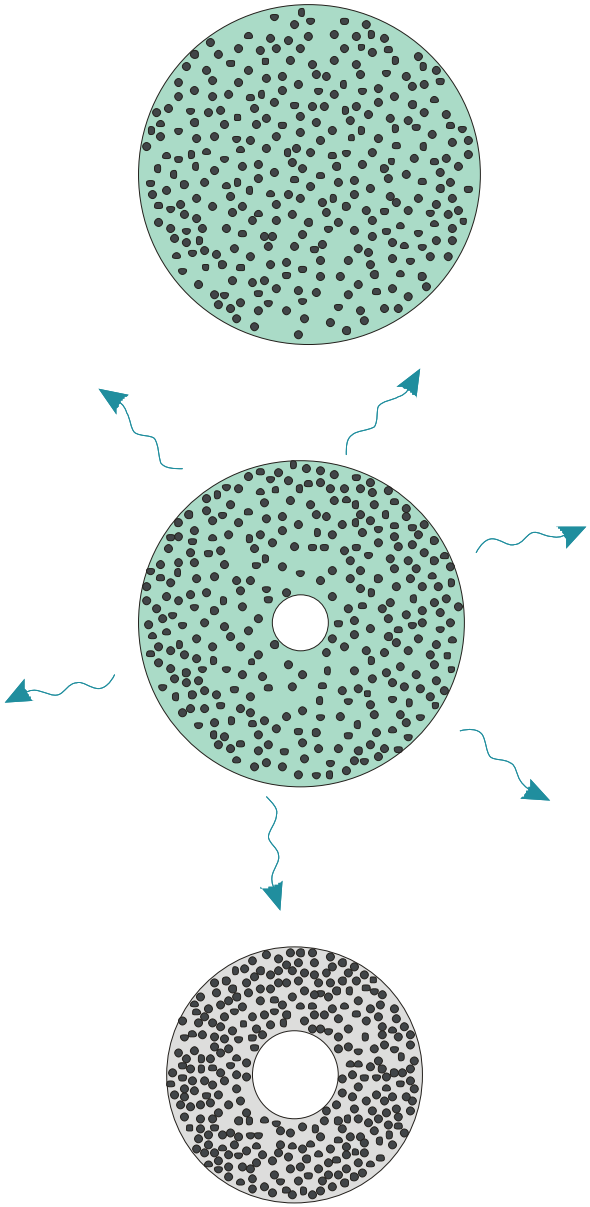
Droplet drying



Slurry droplet
Water + ceramic particles + binder
Distributed homogeneously

Water evaporation
Droplet shrinkage
Pore formation

Dense package,
Stop of particle mobility
→ Undesired shape of granule

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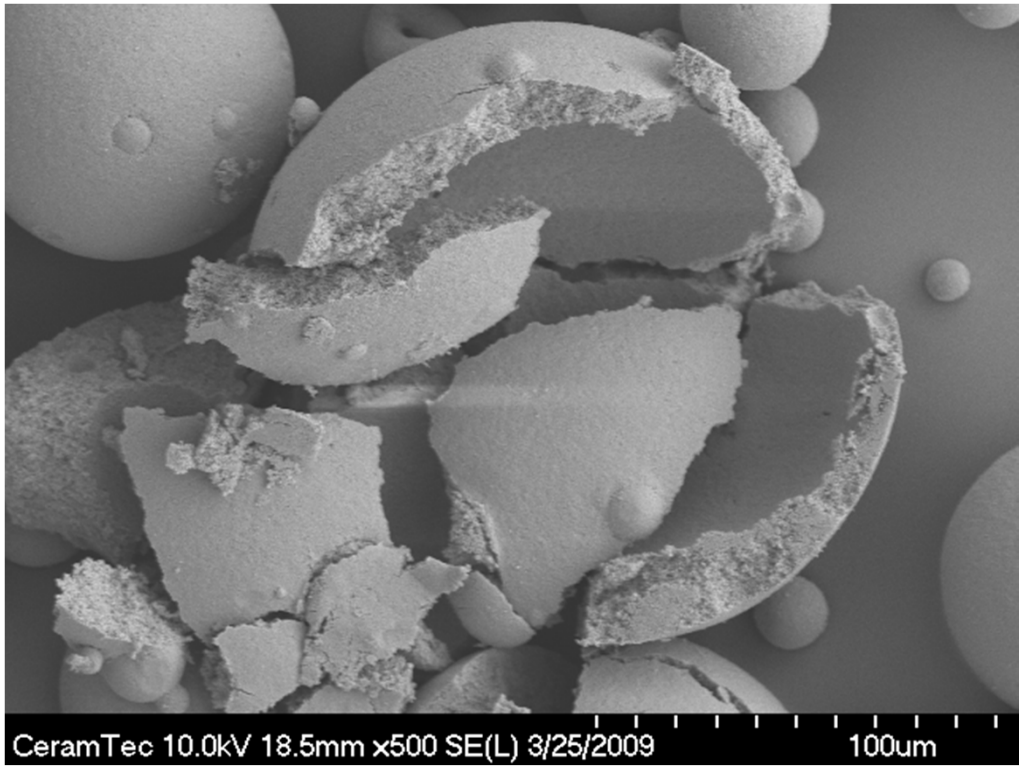
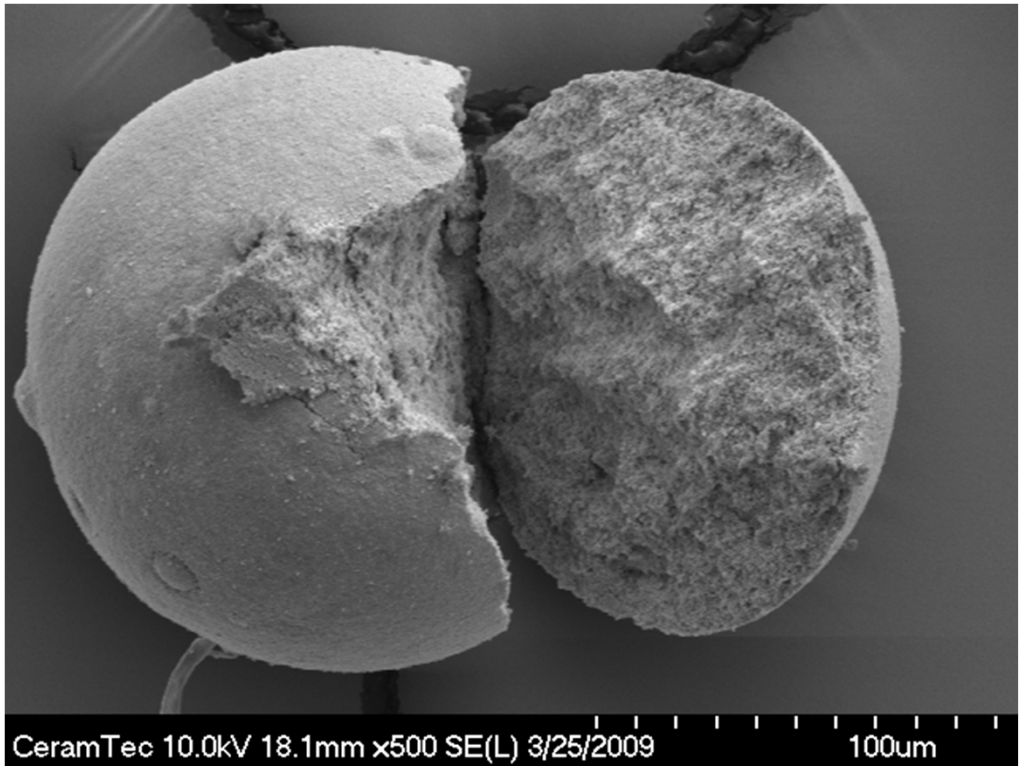
Granules

Hollow



Homogeneous



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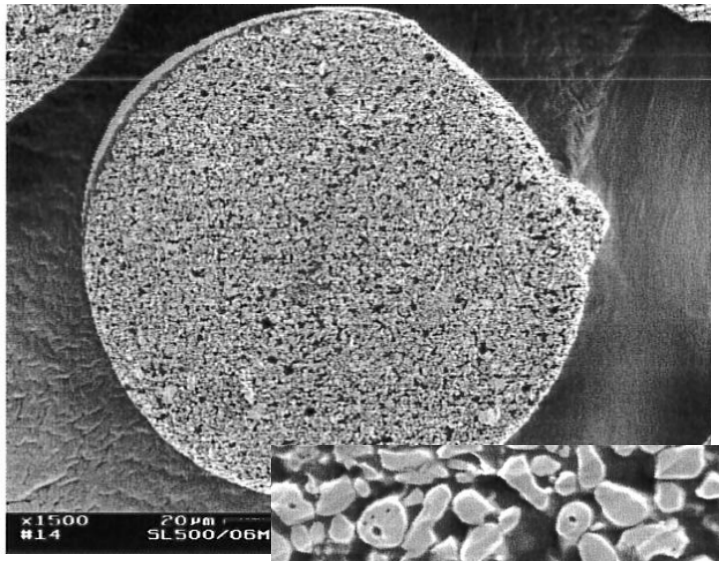
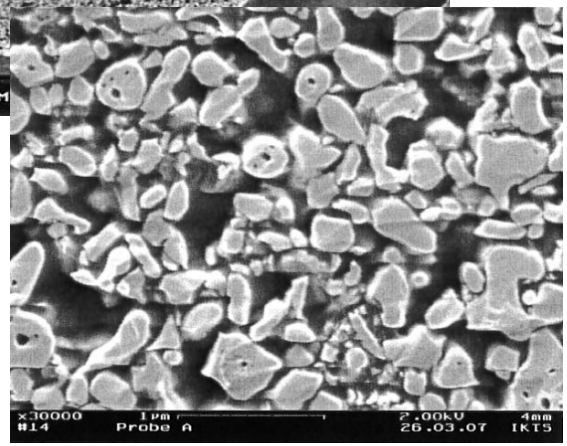
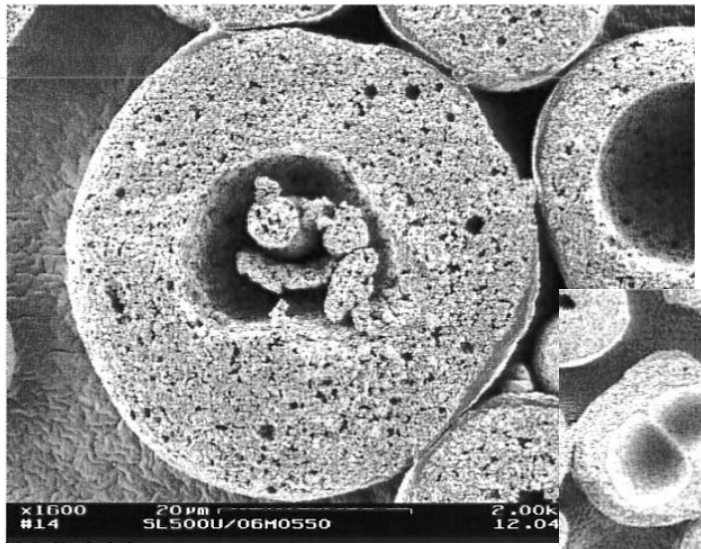
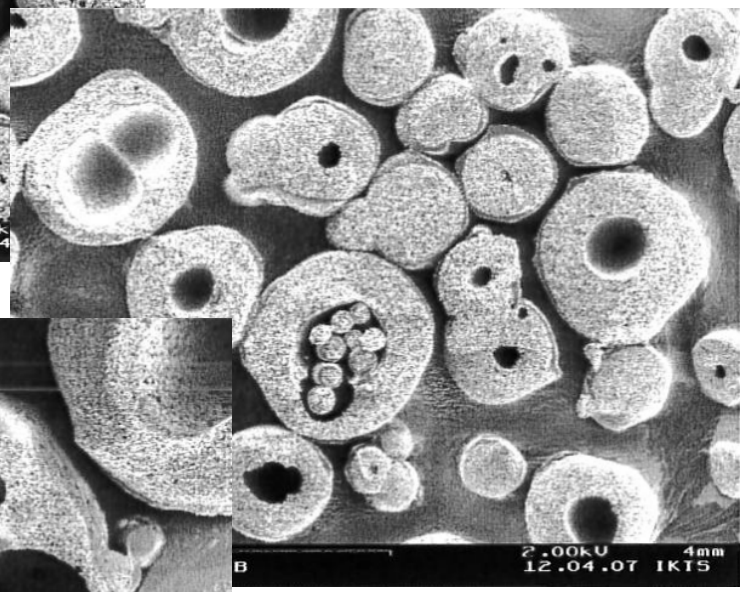
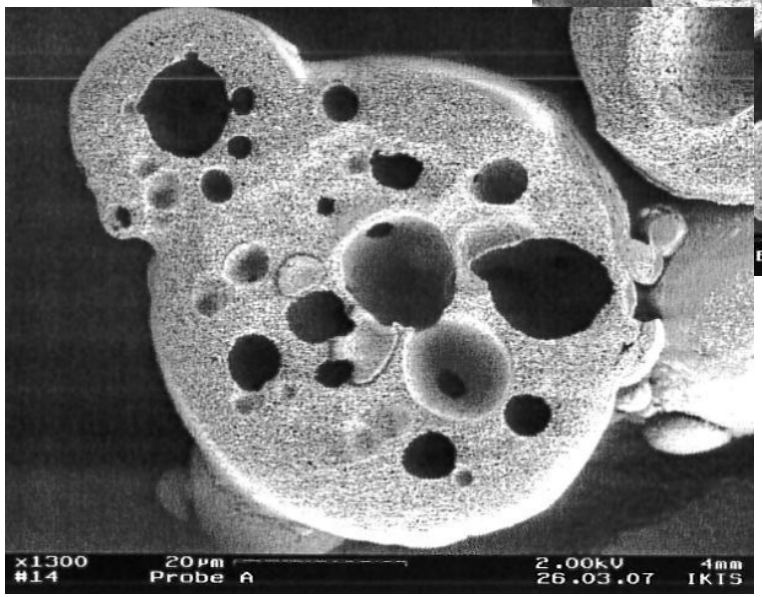
Granule Morphology











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„Perfect Granules“ ?

Green strength
Good adhesion

Homogeneity
Avoid segregation

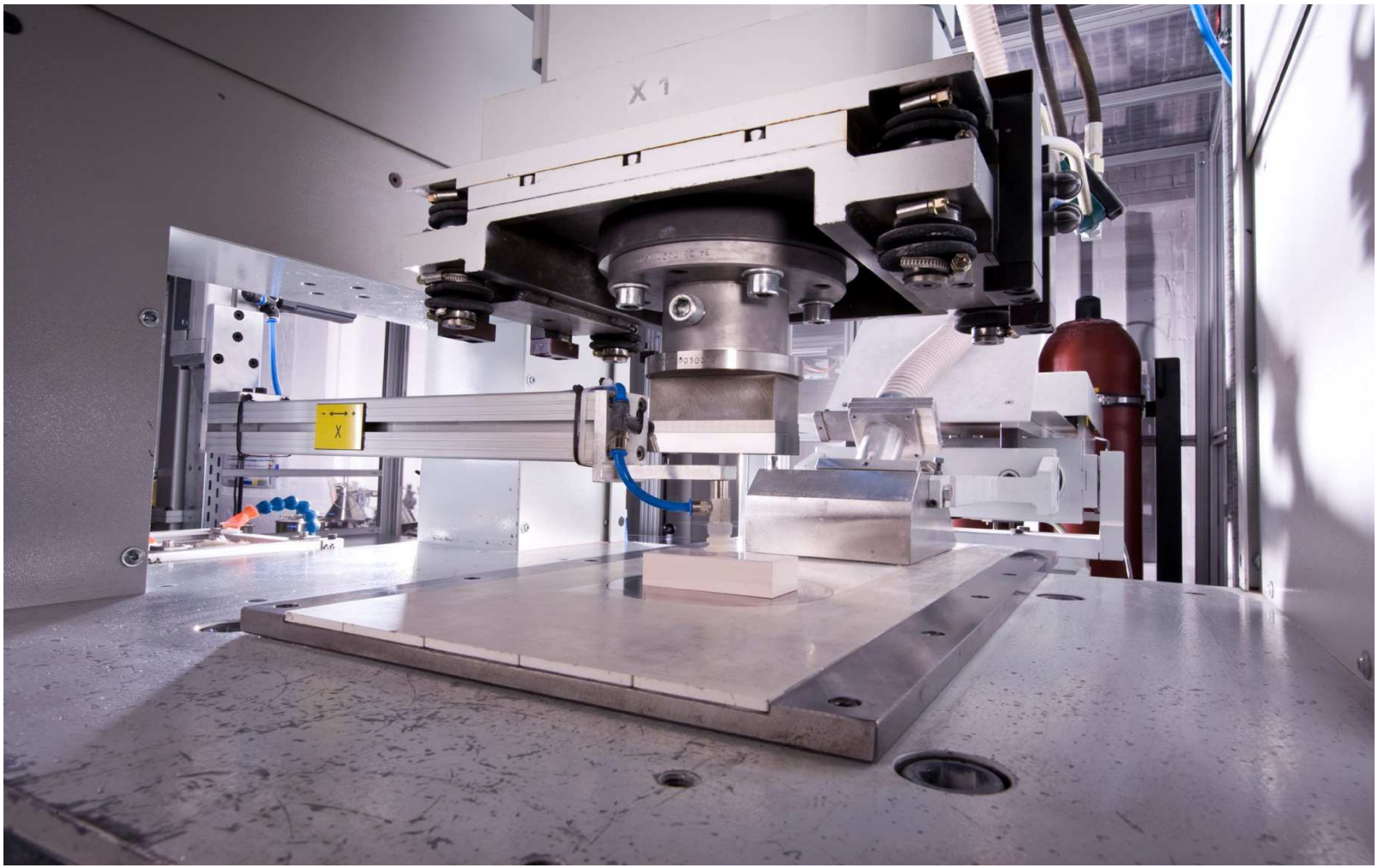
Pressing performance
No die wall sticking

Green shaping
Smooth surface machining

Deformation
Soft granules

Flowability
Compact granules

Axial pressing



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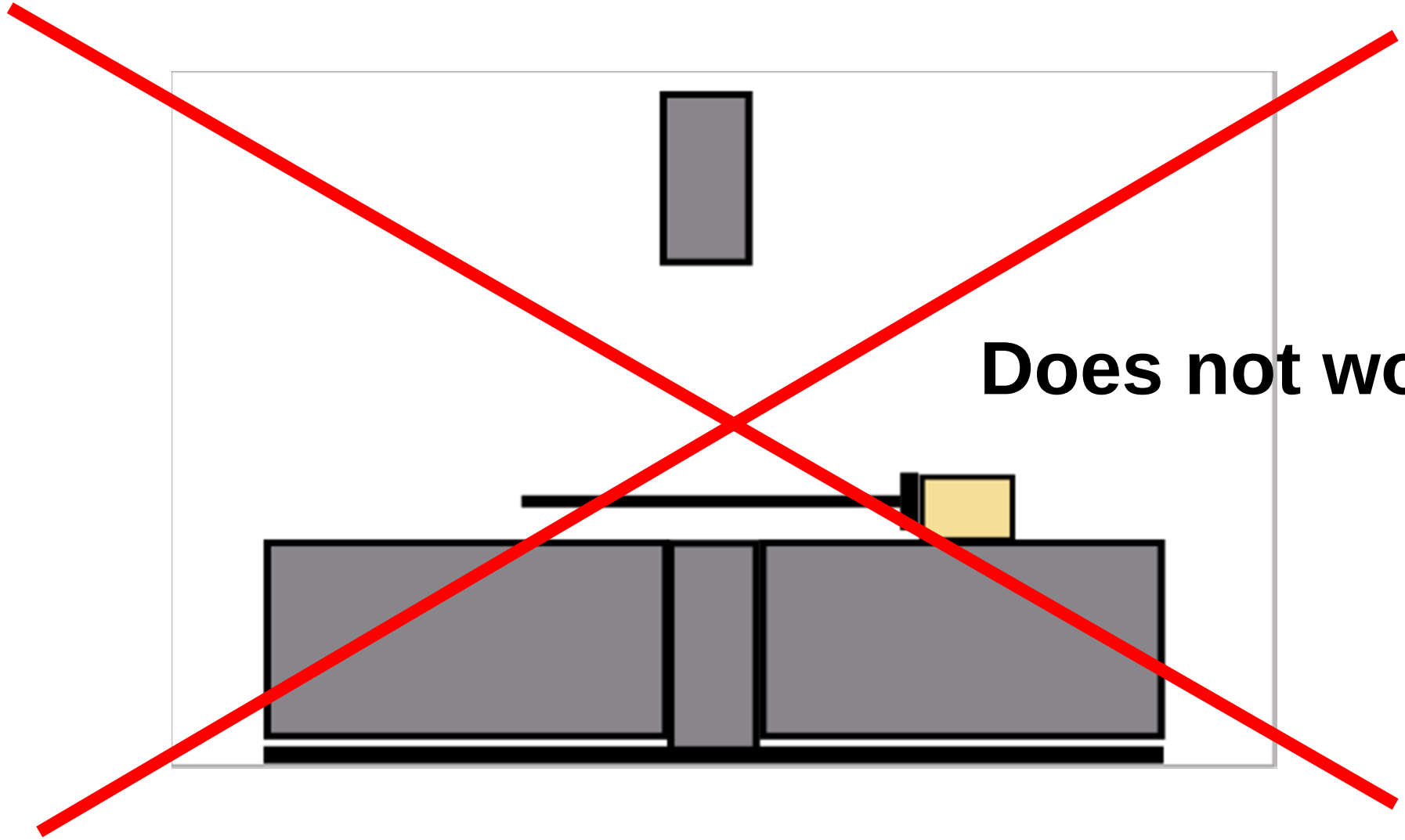
Axial pressing



Does not work!

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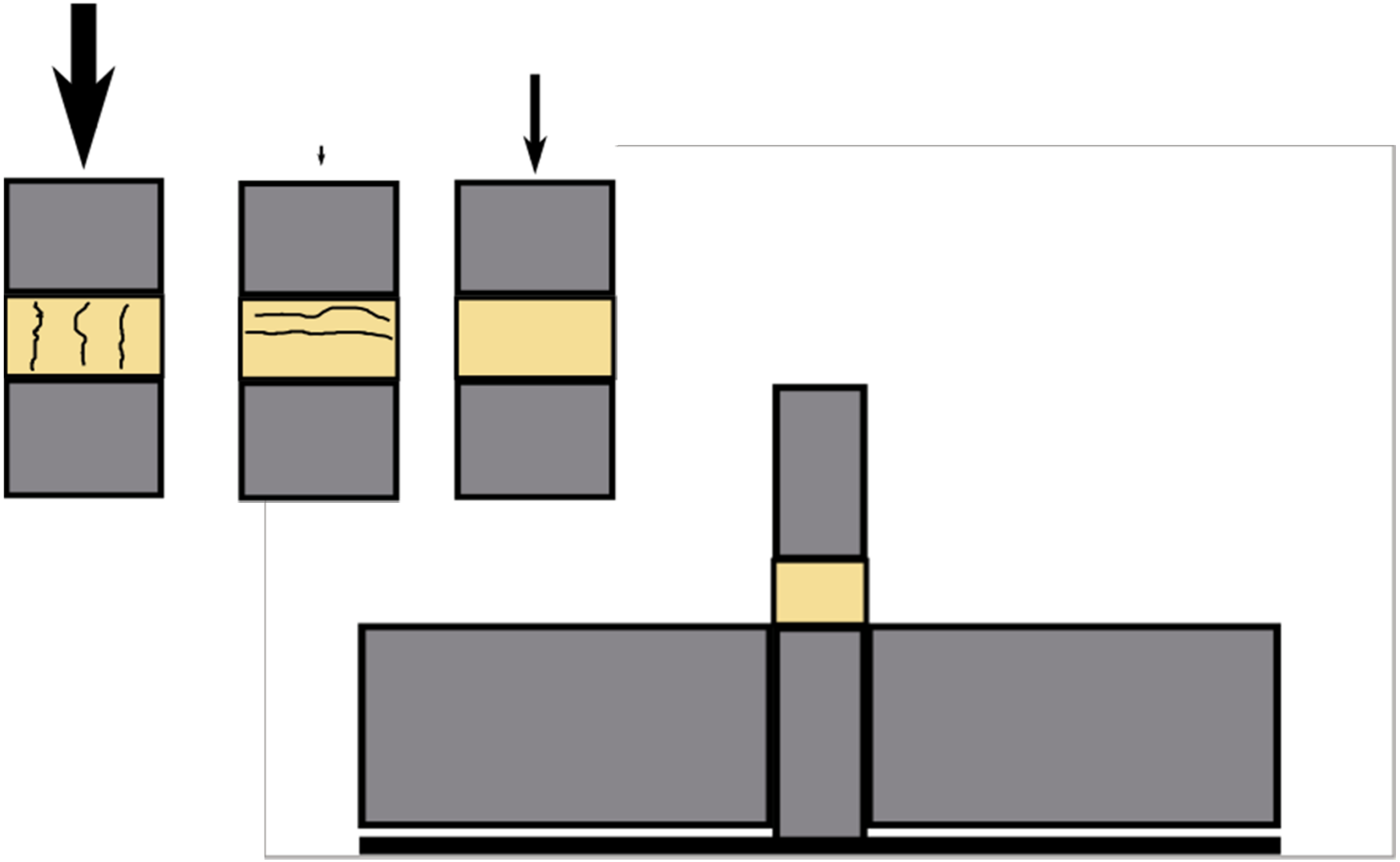
Good axial pressing



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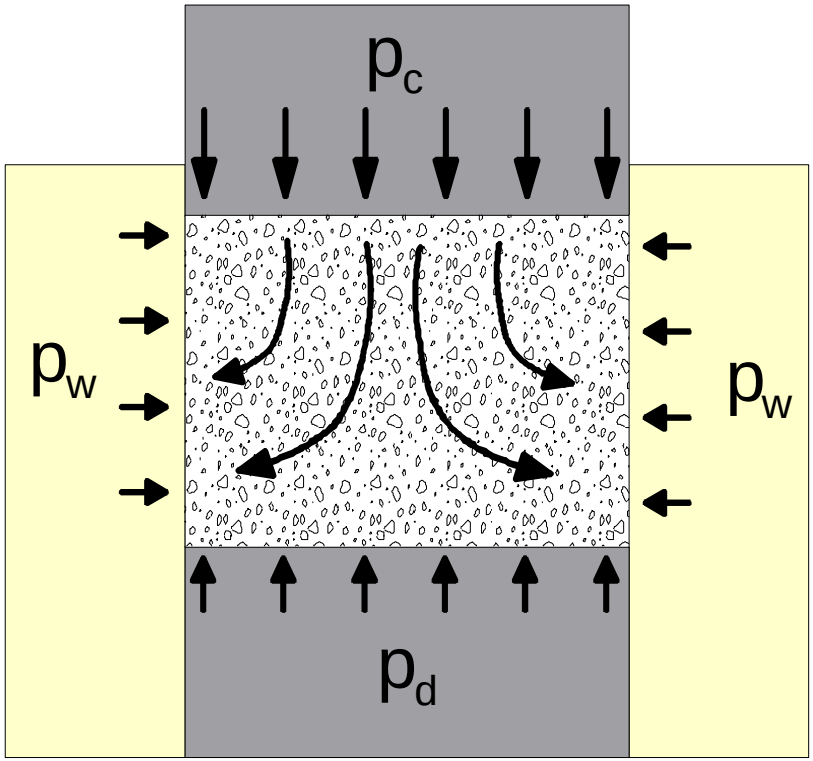
Powder Test Center (PTC)

Upper punch
Position and load control



Lower Punch
Fixed position
Load control

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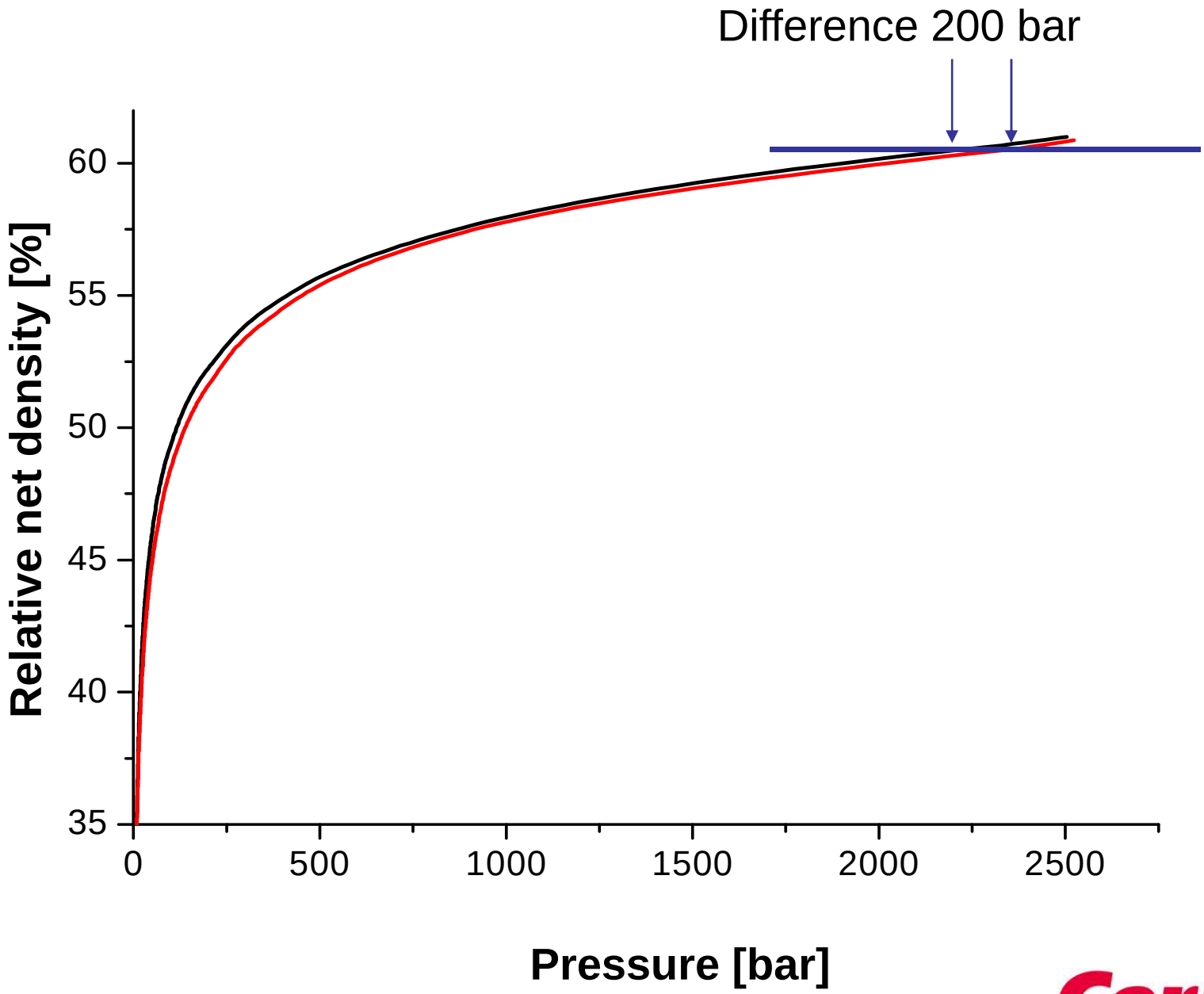
Problem at low pressure coefficient



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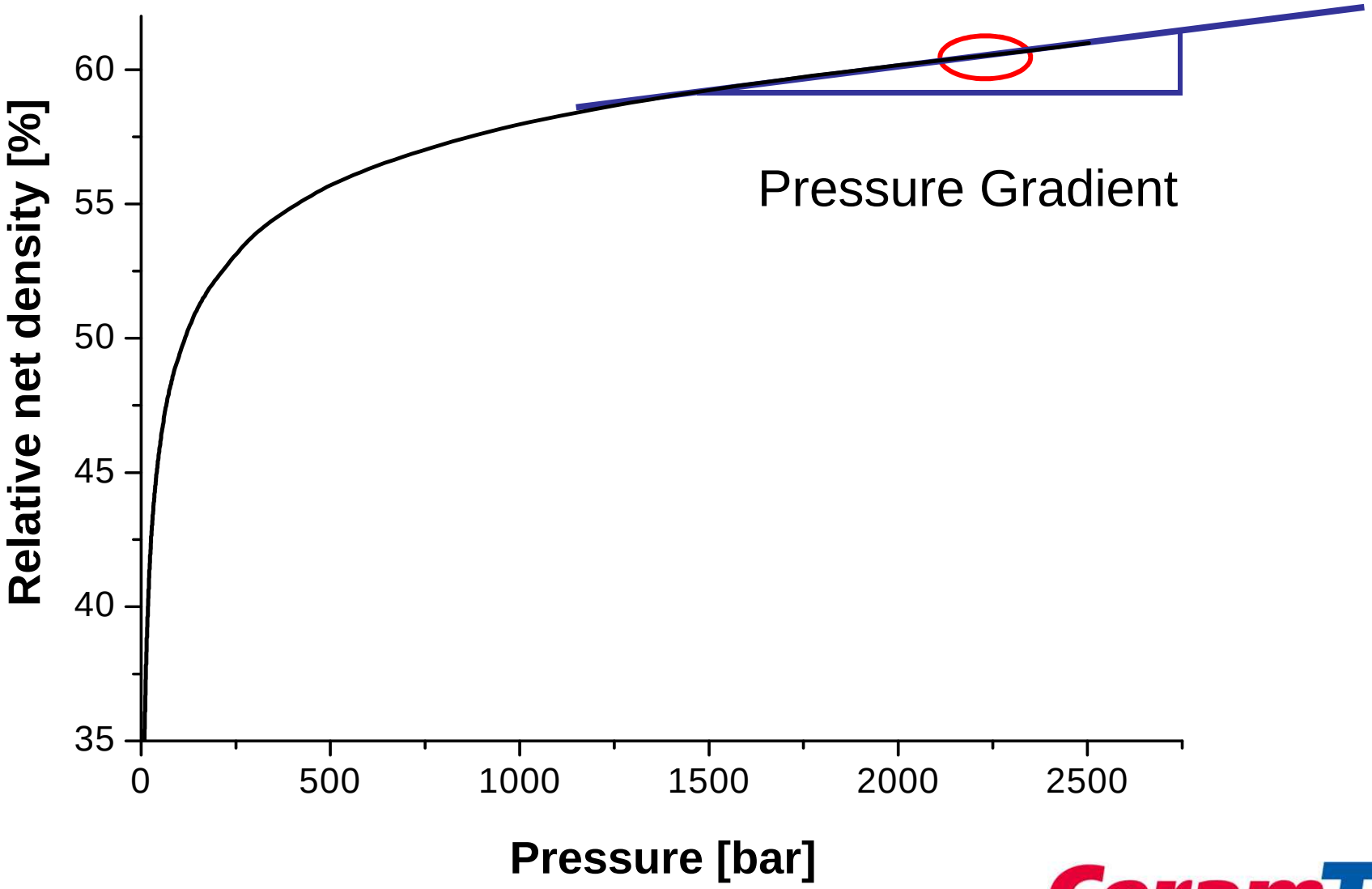
Evaluation PTC-Curve

Pressure gradient

High: Prozess robust vs. compressibility deviations

Low: Prozess robust vs. pressure deviations



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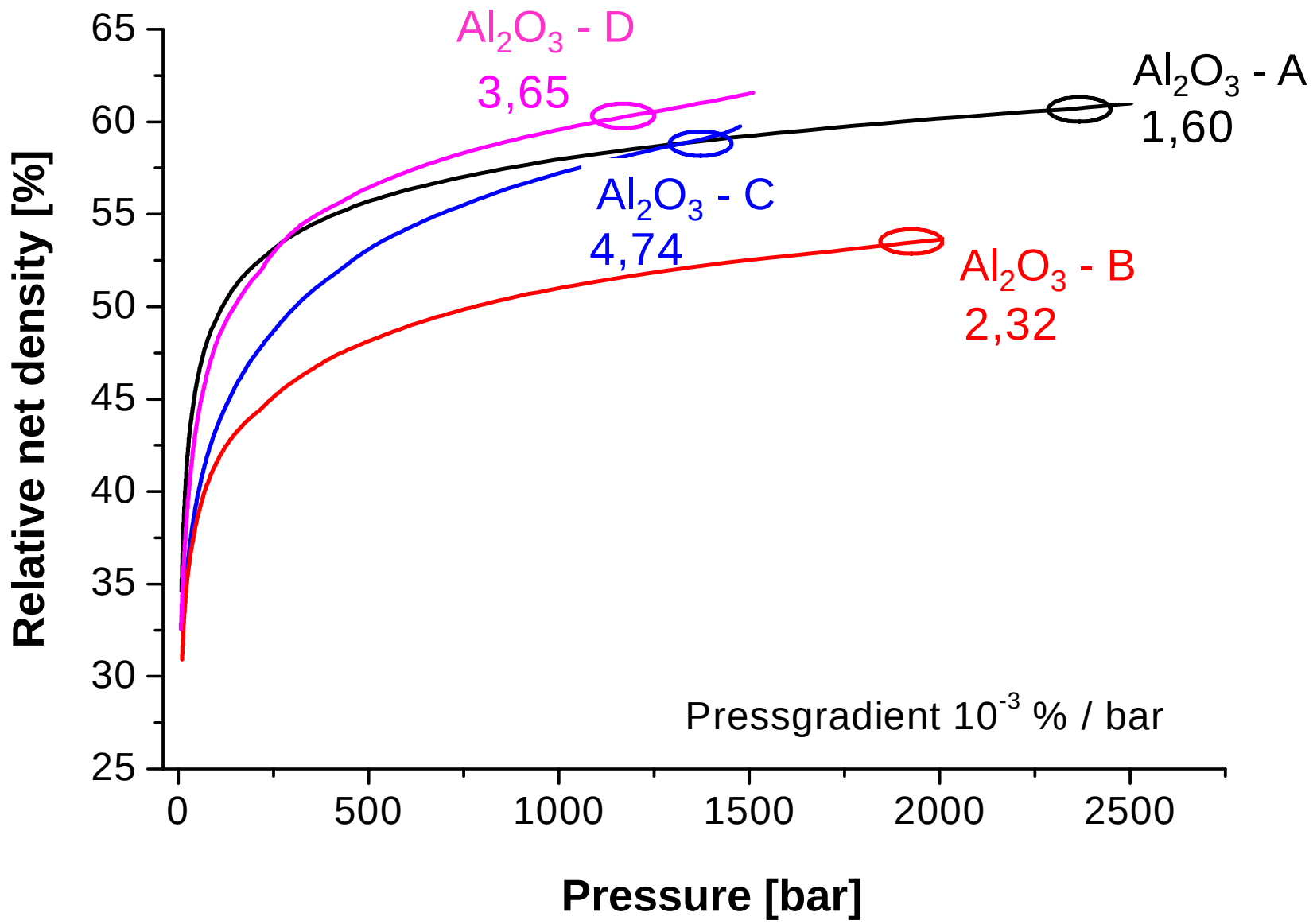
Different Powders



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Different types of „Ready to press powder“

Quick pressing

Complex shape
Direct pressing
Perfect flowability
Easy sintering

Green strength

Simple pressing shape
High performance green shaping
High edge strength

Soft pressing

Combination
Direct pressing, tight tolerances
Minimize defects

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Green shaping

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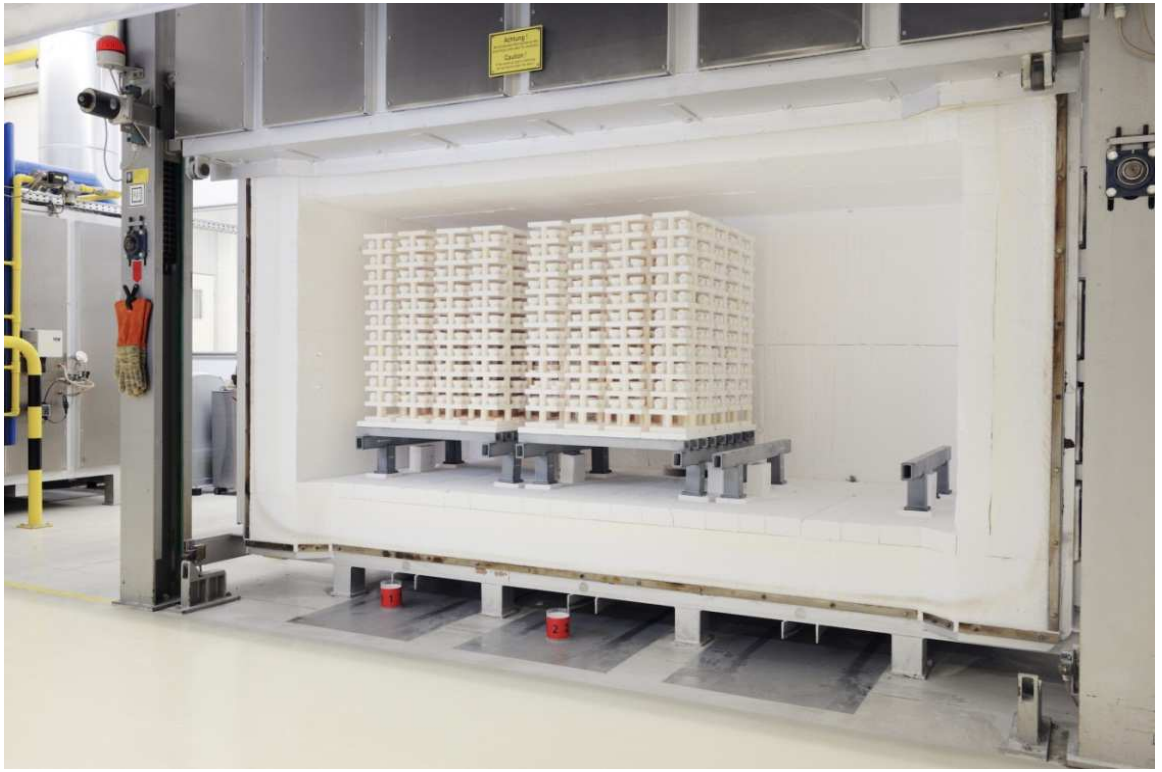
Sintering

Electrical or gas furnace



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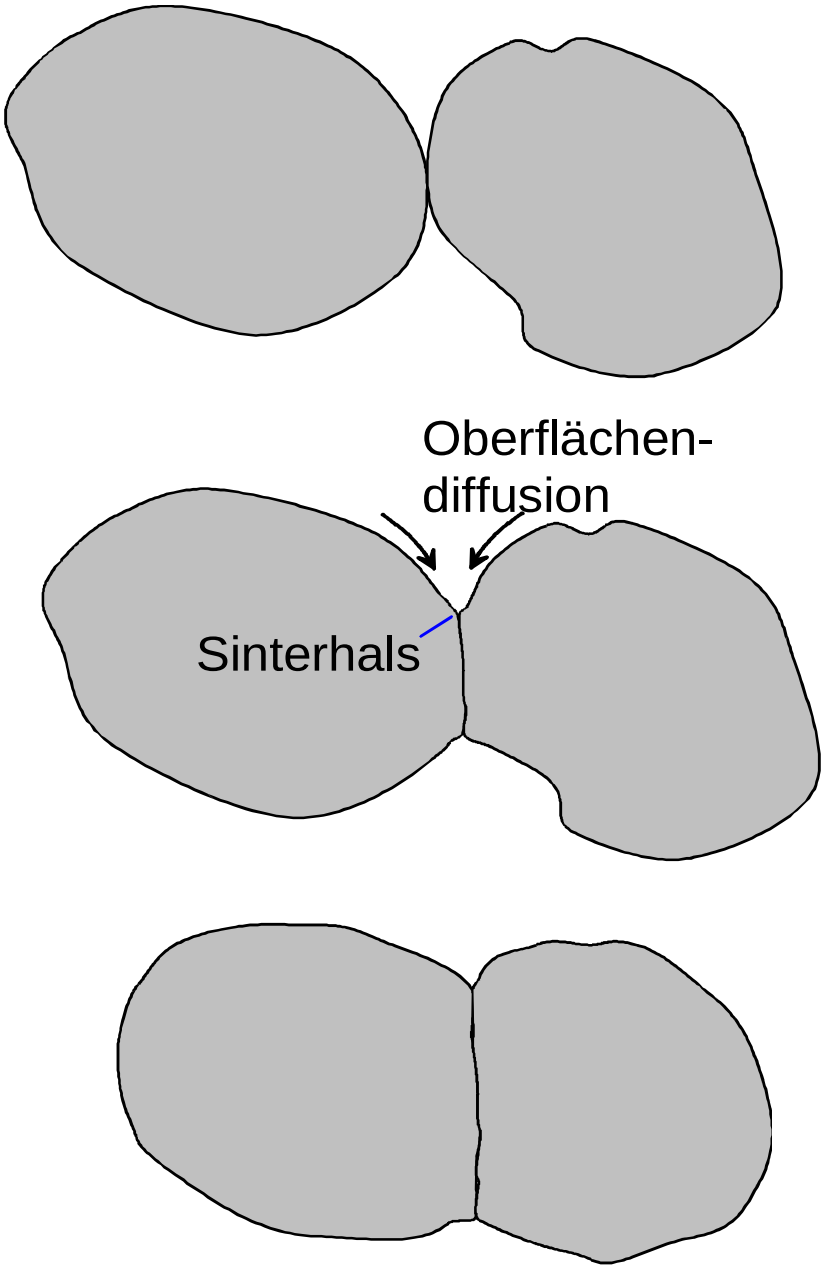
Mechanism of sintering



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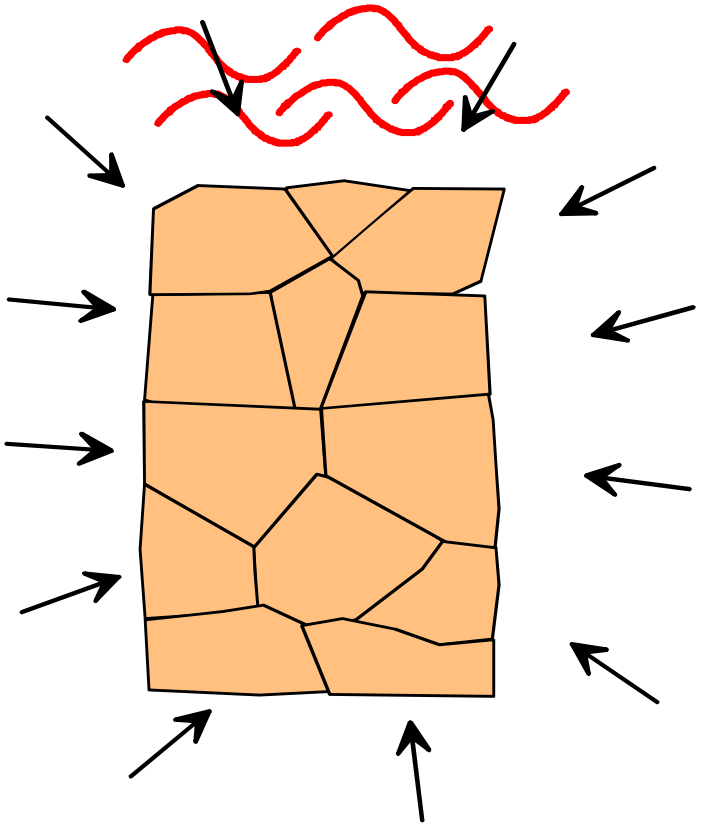
Hot Isostatic Pressing

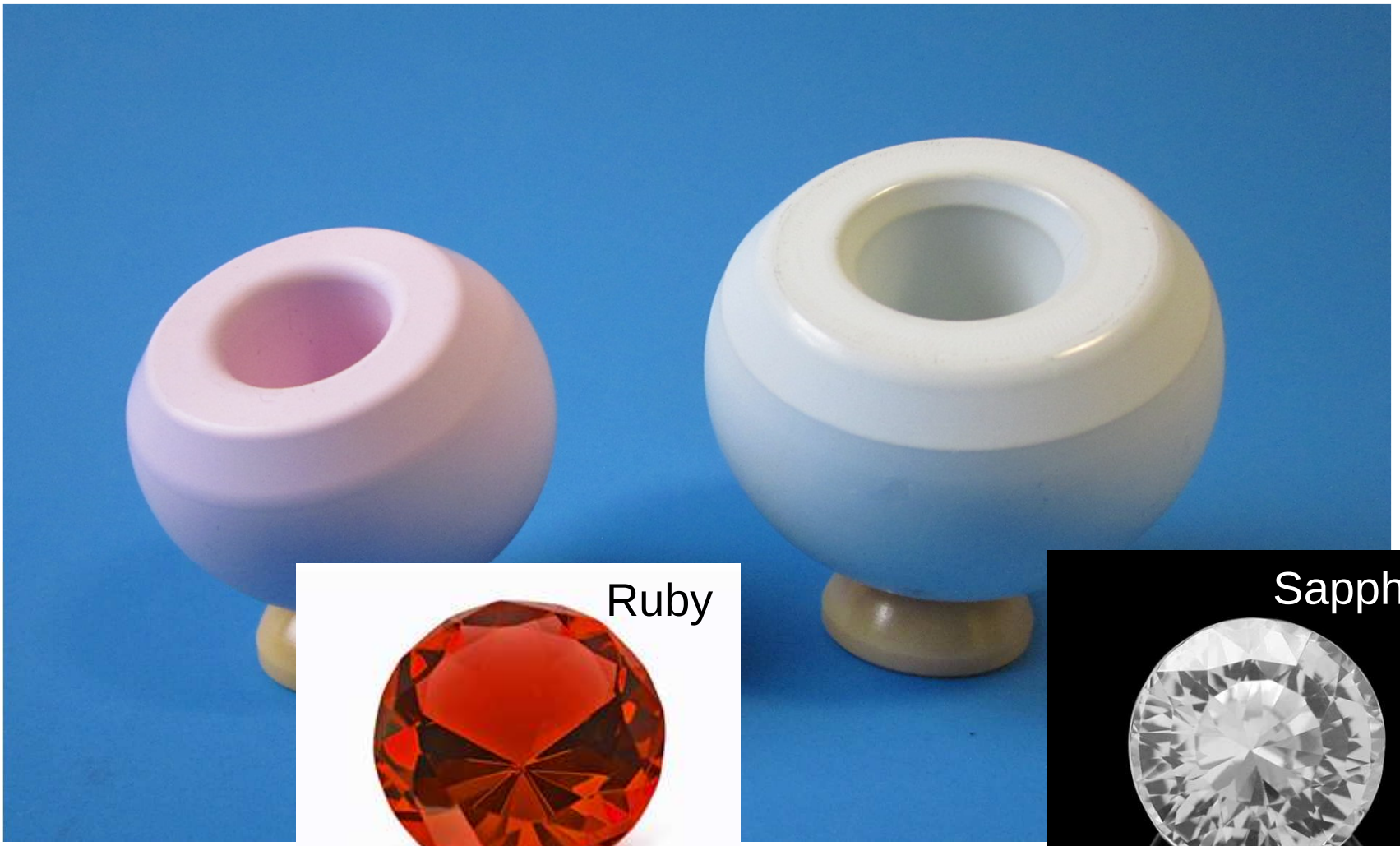


1. Powder compact
   Densification ~ 55%

2. Pressureless sintering
   Densification 95 – 99%
   Closed residual porosity
   Grain & large pore growth

3. Hot isostatic pressing
   Gas pressure, sintering temperature
   Densification up to 100%

Chemical reaction at sintering



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Raw material specification

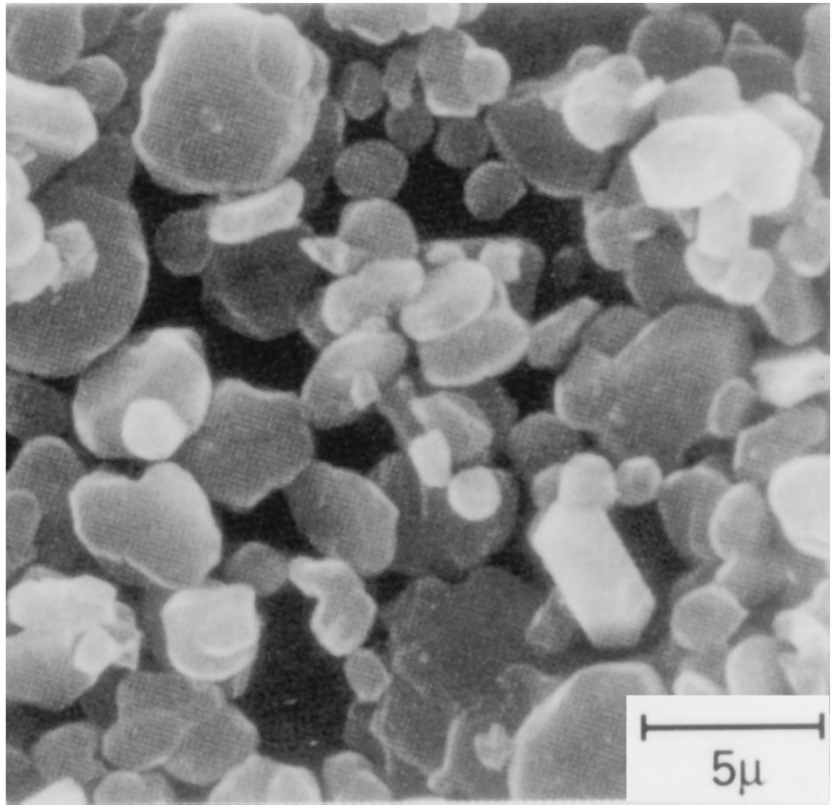
Impurities of Alumina

Mg, Fe, Na, Si, ...

Specific surface BET

Particle size

Others.....



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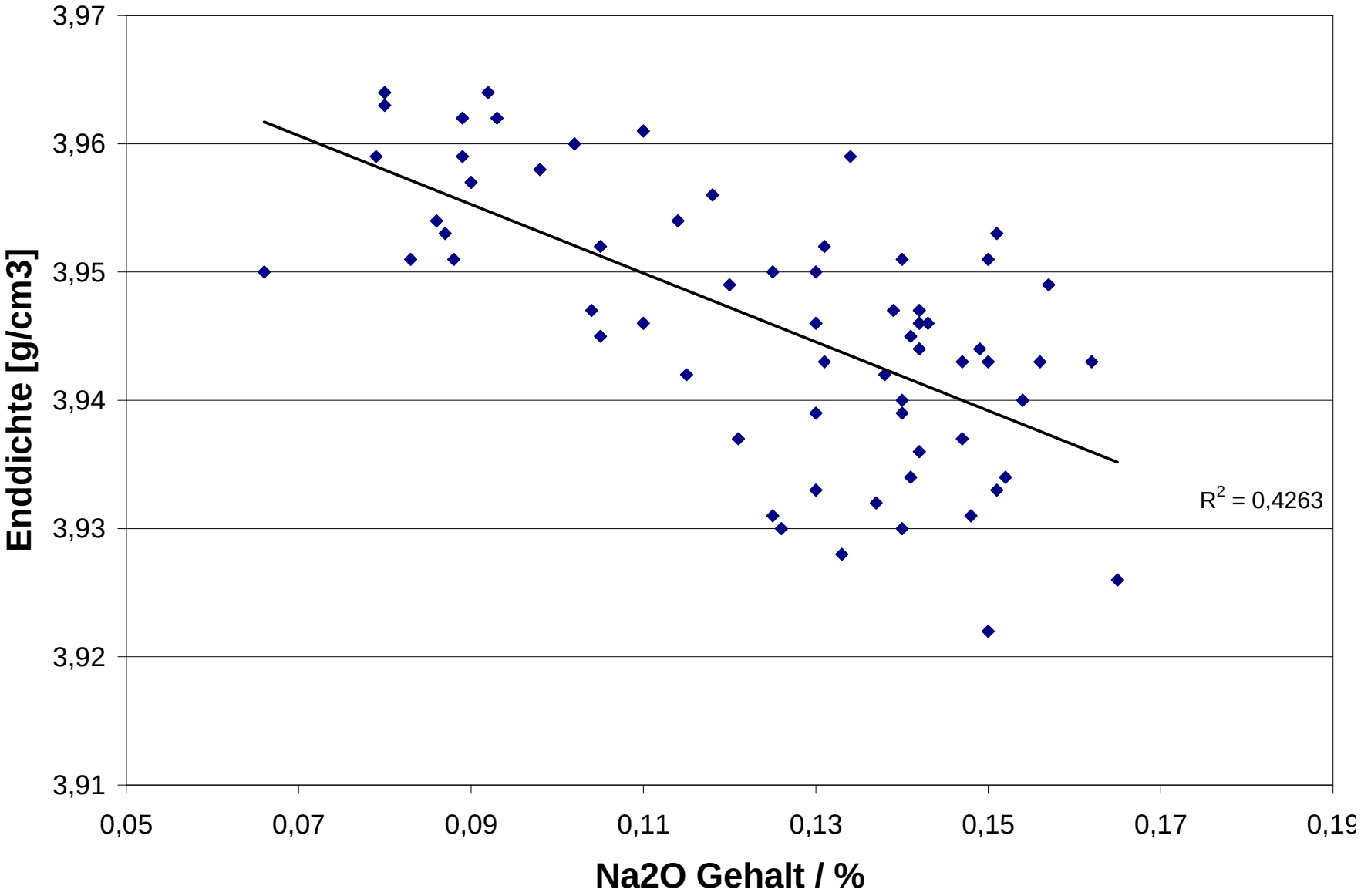
Correlation analysis



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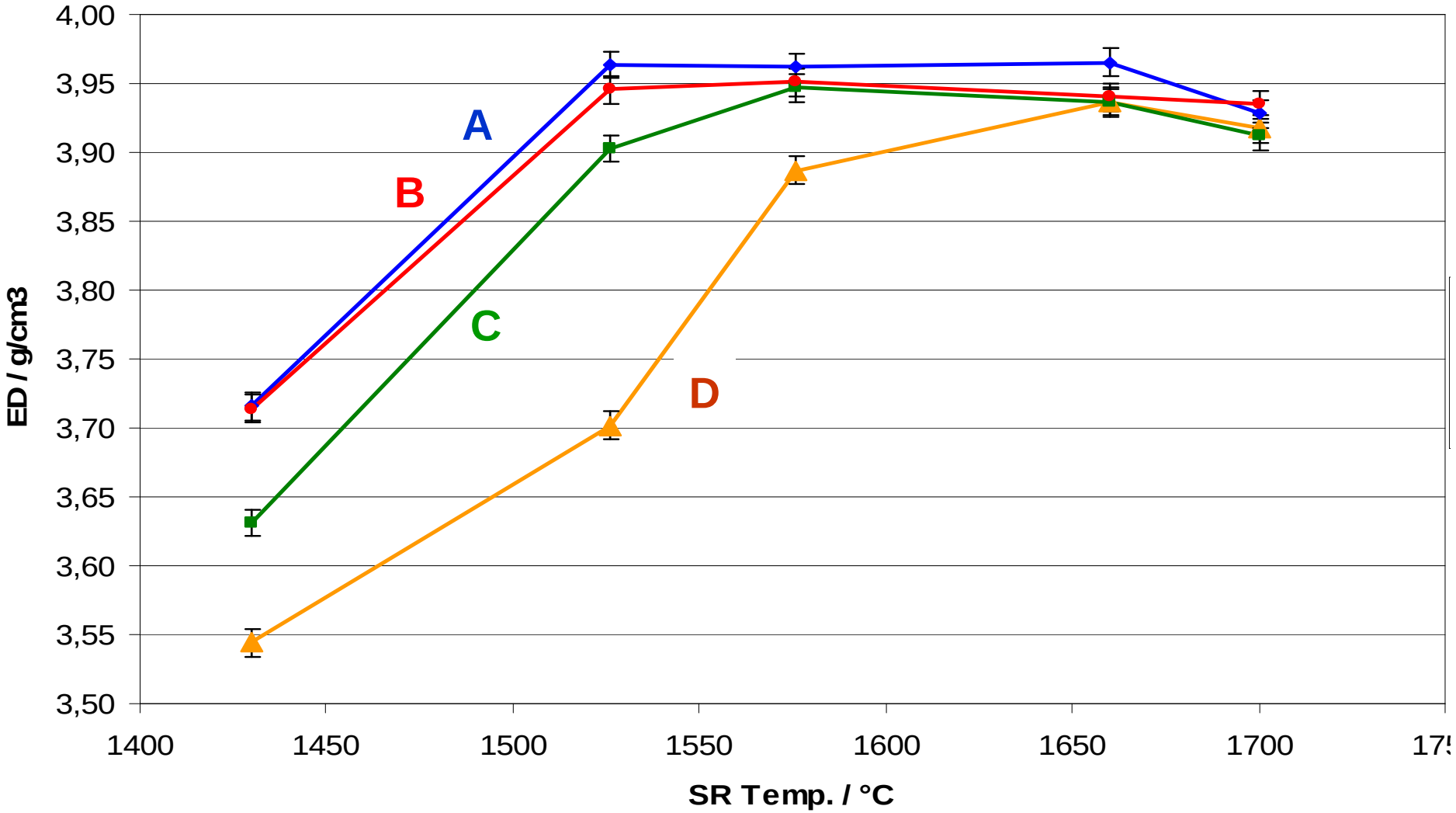
„Robust“ Sintering



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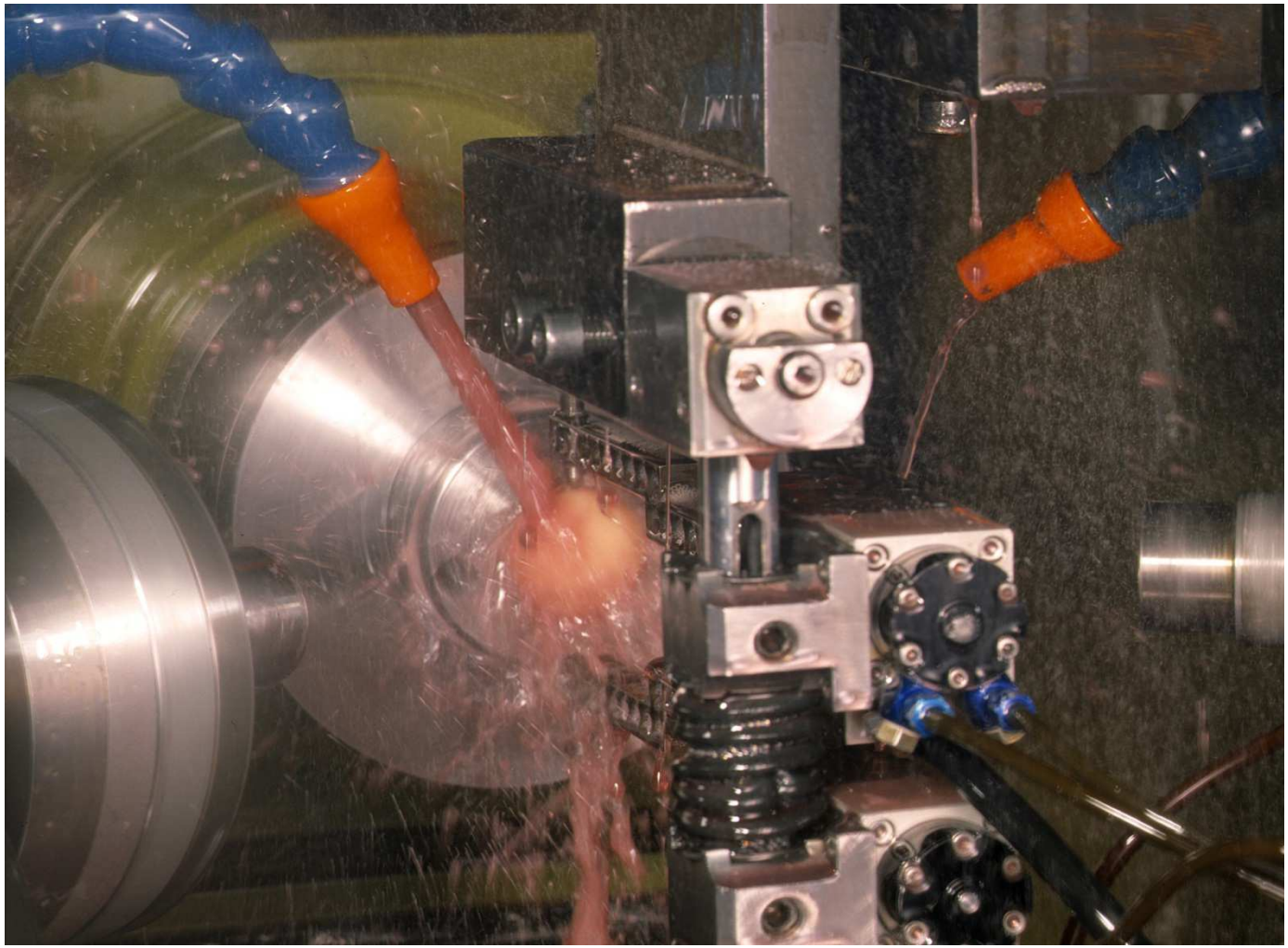
Machining: Grinding

- Diamond tools
- High precision
- Expensive (>30% TC)
- Avoid if you can



Machining: Polishing

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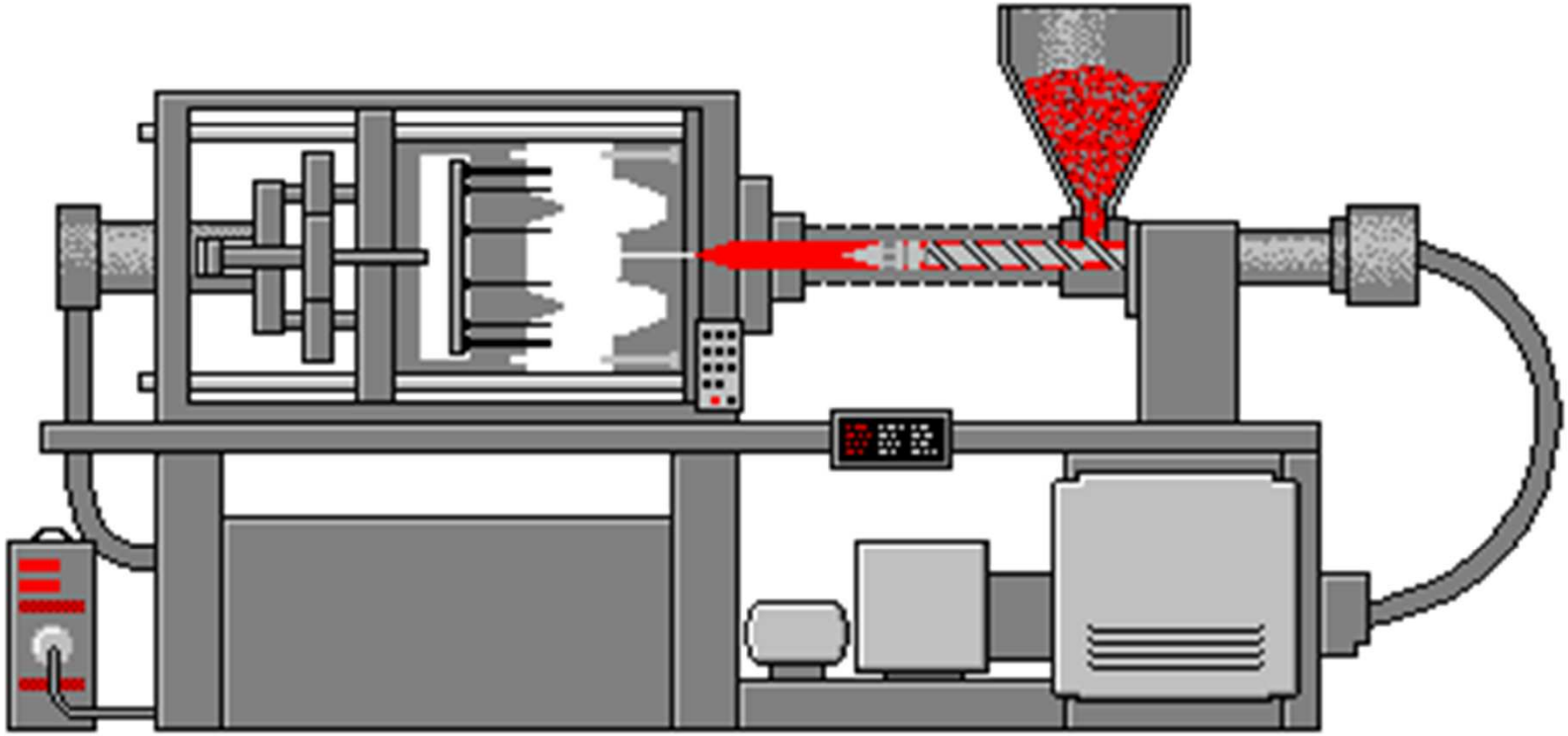
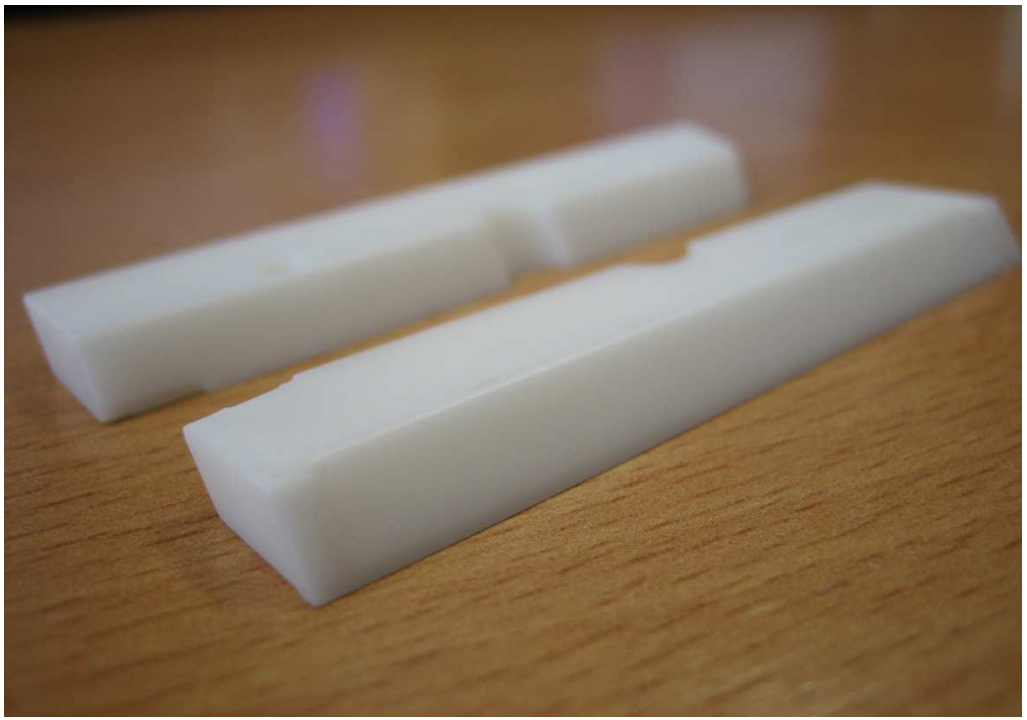
Injection molding

Clamping Injection Cooling Ejection



Successful injection molding ?

Baby tooth cover



Meat chopper knife

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Complexity of technology

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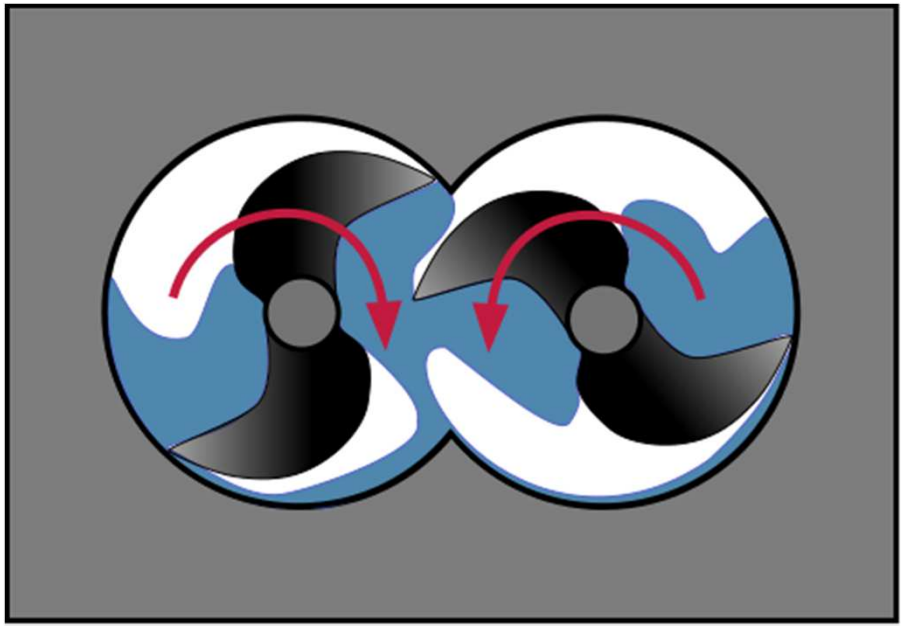
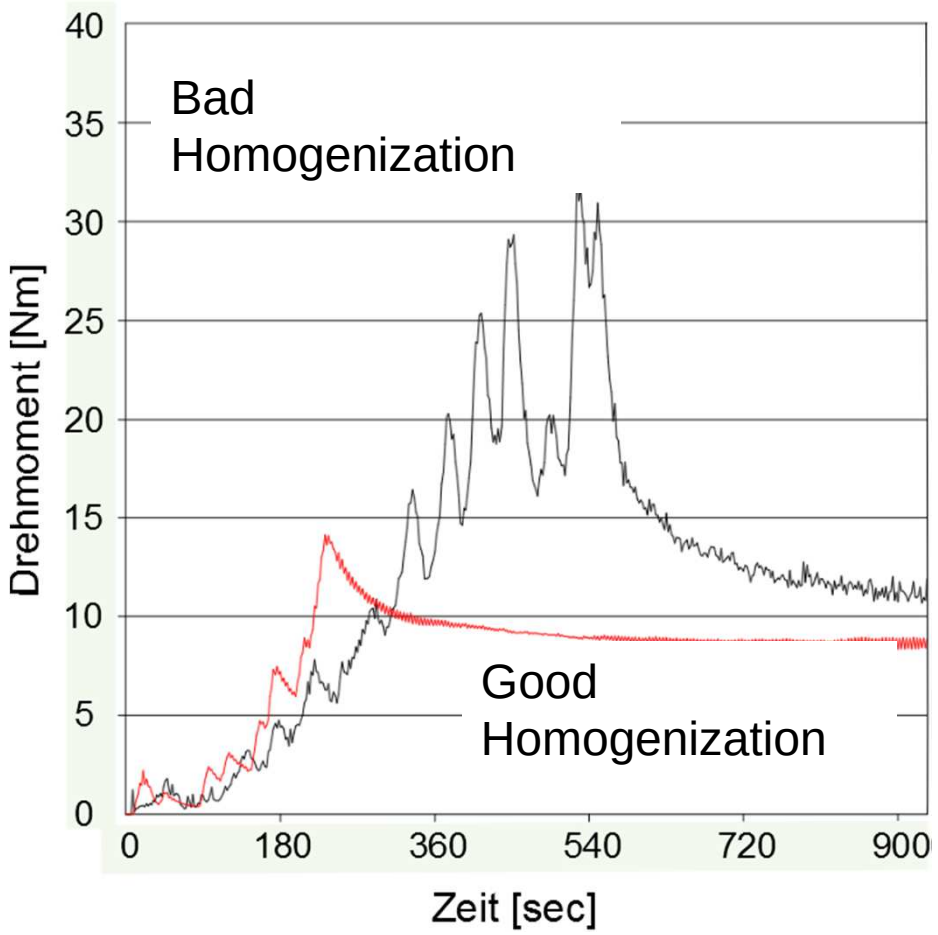
Development / assessment of injection molding feedstock

Laboratory heavy duty mixer





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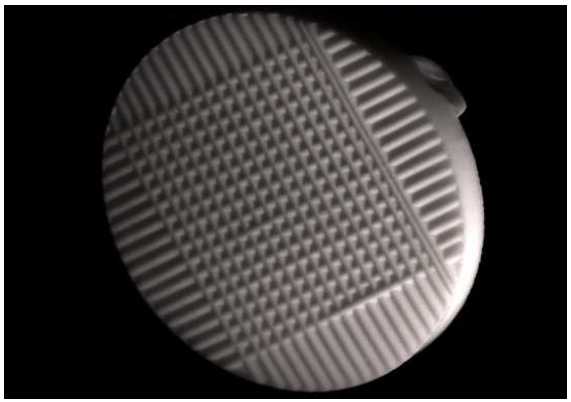
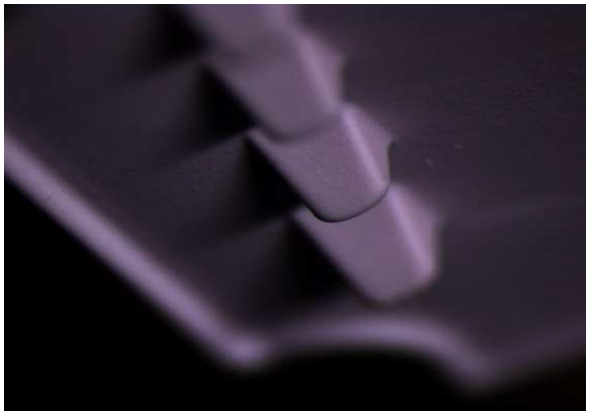
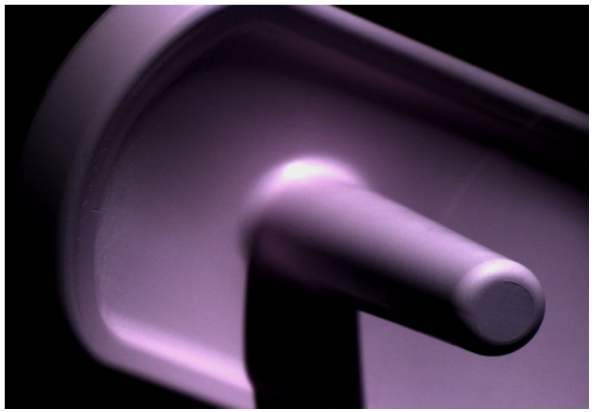
Injection molding components







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Size vs. complexity

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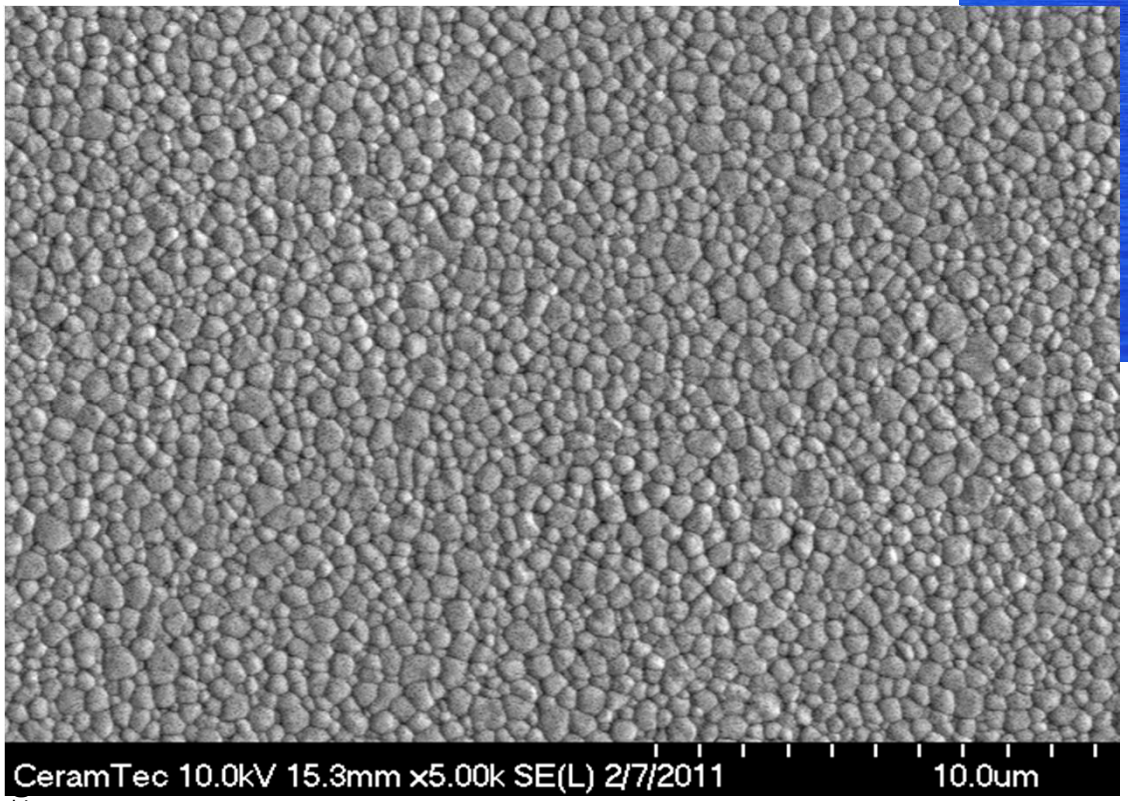
Fracture

Microcstructure of zirconia



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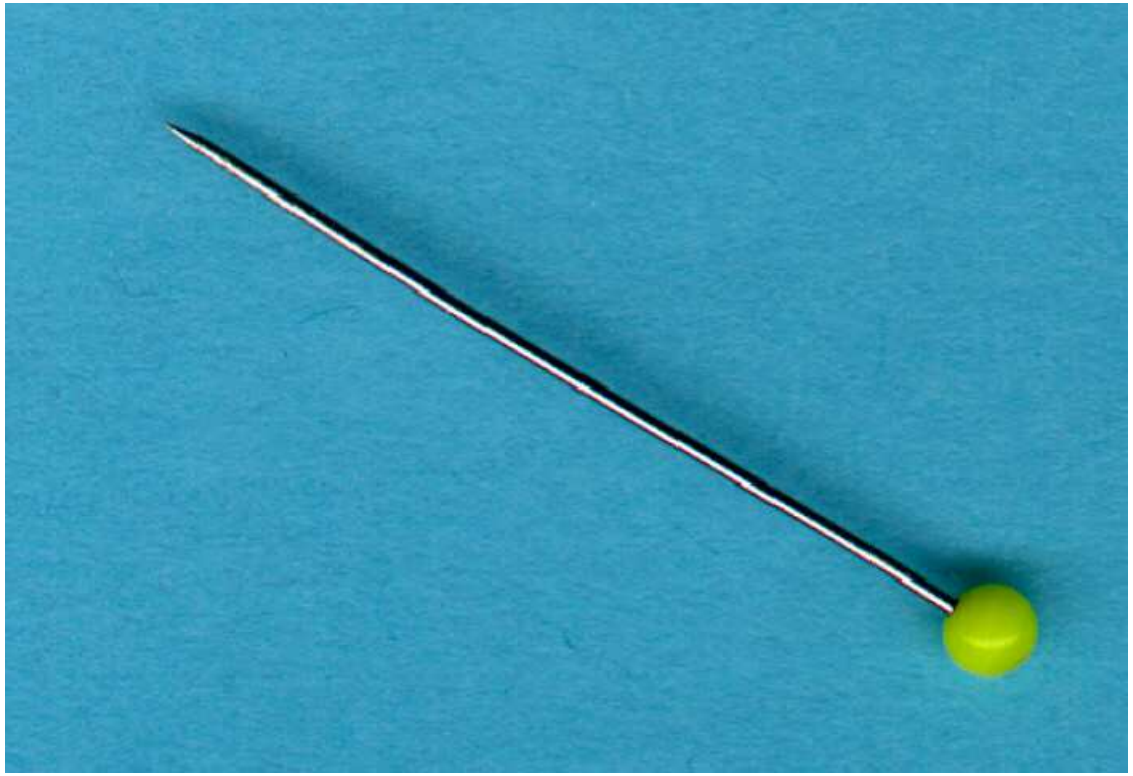
How many grains in 1 mm^3 ?



120 Billion
120.000.000.000

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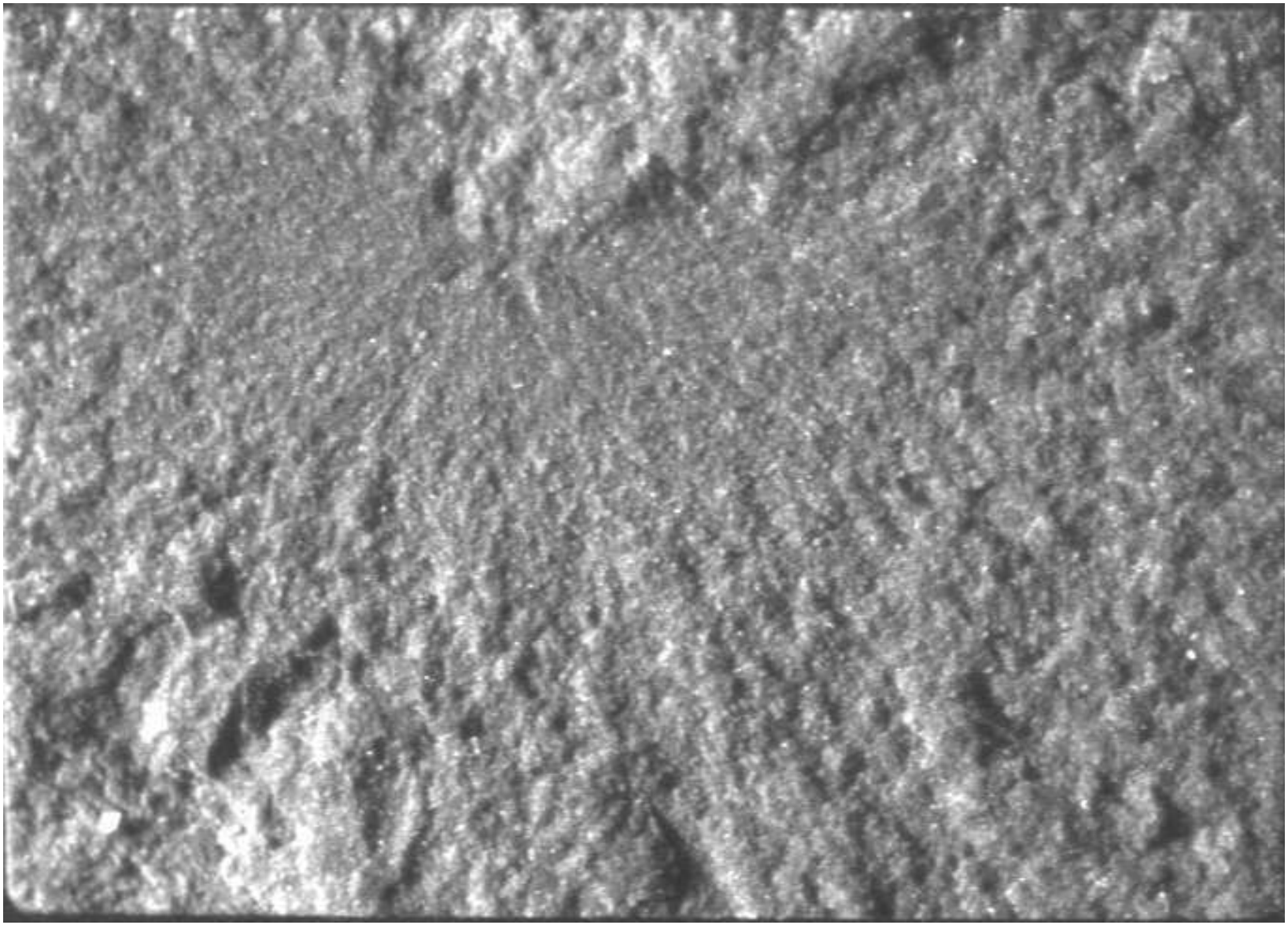
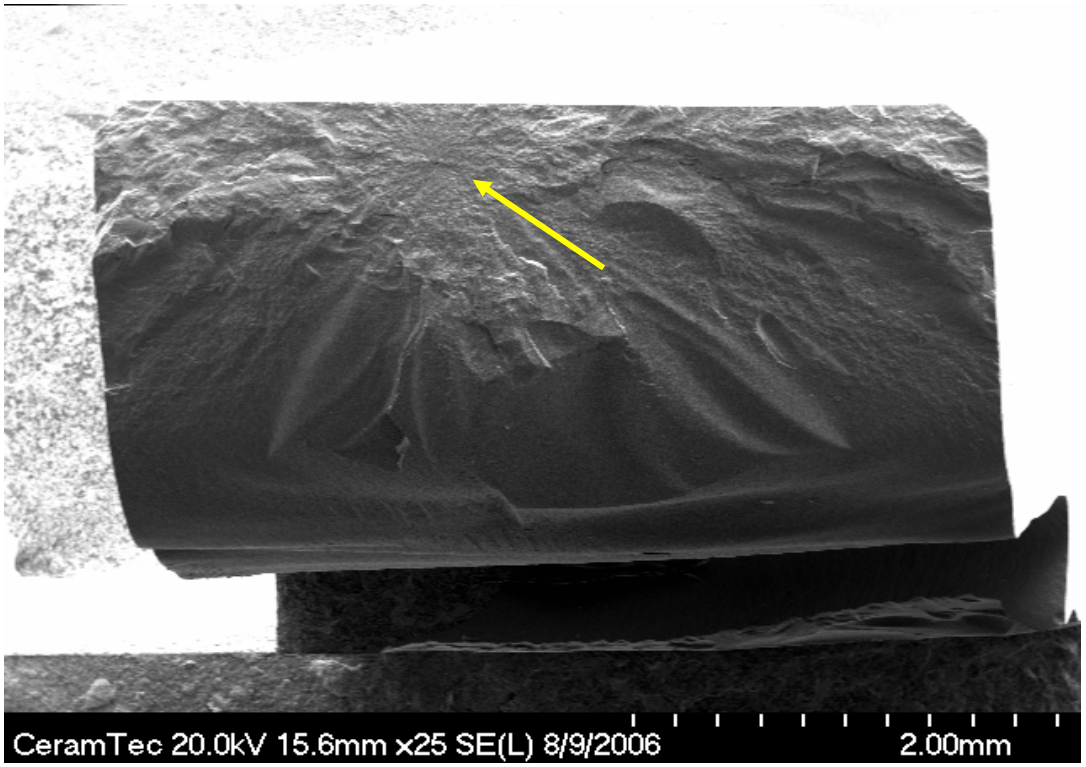
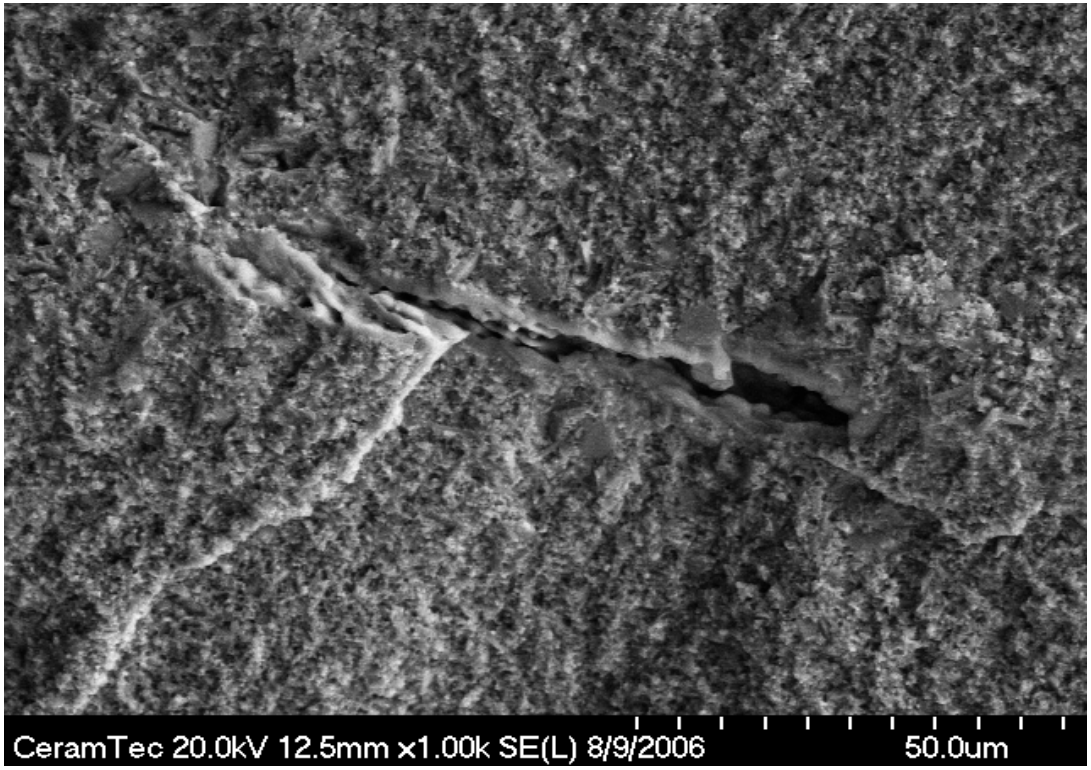
Natural defect



CeramTec

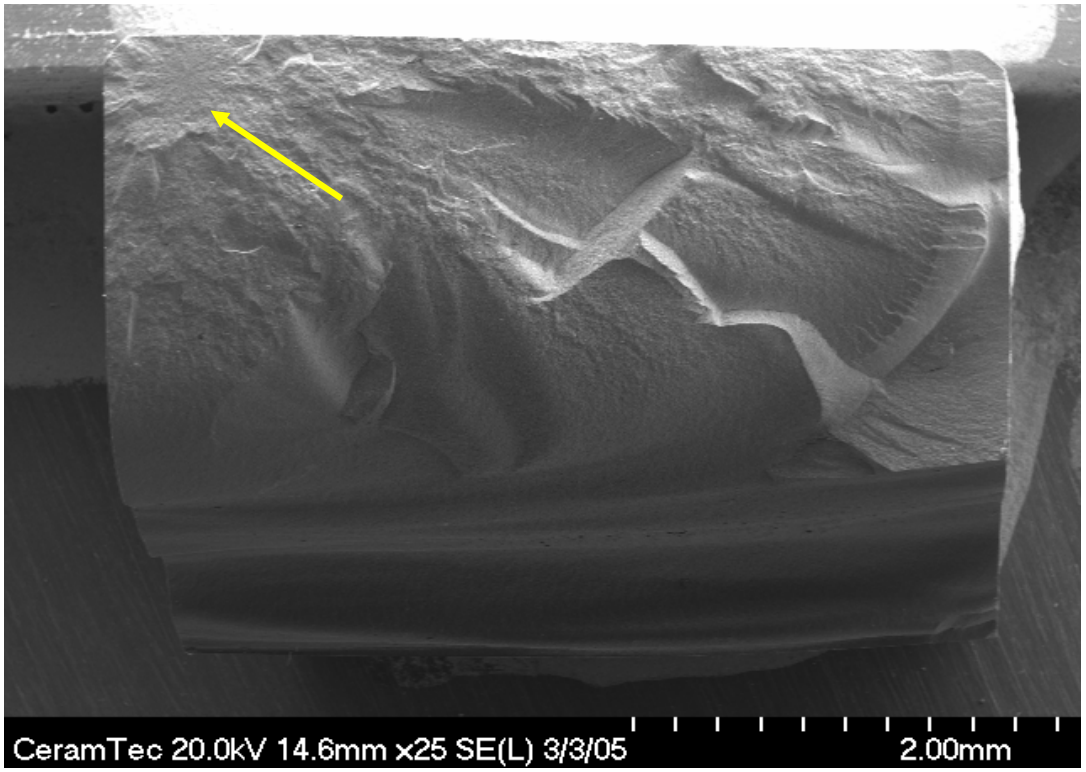
Natural processing defects

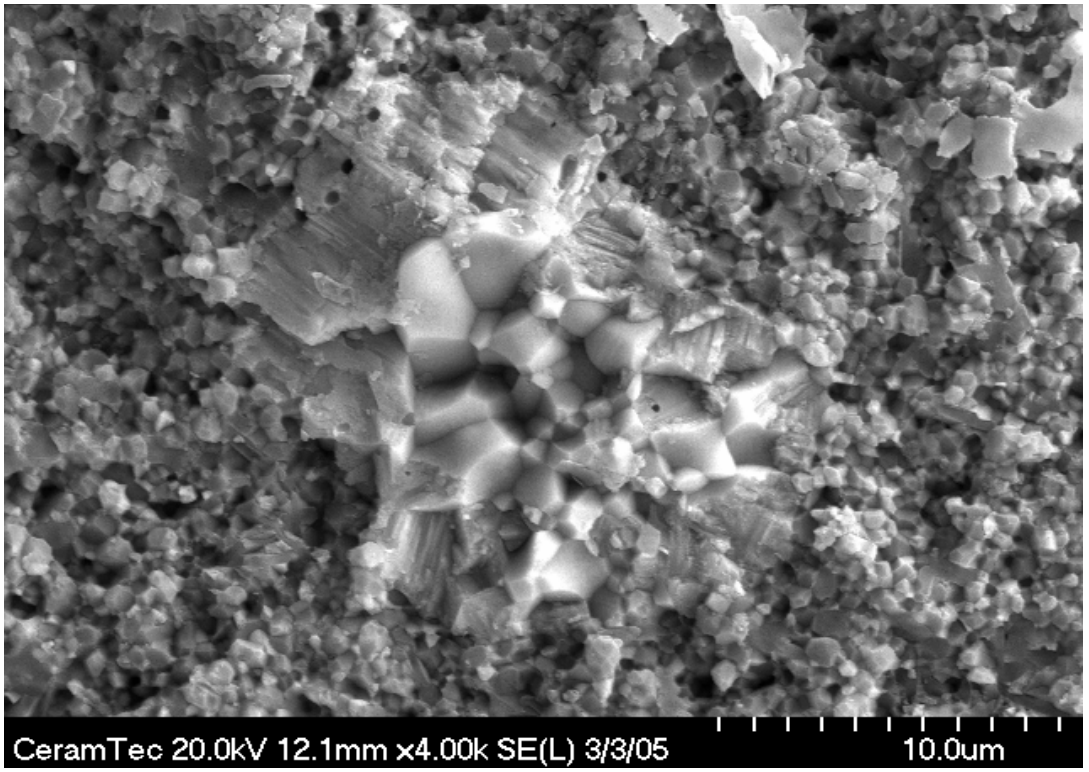




CeramTec

Natural processing defects





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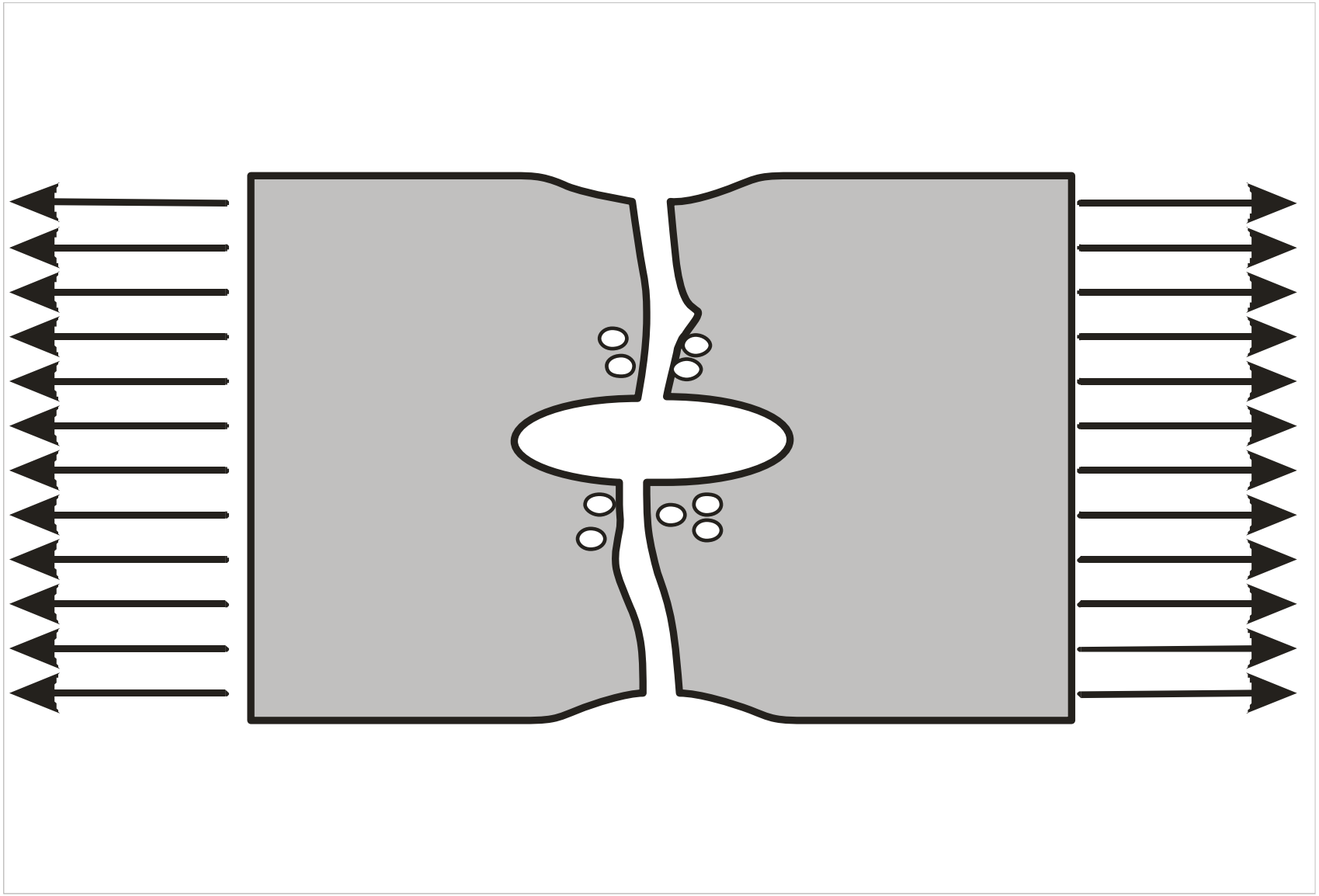
Fracture of ductile materials

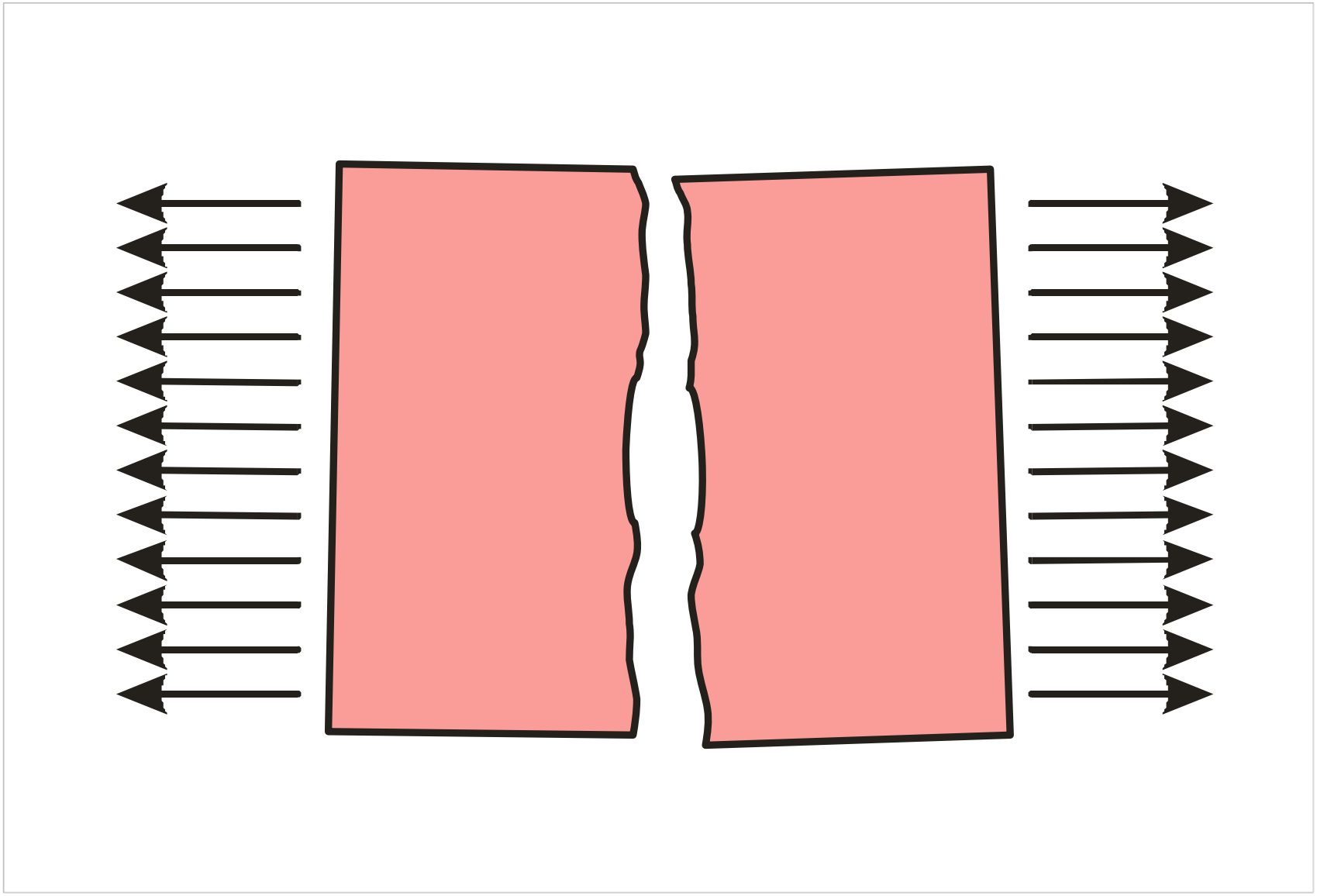


Plastic deformation of metals

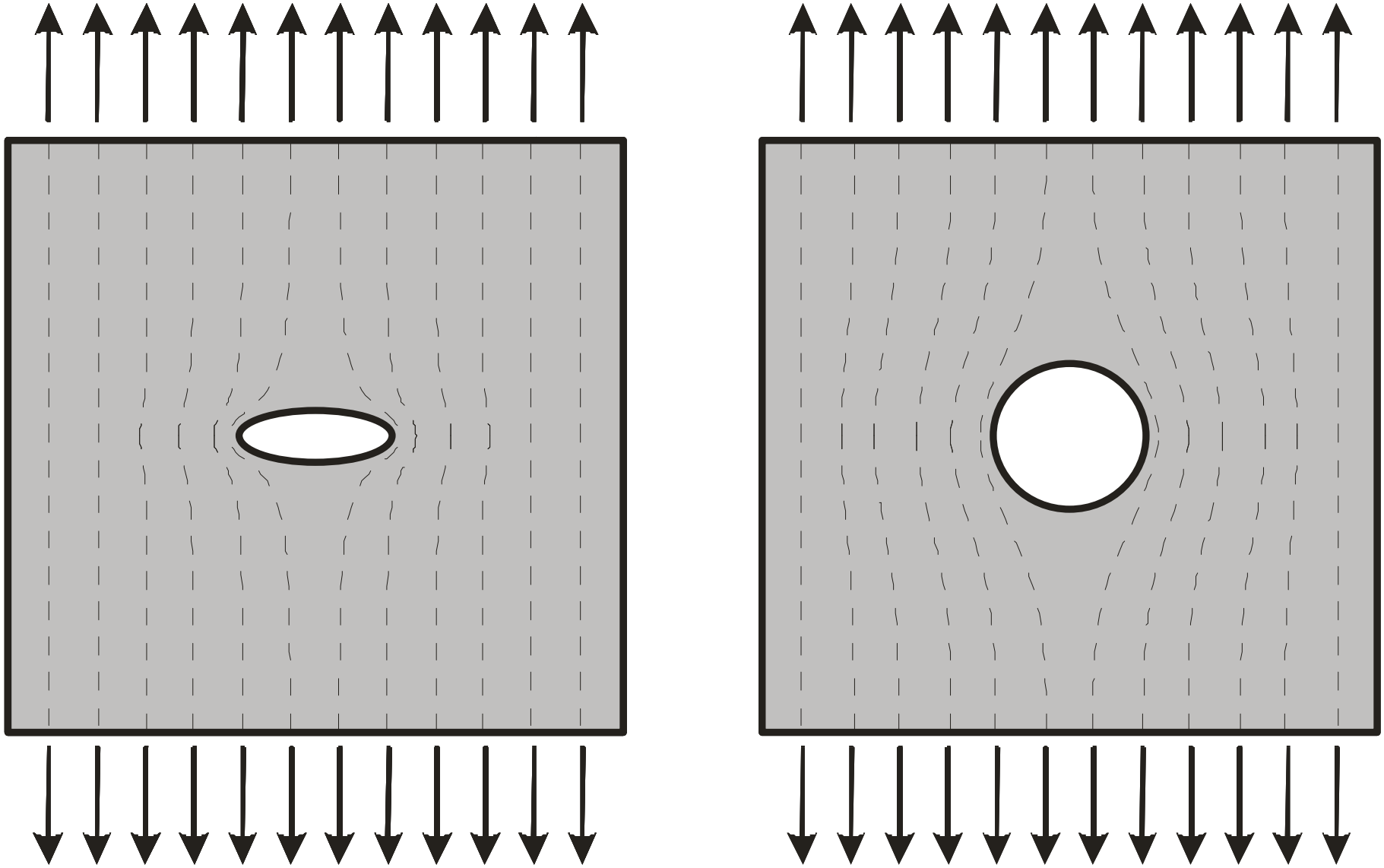
Rounding of notch tip

Reduce notch effect

Fracture of brittle materials



Notch effect



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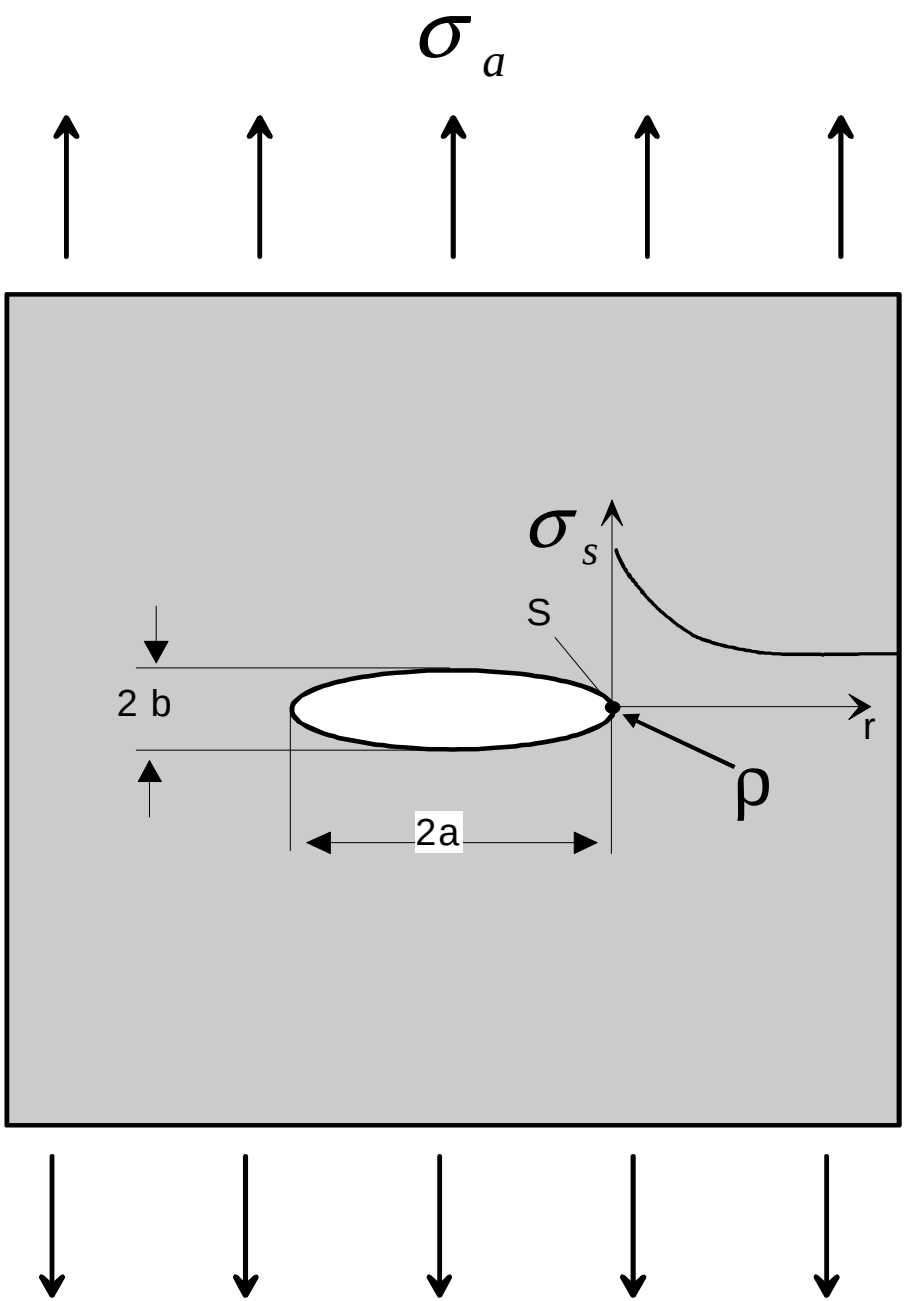
Stress increase at a notch



„Notch number“

$$\alpha = \frac{\sigma_s}{\sigma_a}$$

Notch number for oval shaped notch

$$\alpha = 1 + 2\sqrt{a/\rho}$$

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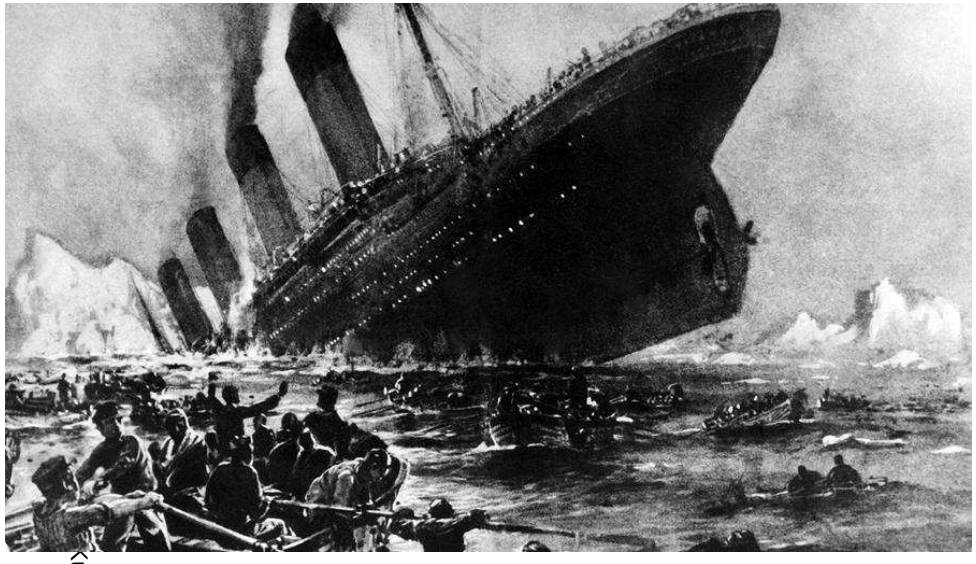
Fracture mechanics

Strength in presence of cracks



First approach: Griffith, ~ 1903
Re-developed in USA ~ 1950s

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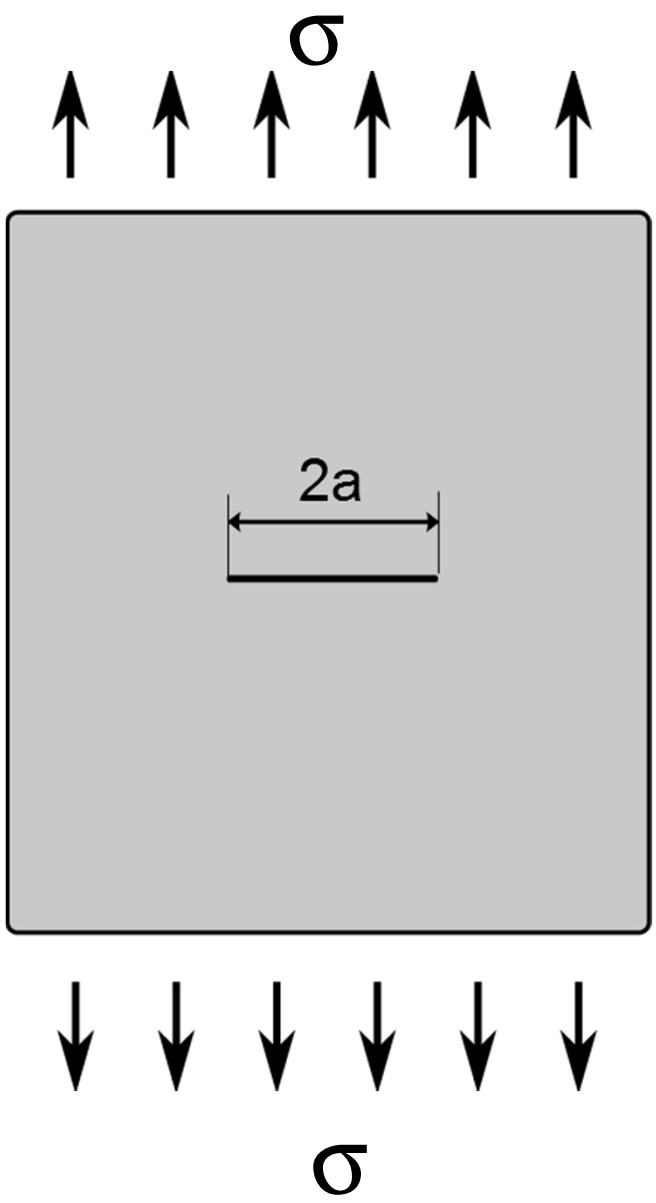
Strength in presence of a crack



$$\sigma_c = \frac{K_{IC}}{\sqrt{a_c} \cdot f}$$

σ_c = stress at the moment of fracture

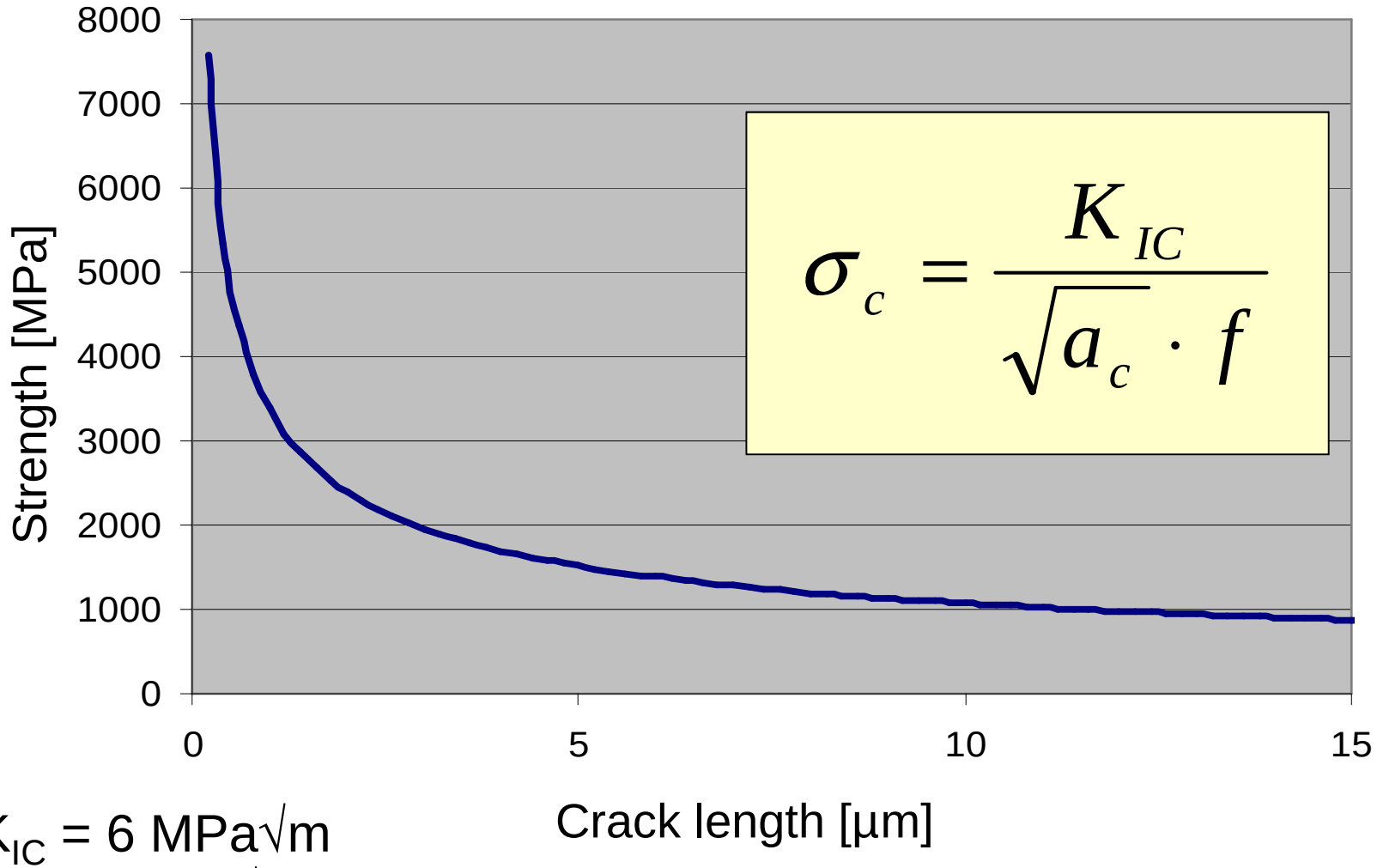
a_c = crack length at the moment of fracture

f = geometric factor

Fracture Toughness of different materials

Material	Composition	K_{IC} [MPa $m^{1/2}$]
Diamond	C	4
Silicon carbide	SiC	3 – 7
Silicon nitride	Si3N4	4 – 10
Alumina	Al2O3	2 – 8
Zirconia	ZrO2:(Y,Ce)	3 – 20
Fiber reinforced ceramics		10 – 40
Glas		0,5 – 1,5
Ice	H2O	0,1
Steel	Fe(C, …)	20 – 100
Cemented carbide	WC-Co	10 – 25
Concrete		1 – 1,5

Strength vs. Crack size



K_{IC} = 6 MPa$\sqrt{m}$
f = 1,77 (= $\sqrt{\pi}$)

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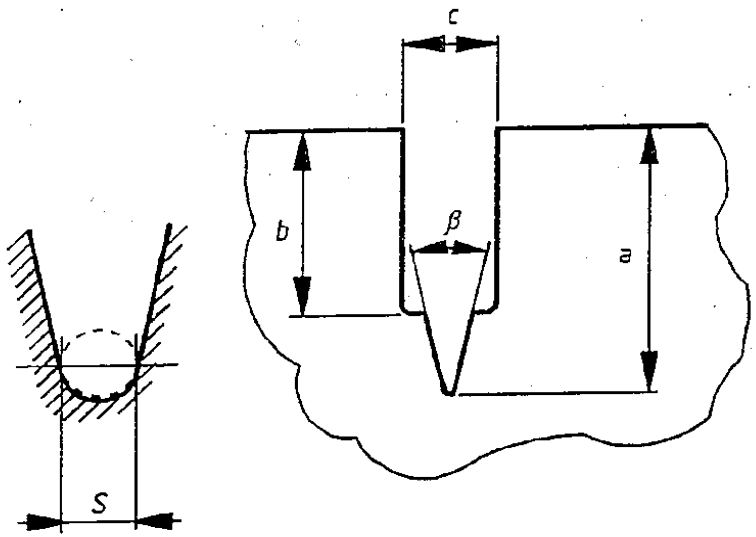
Sharp notch (simulates a crack)

Single **E**dge **V**-**N**otch **B**eam Test

Notch for SEVNB-Test

Razor blade method



Legende

a = 0,8 mm bis 1,2 mm

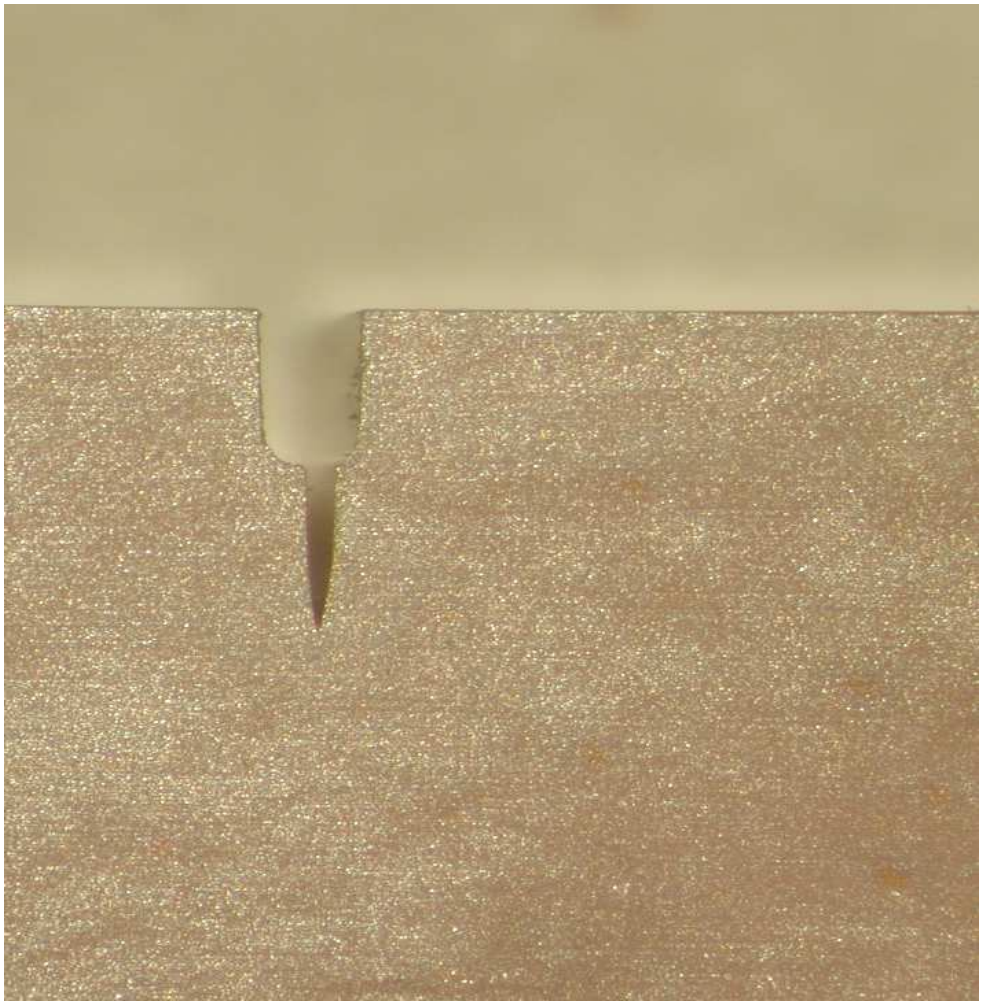
$b \approx$ 0,5 mm

c > Breite der Rasierklinge

$a - b > c$

$\beta \approx 30°$ oder so klein wie möglich

S = Breite des V-Kerbs



011-75

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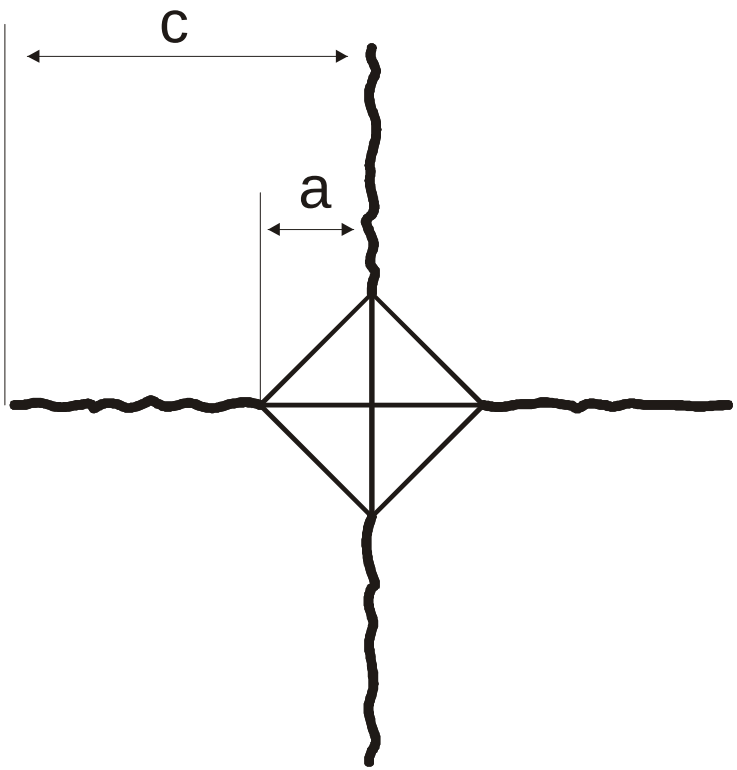
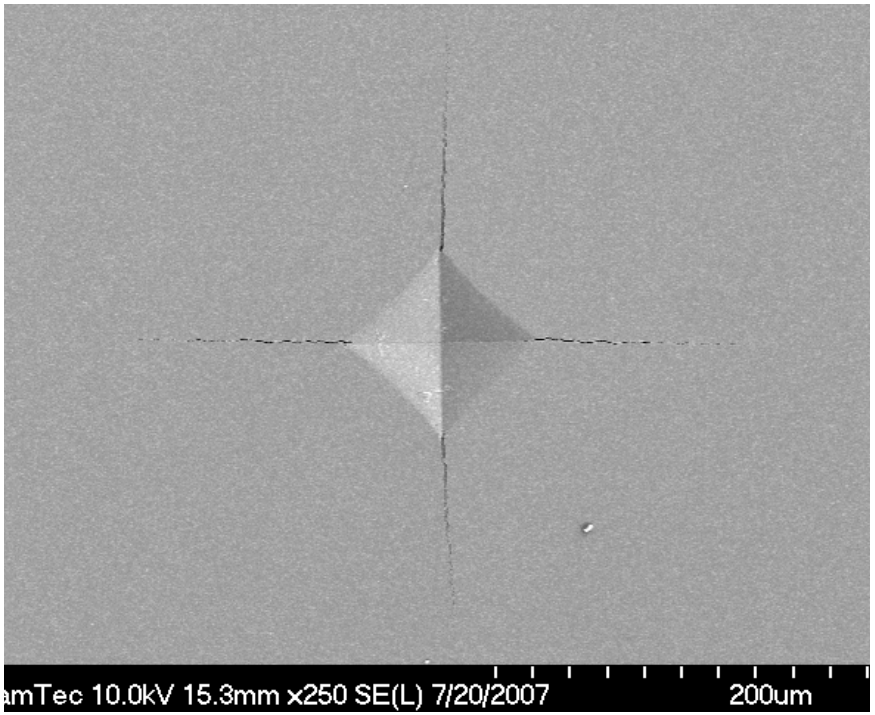
Estimate Fracture toughness





Palmquist-crack (c/a < 2,5) $$K_{IC} = 0.018\, H \sqrt{a} \left(\frac{E}{H}\right)^{0.4} \left(\frac{c}{a} - 1\right)^{-1/2}$$

Median-crack (c/a ≥ 2,5) $$K_{IC} = 0.067\, H \sqrt{a} \left(\frac{E}{H}\right)^{0.4} \left(\frac{c}{a}\right)^{-3/2}$$

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How to increase the strength of ceramic

$$\sigma_c = \frac{K_{IC}}{\sqrt{a_c} \cdot f}$$

Microstructure design:
Increase toughness

Ceramic technology:
Reduce defect size

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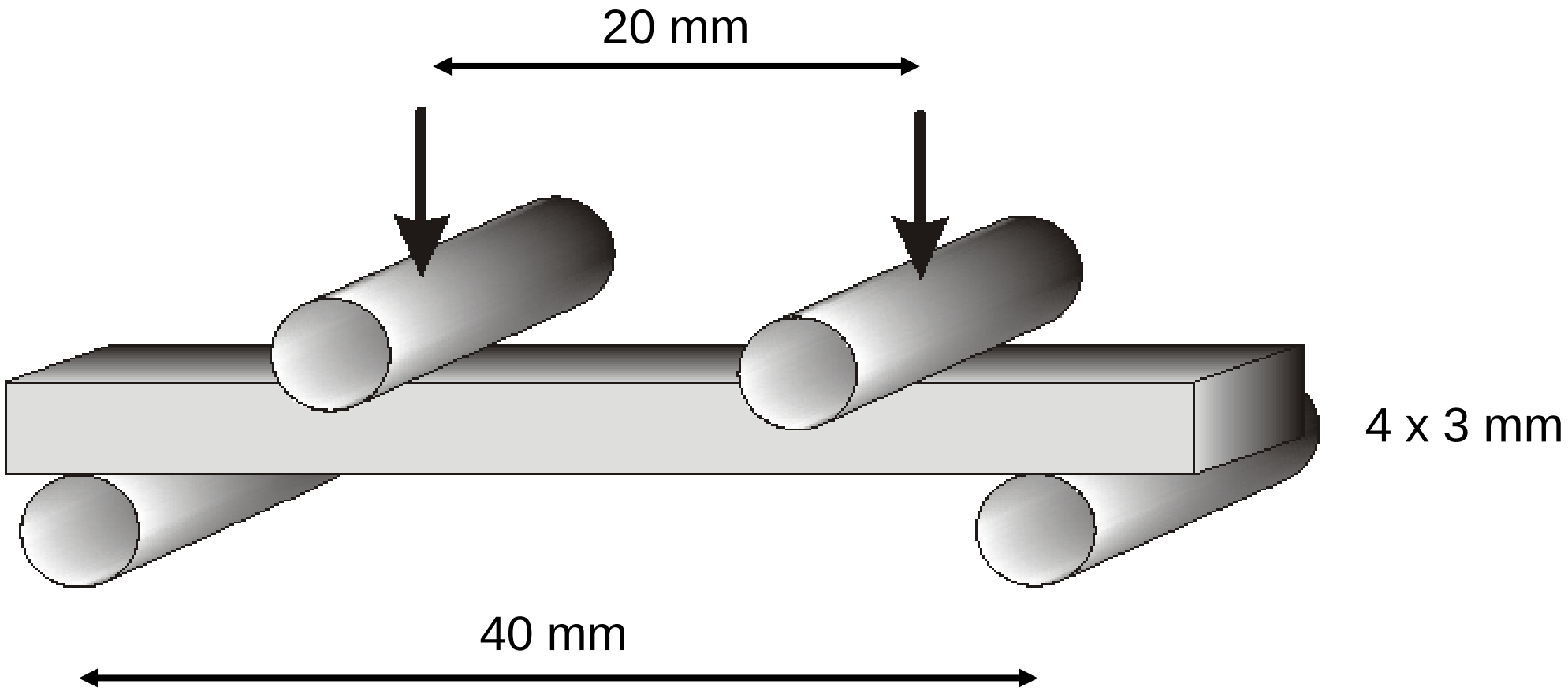
Messurement of strength

ISO standard 4 point bending test



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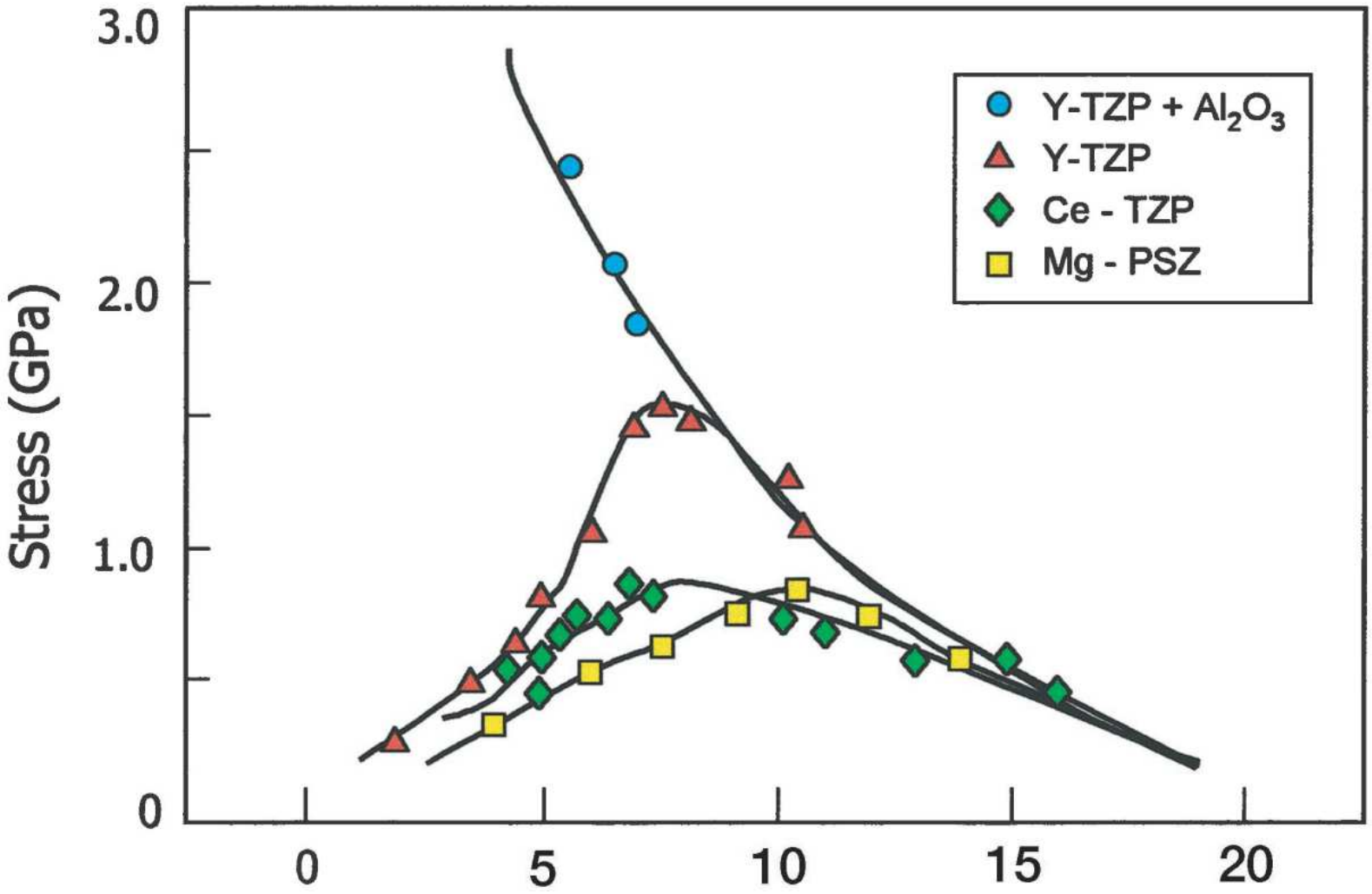
Increase strength

via

increase of toughness !

$$\sigma_c = \frac{K_{IC}}{\sqrt{a_c \cdot f}}$$

Correlation Toughness vs. Strength



Transformation Toughening in Zirconia-Containing Ceramics

Richard H. J. Hannink*

CSIRO Manufacturing Science and Technology, Clayton South MDC, Victoria, 3169, Australia

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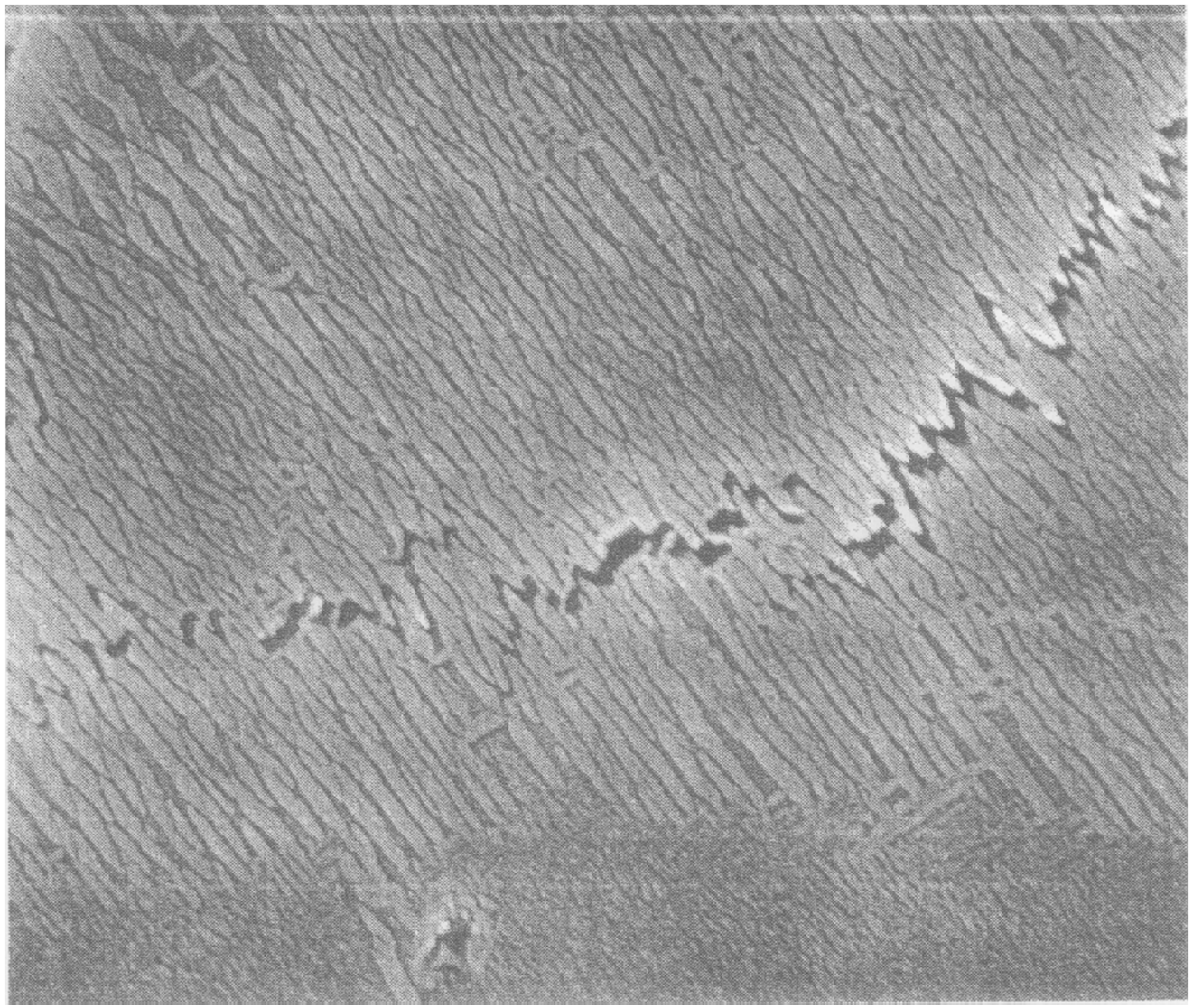
Elongated grains → crack bridging



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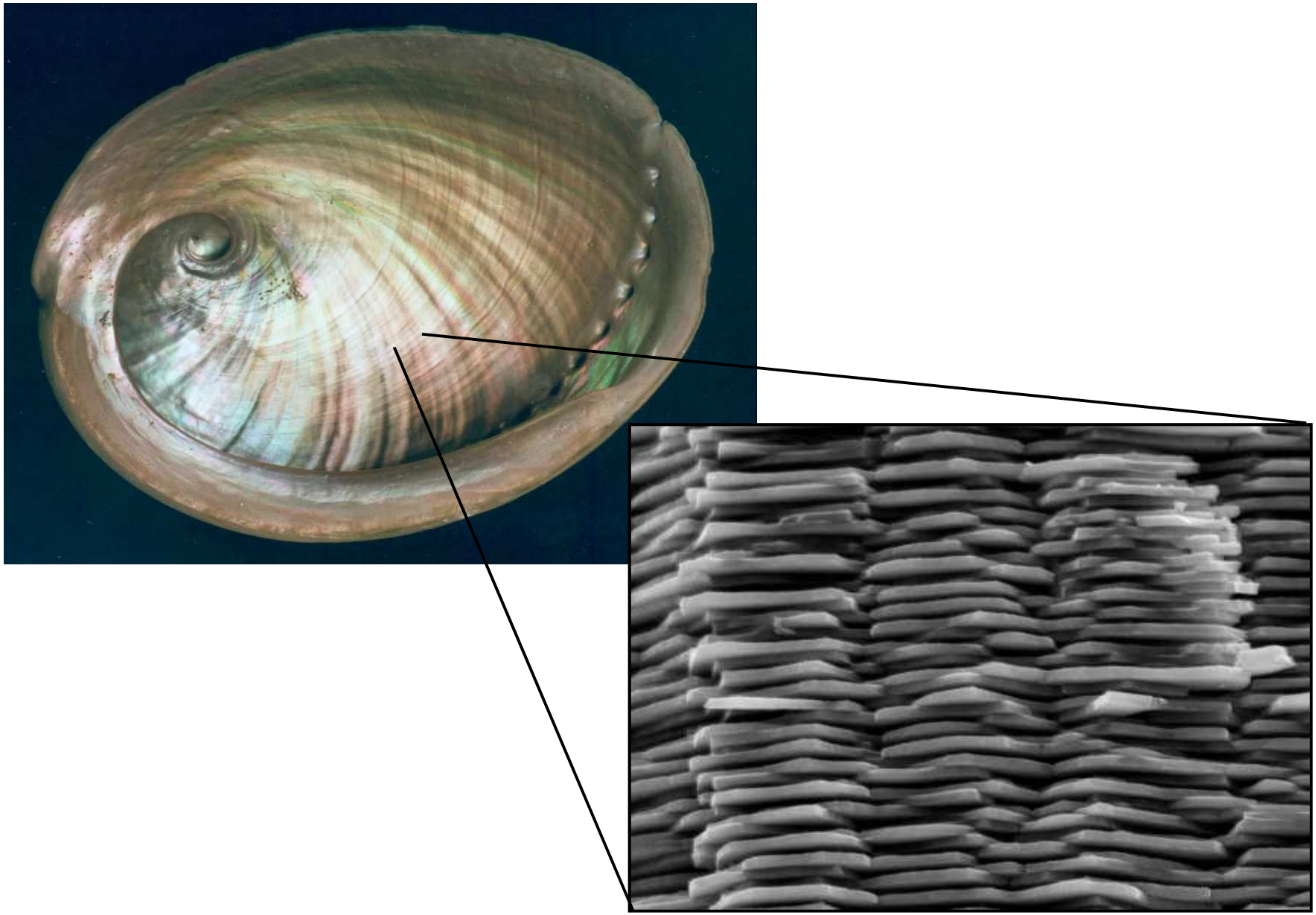
Nacre – mother of pearl



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ß-Silicon Nitride needle shaped crystals

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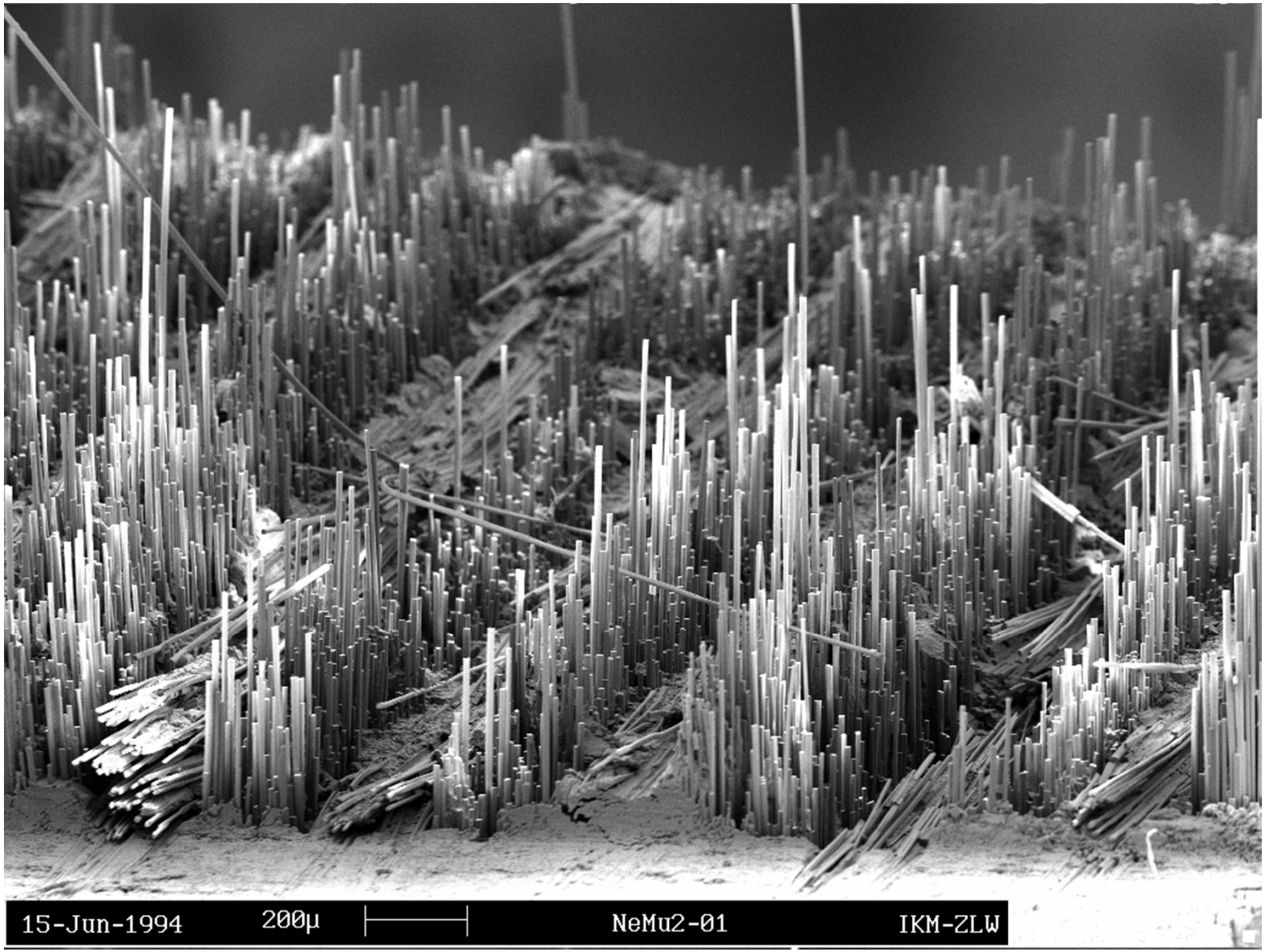
“Tough ceramic“
Fiber reinforcement



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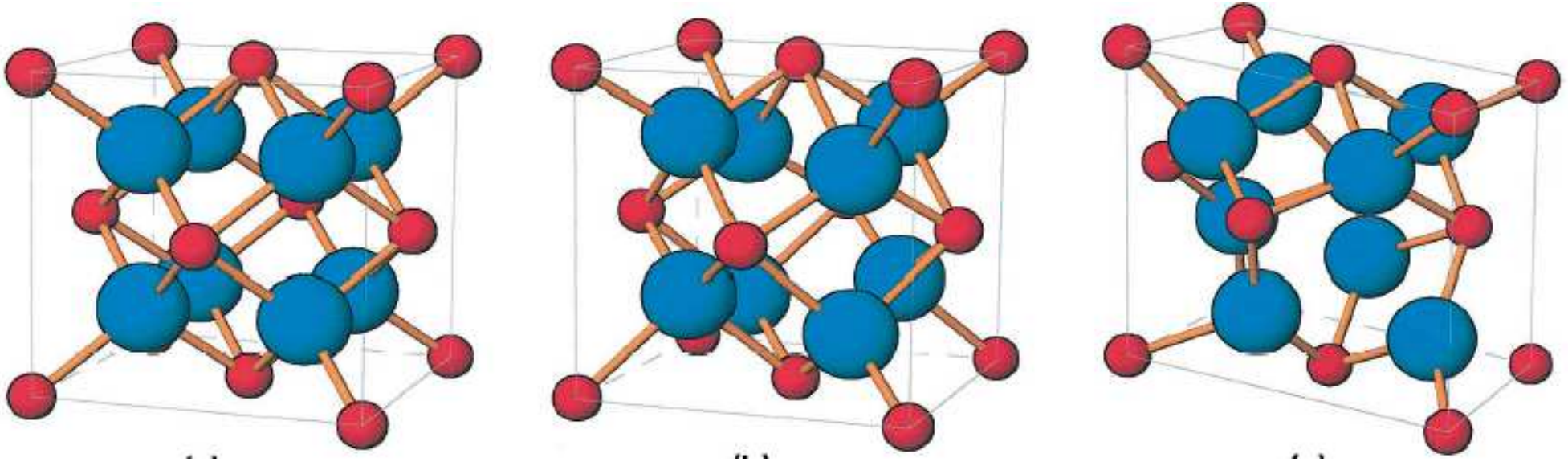
Phase transformation toughening Zirconia



Cubic

Tetragonal

Monoclinic

Oxygen

Zirkonium

Volume increase + 4%

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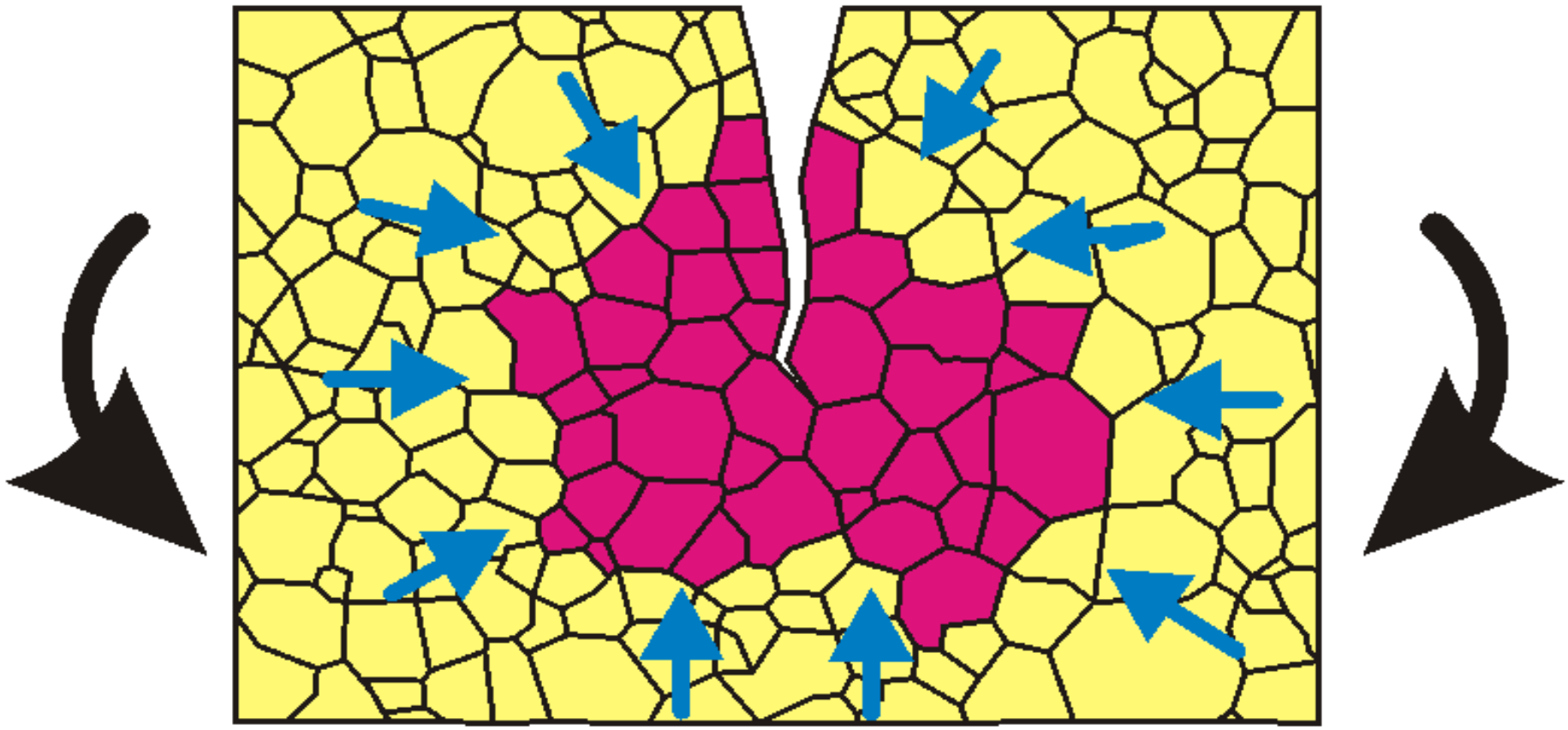
Phase transformation toughening Zirconia



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Increase strength

via

reduction of defects !

$$\sigma_c = \frac{K_{IC}}{\sqrt{a_c} \cdot f}$$

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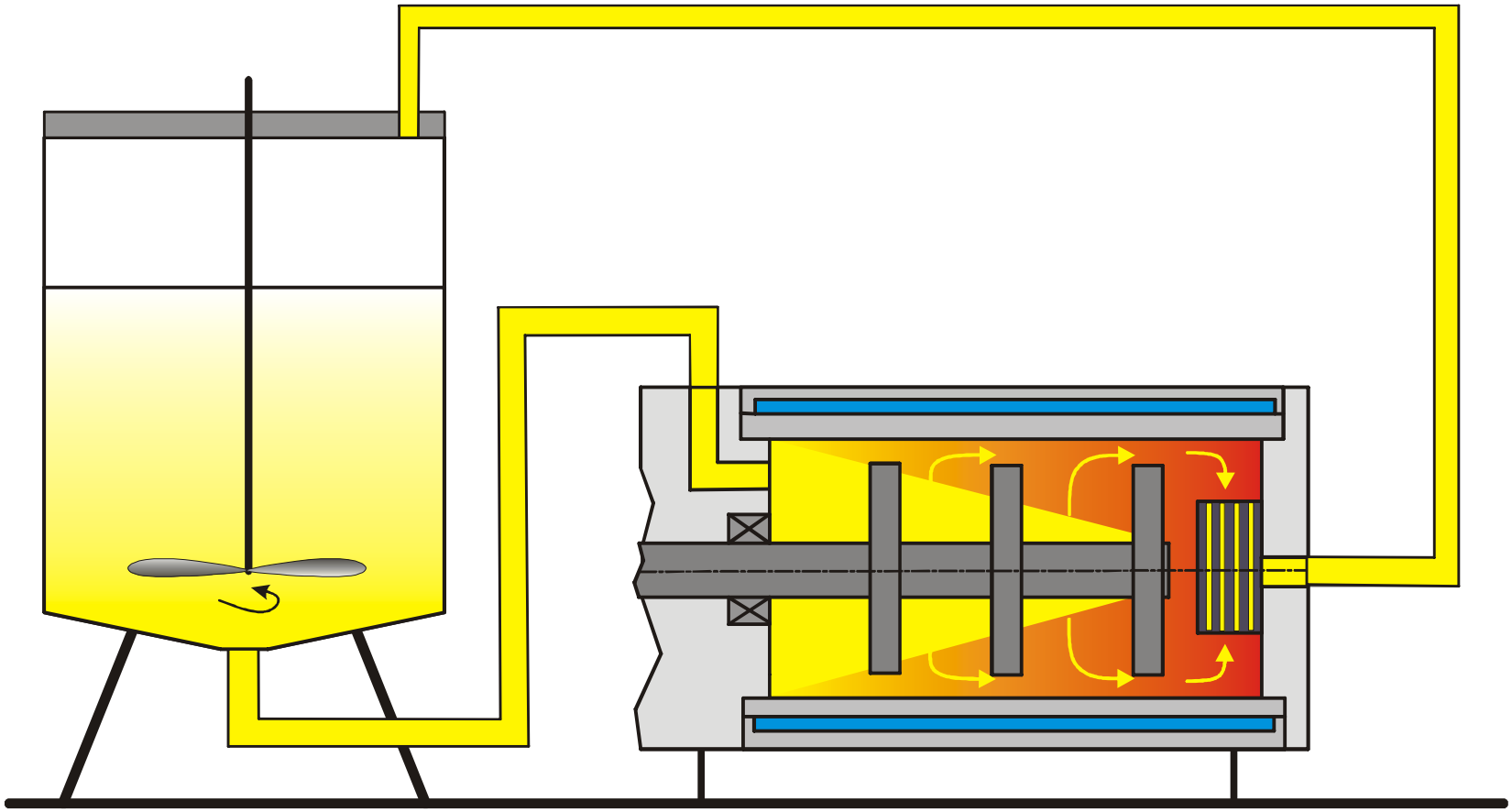
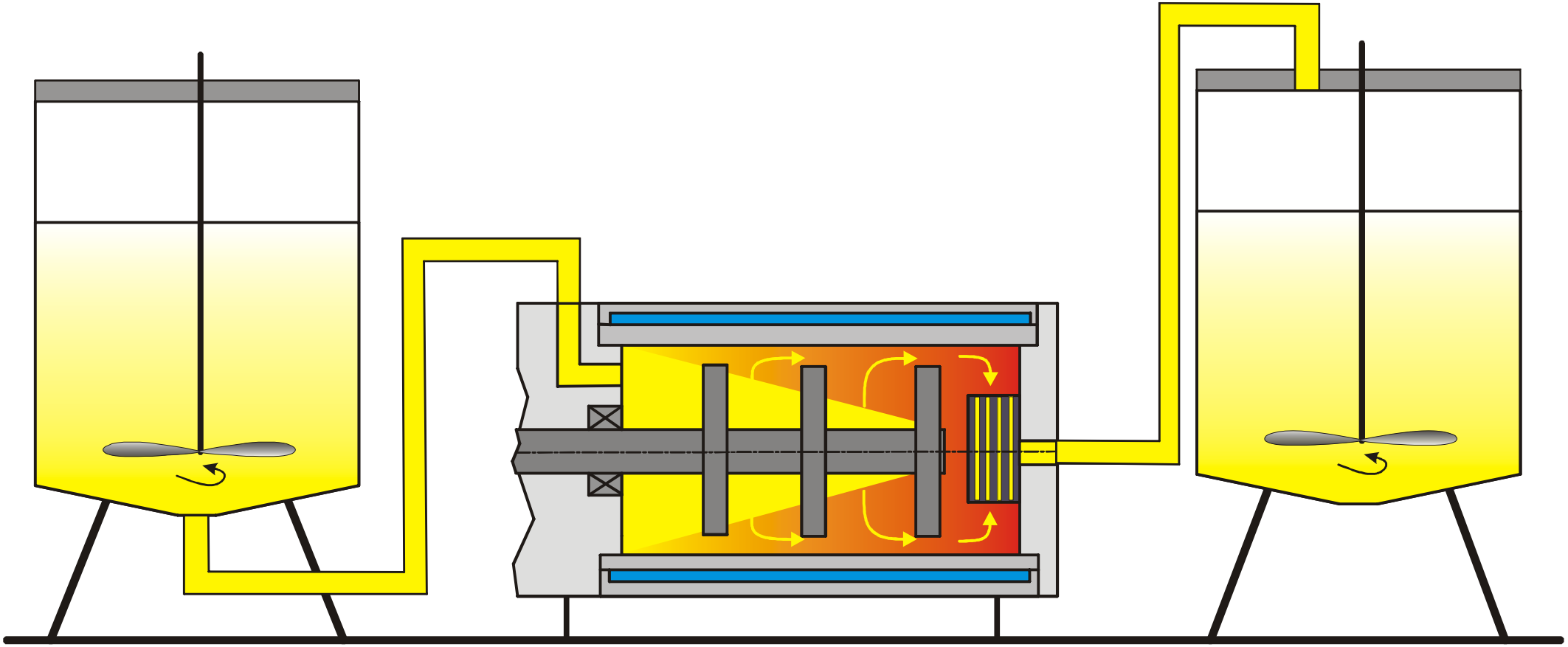
Wet milling
Circulation mode



CeramTec

Wet milling
Reciprocating mode



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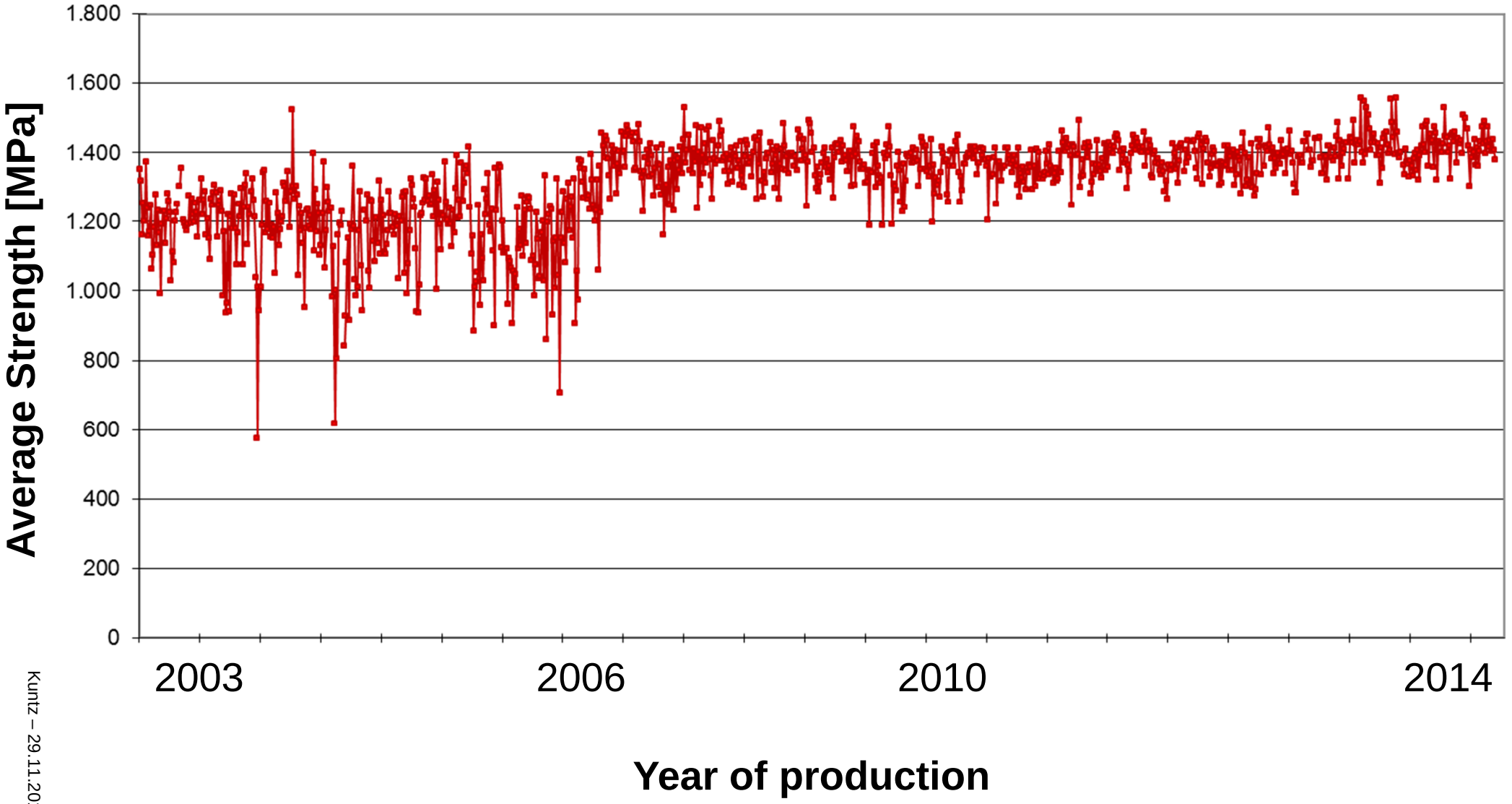
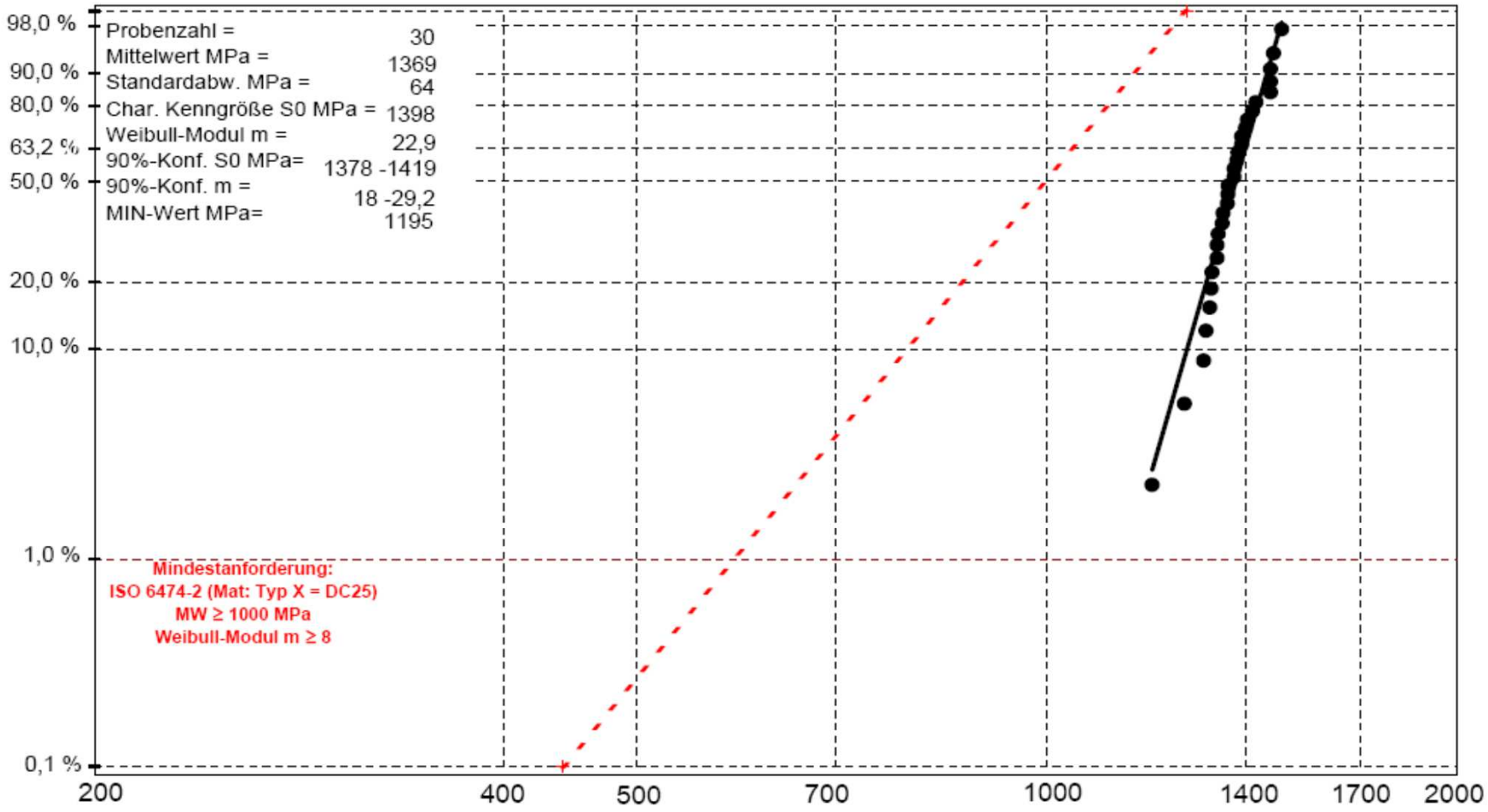
Strength of BIOLOX®*delta*

Each point represents average of 30 bending tests



CeramTec

Strength Distribution of BIOLOX®*delta*



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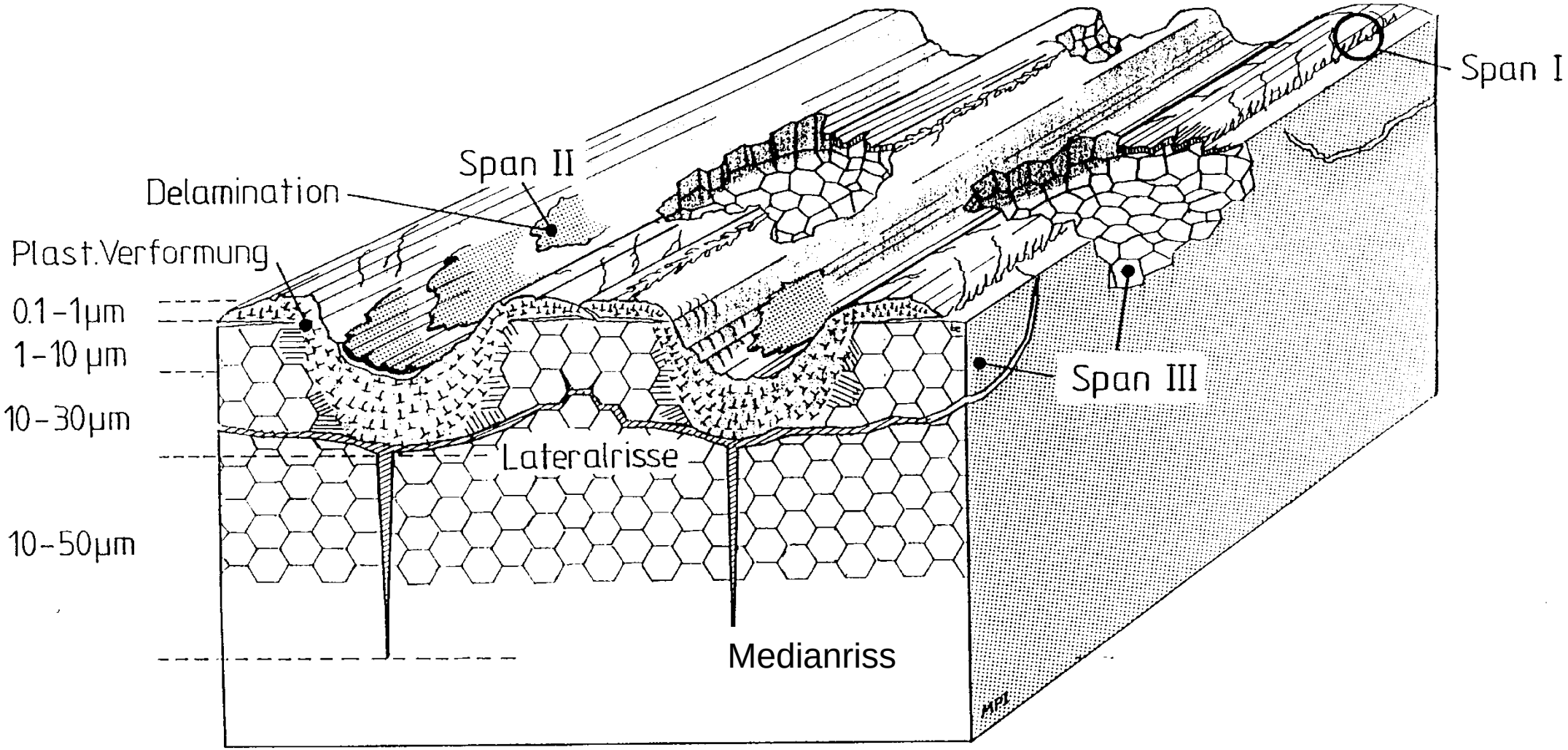
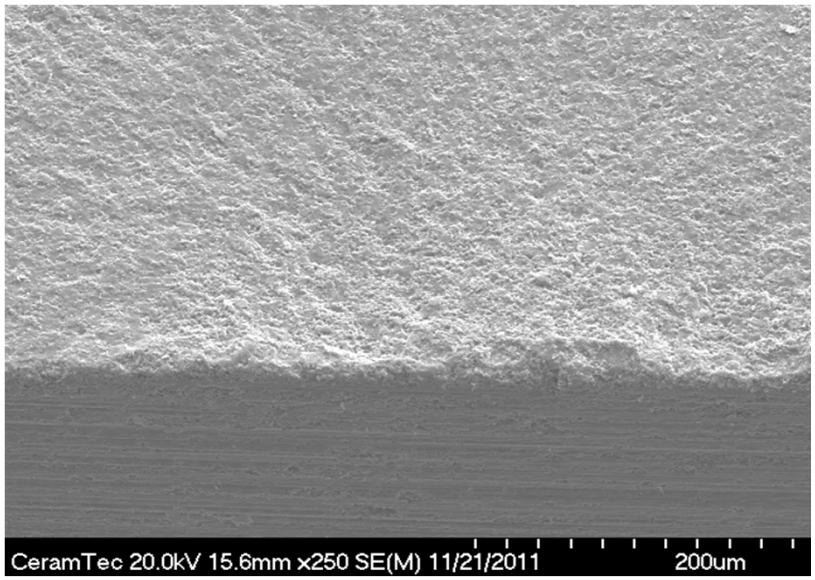
Damage at machining

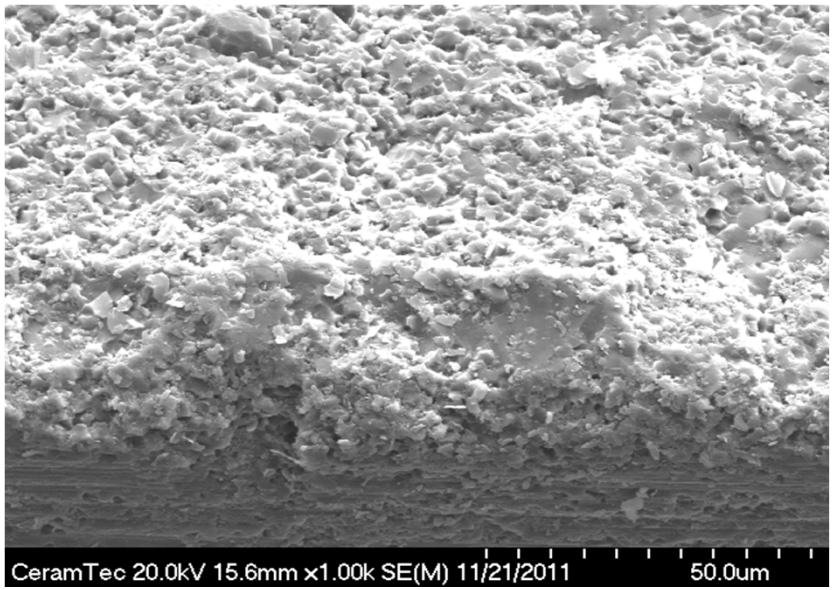


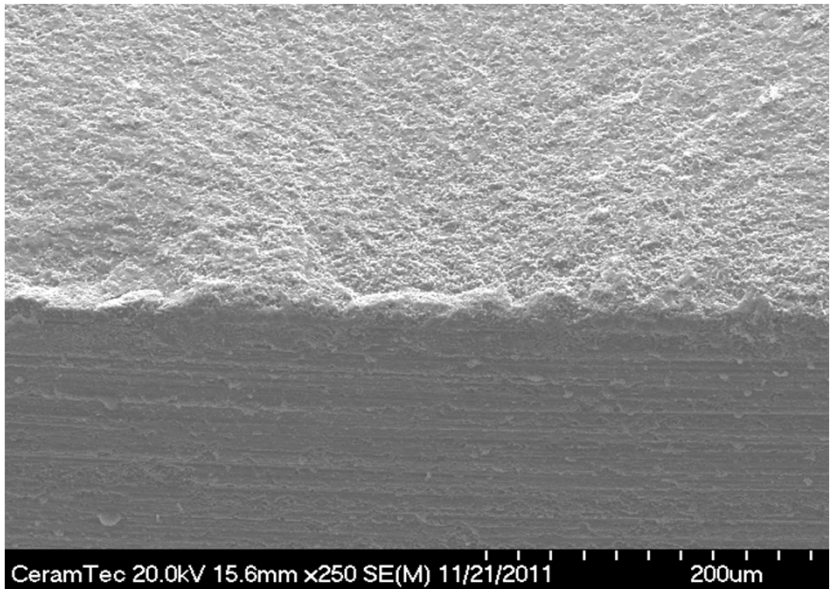
Telle, 1994

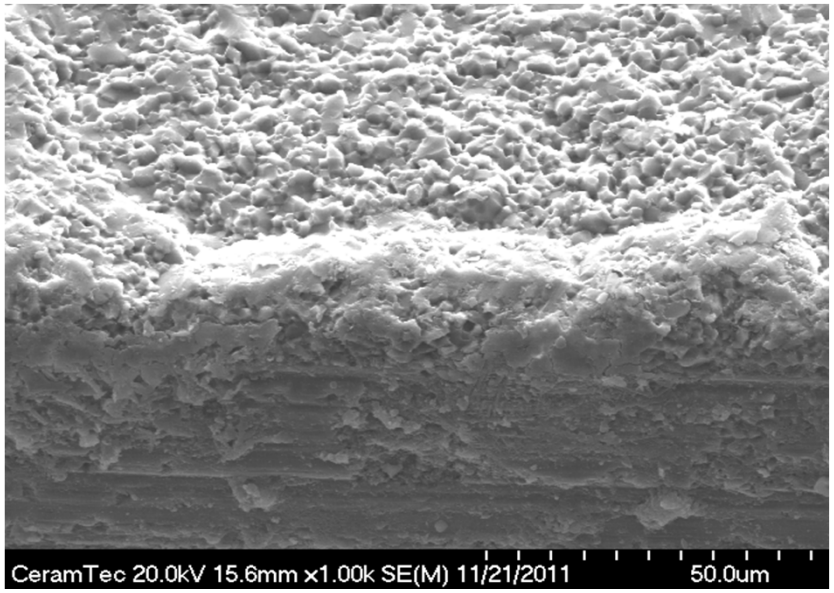
CeramTec

Natural machining defects









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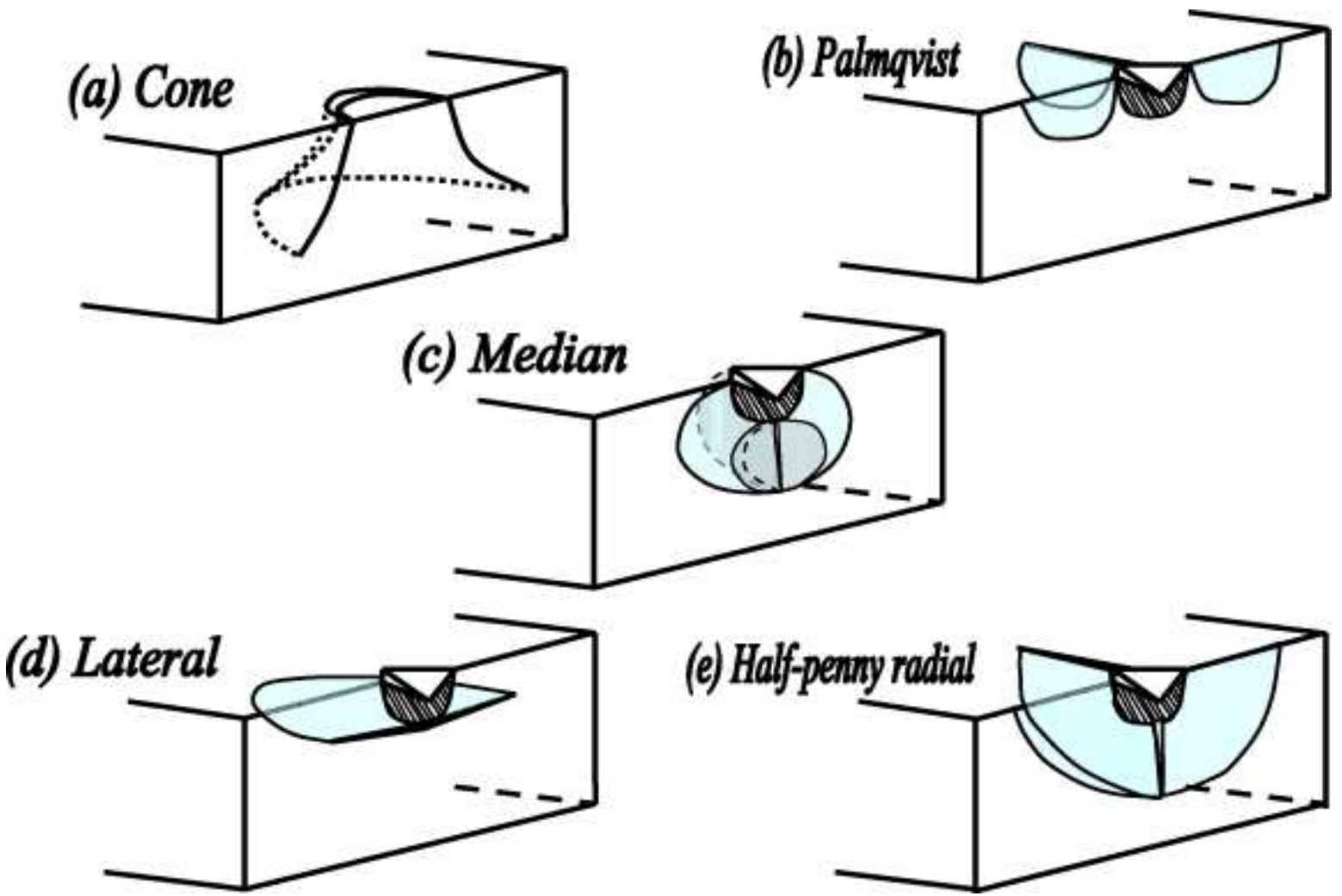
Damaging at point load



Journal of Physics D: Applied Physics Volume 45 Number 20
Jiinju Chen 2012 J. Phys. D: Appl. Phys.
Indentation-based methods to assess fracture toughness for thin coatings

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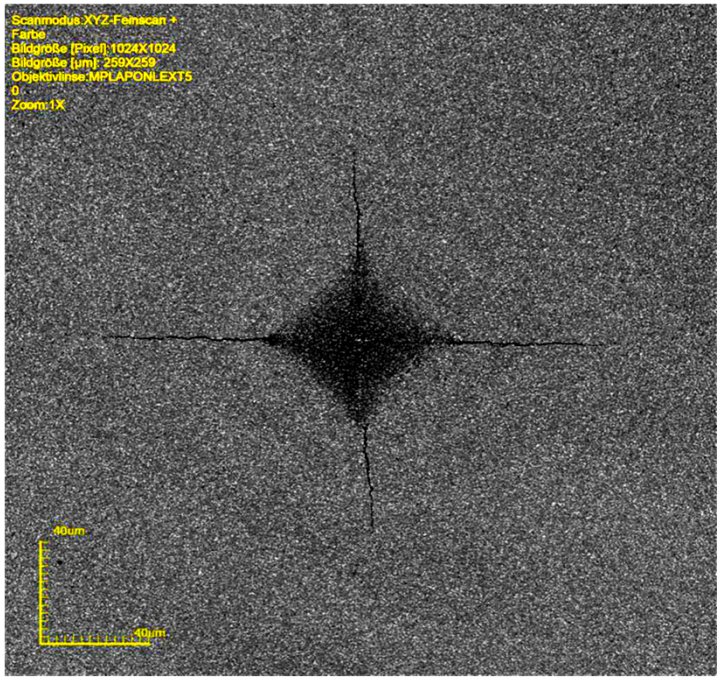
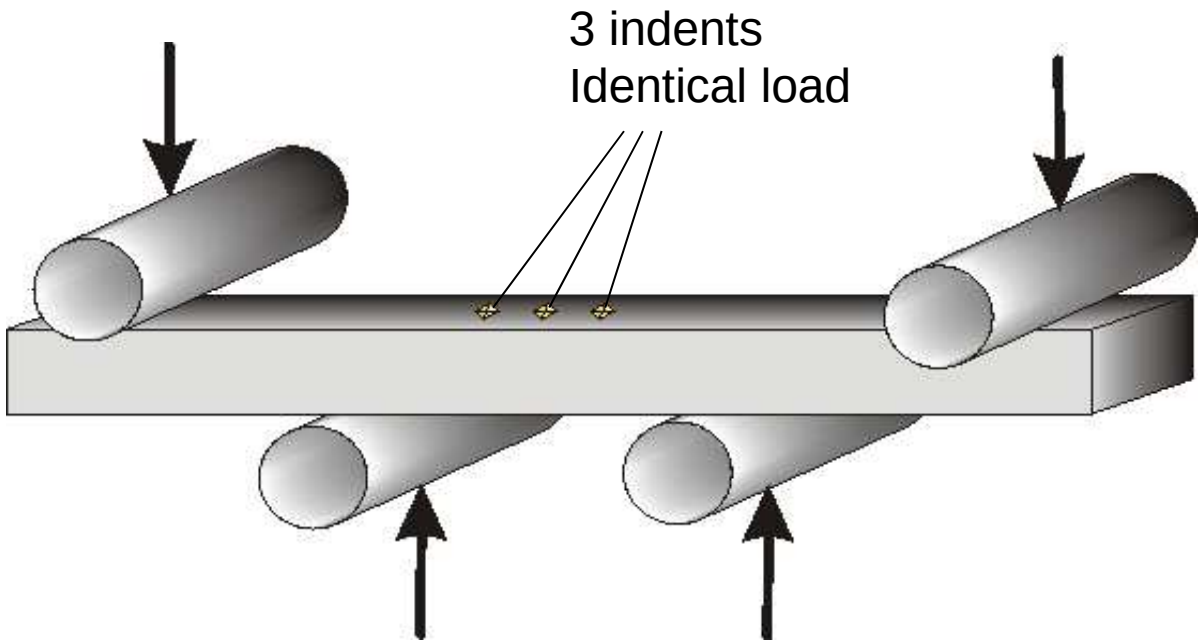
Damage tolerance

Intentional damaging:
Vickers indent with crack





Test protocol:

1. Initial strength (no indent)
2. Indent damaging 3 – 500 N
3. Residual strength after damage

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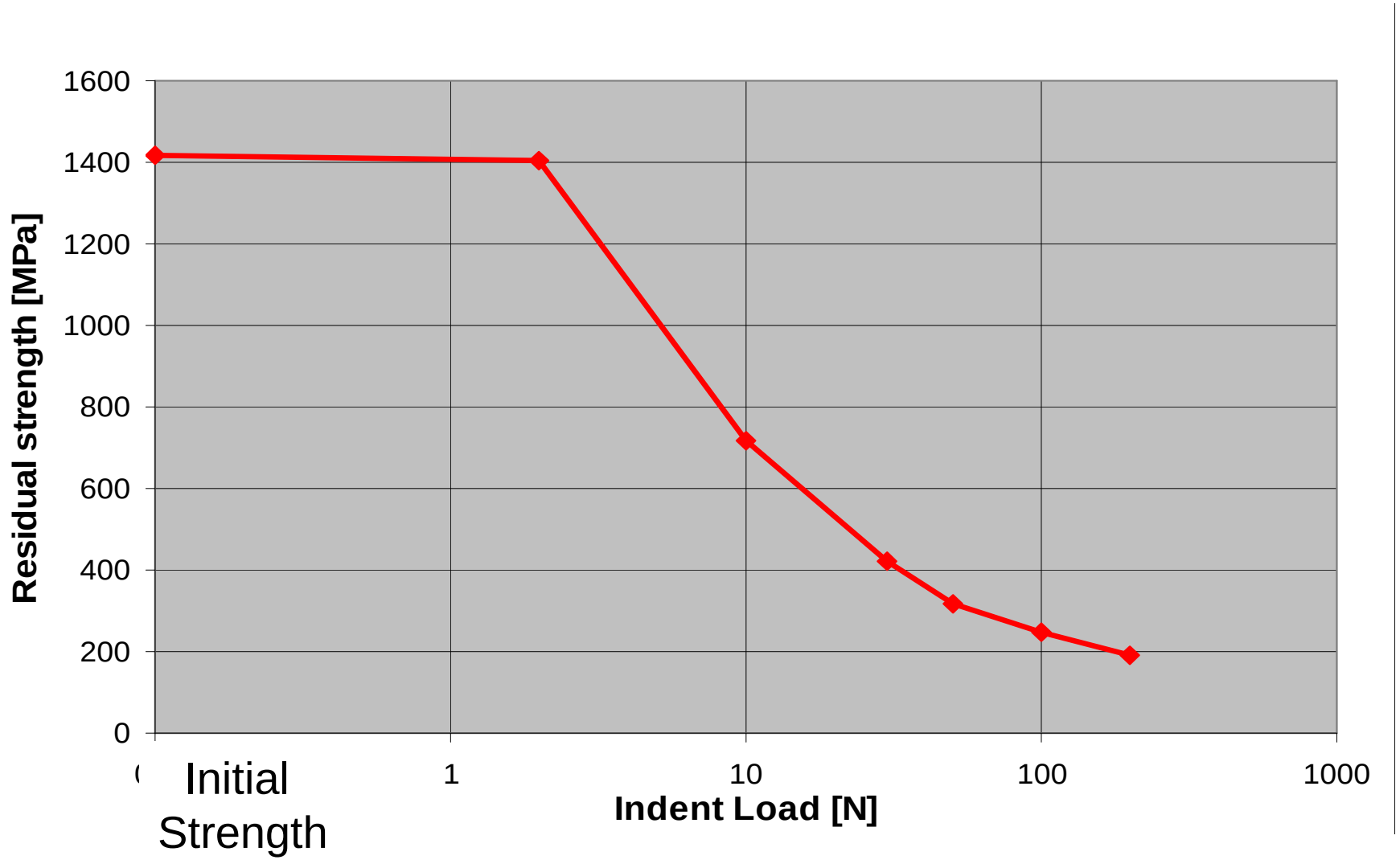
Damage tolerance

BIOLOX®*delta*



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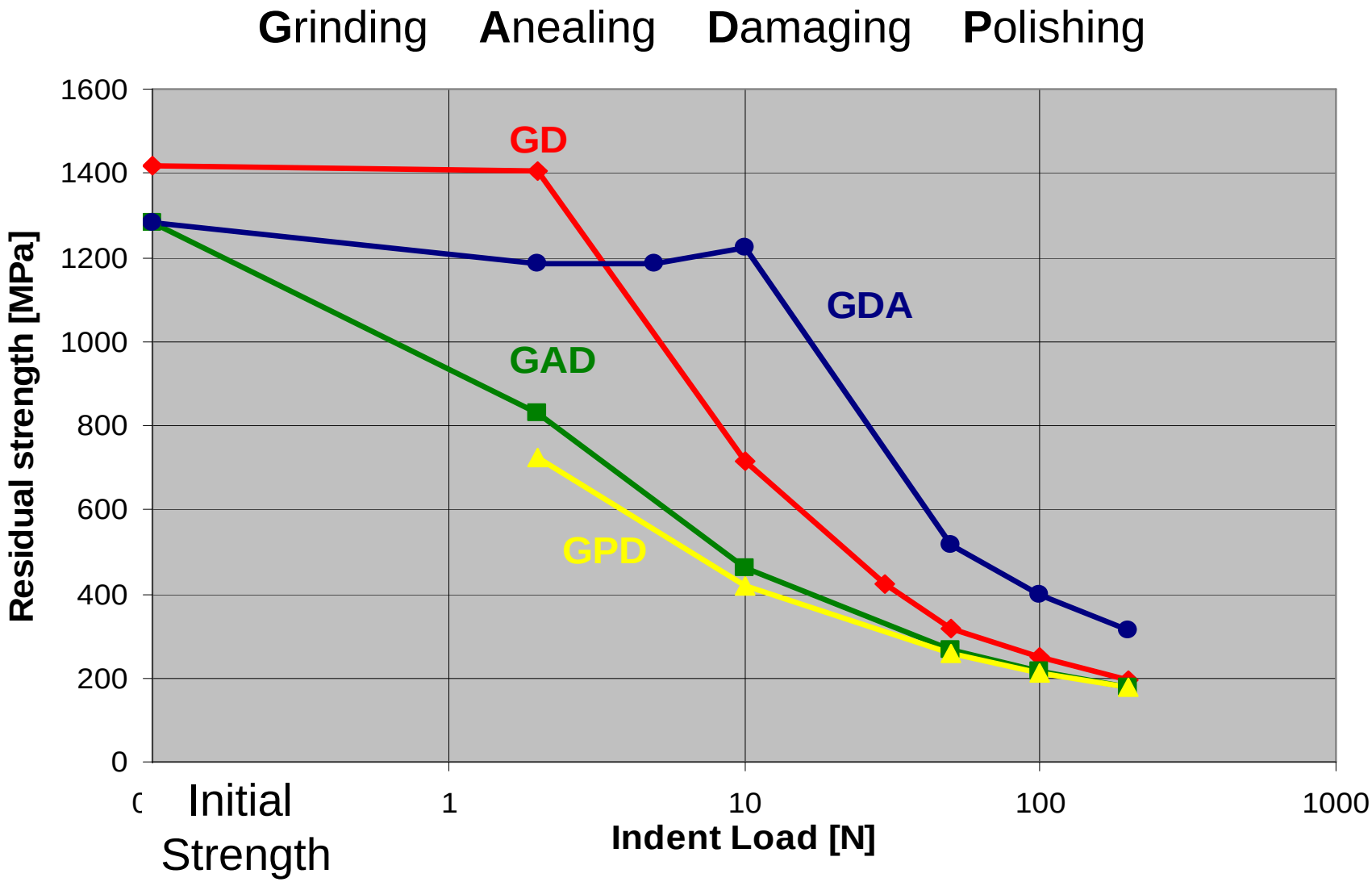
Damage tolerance vs. temperature treatment



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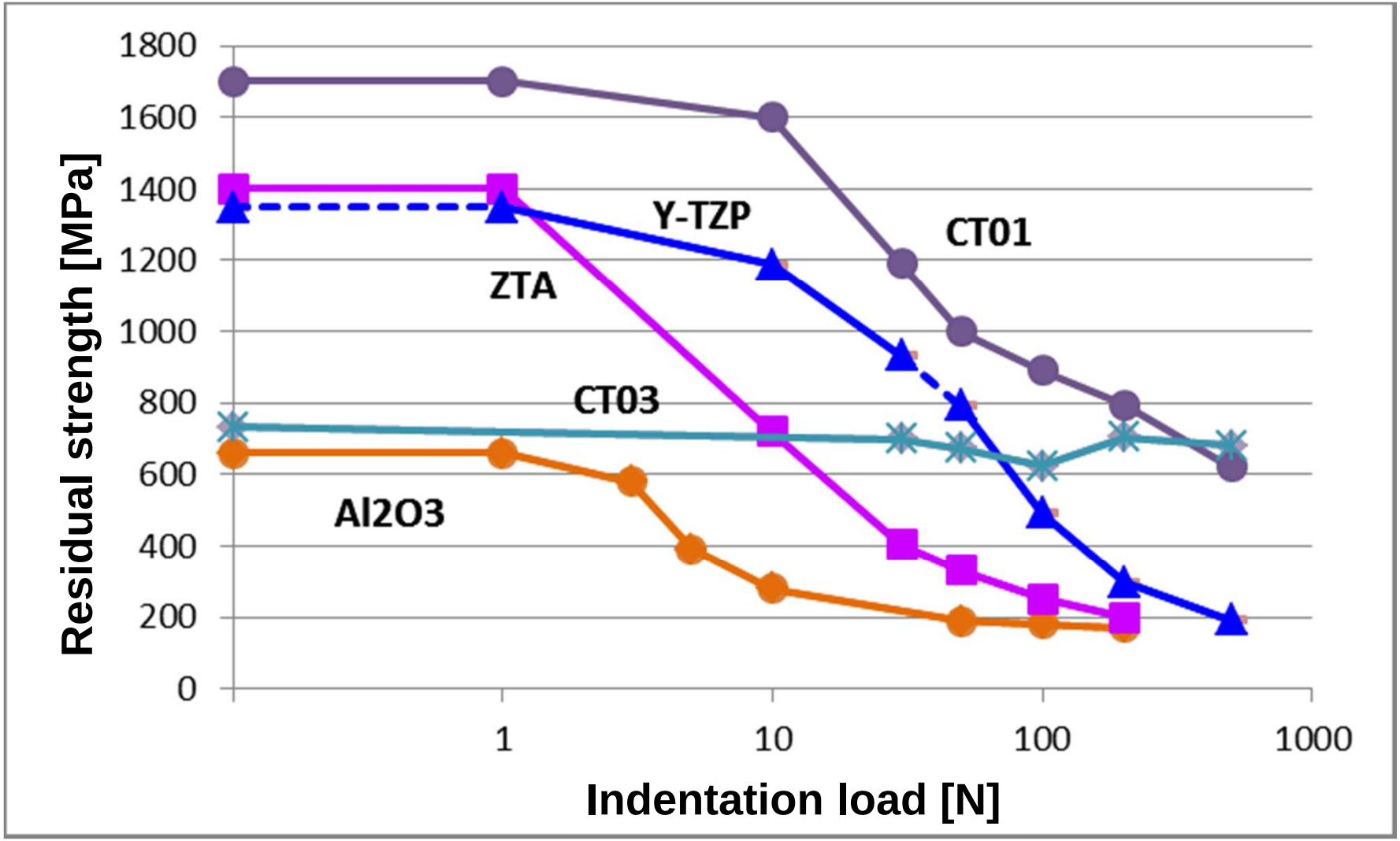
Development of damage tolerant ceramics



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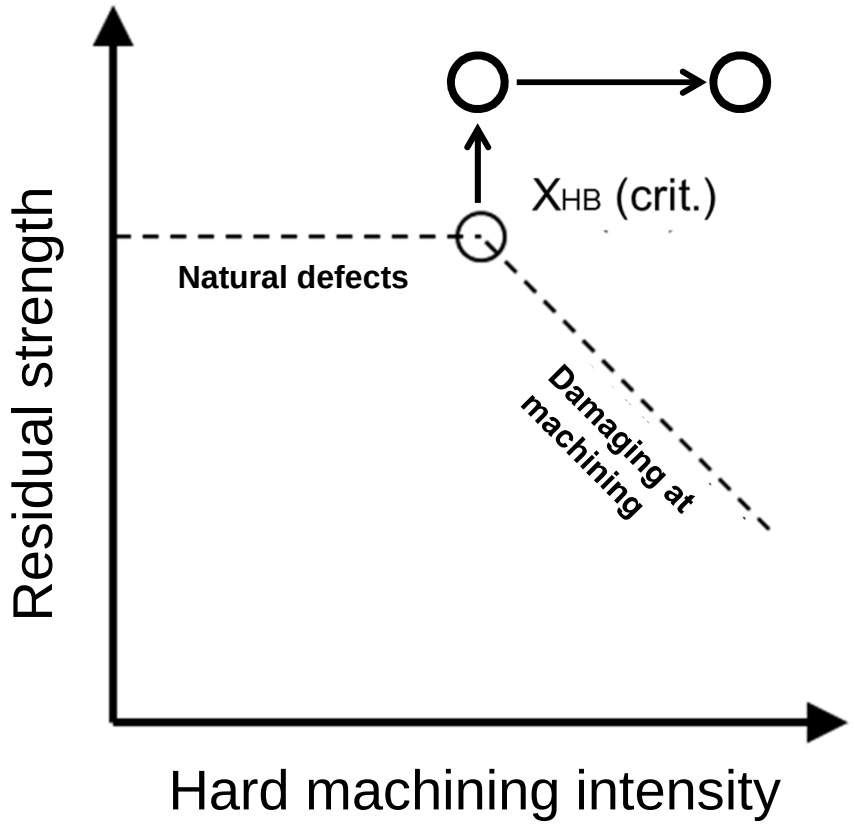
Goal: „Robust Ceramic“



- ***High safety margin***
- ***High cost effectiveness***
- ***Dentists „Acceptance“***

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Some important oxide materials

Revision after 20 years in vivo

Dimensions ✓
Polishing ✓
Strength ✓

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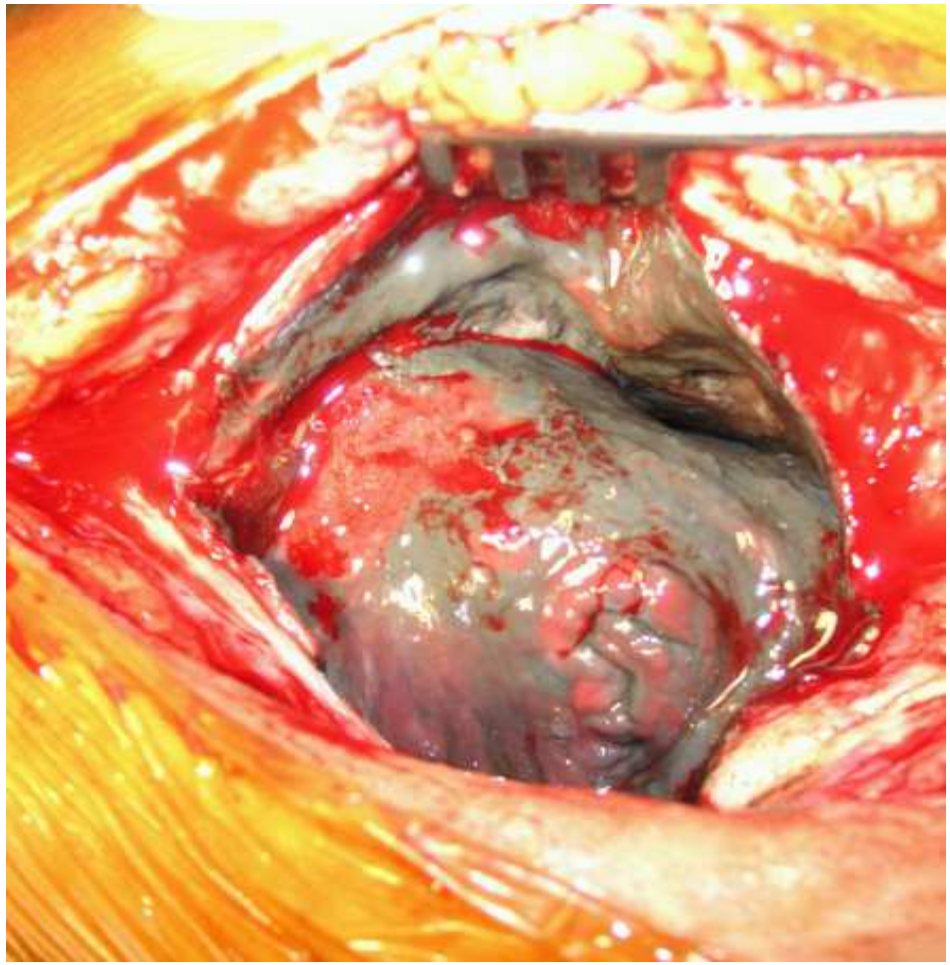
Revision
Metal vs. Polyethylen



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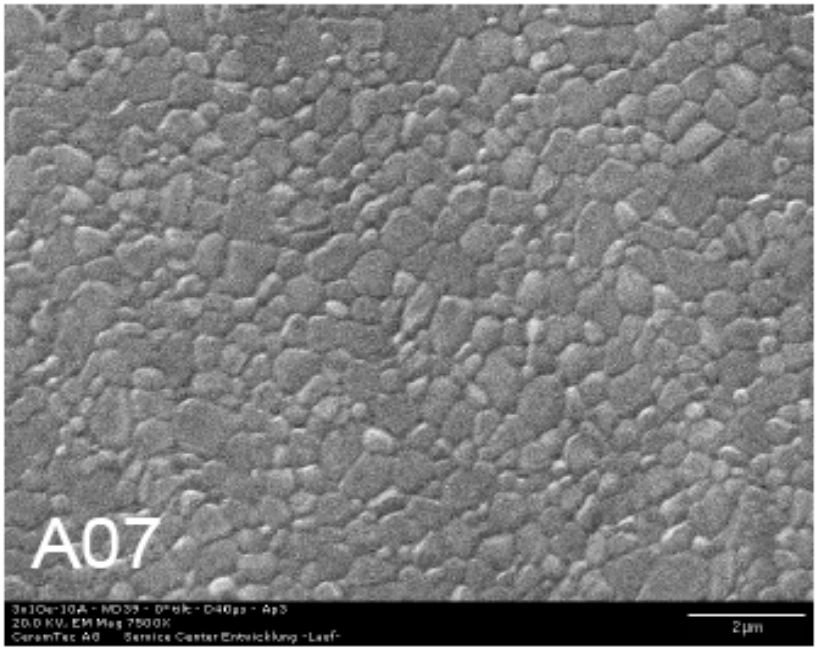
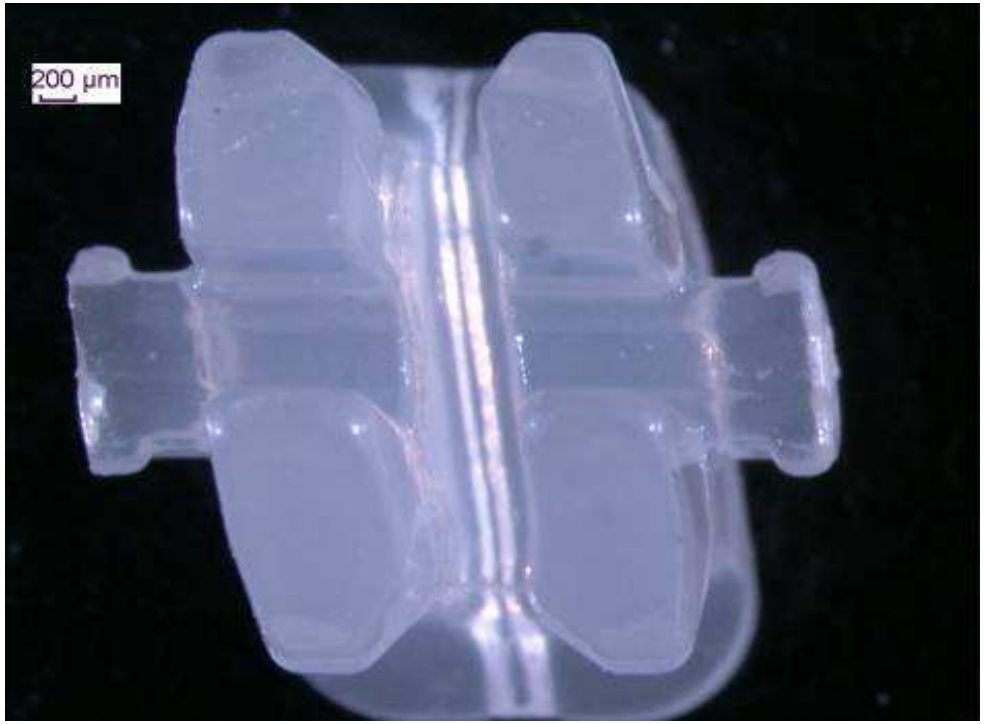
Brackets

Ultra high purity alumina





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Zirconia ZrO_2

Lambda oxygen sensor

Refractory

Kitchen knife

Diamond Imitation

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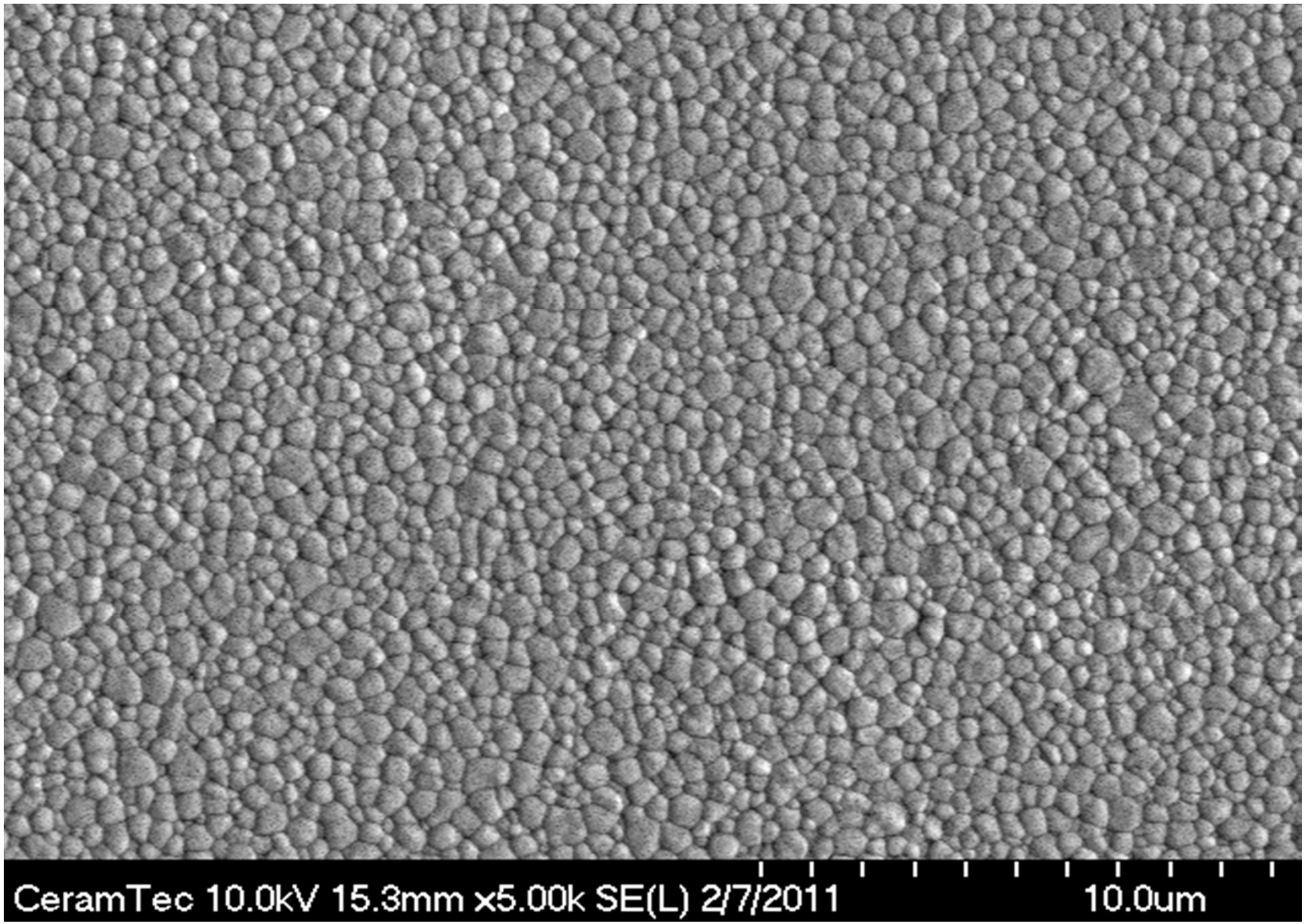
Microstructure 3Y-TZP



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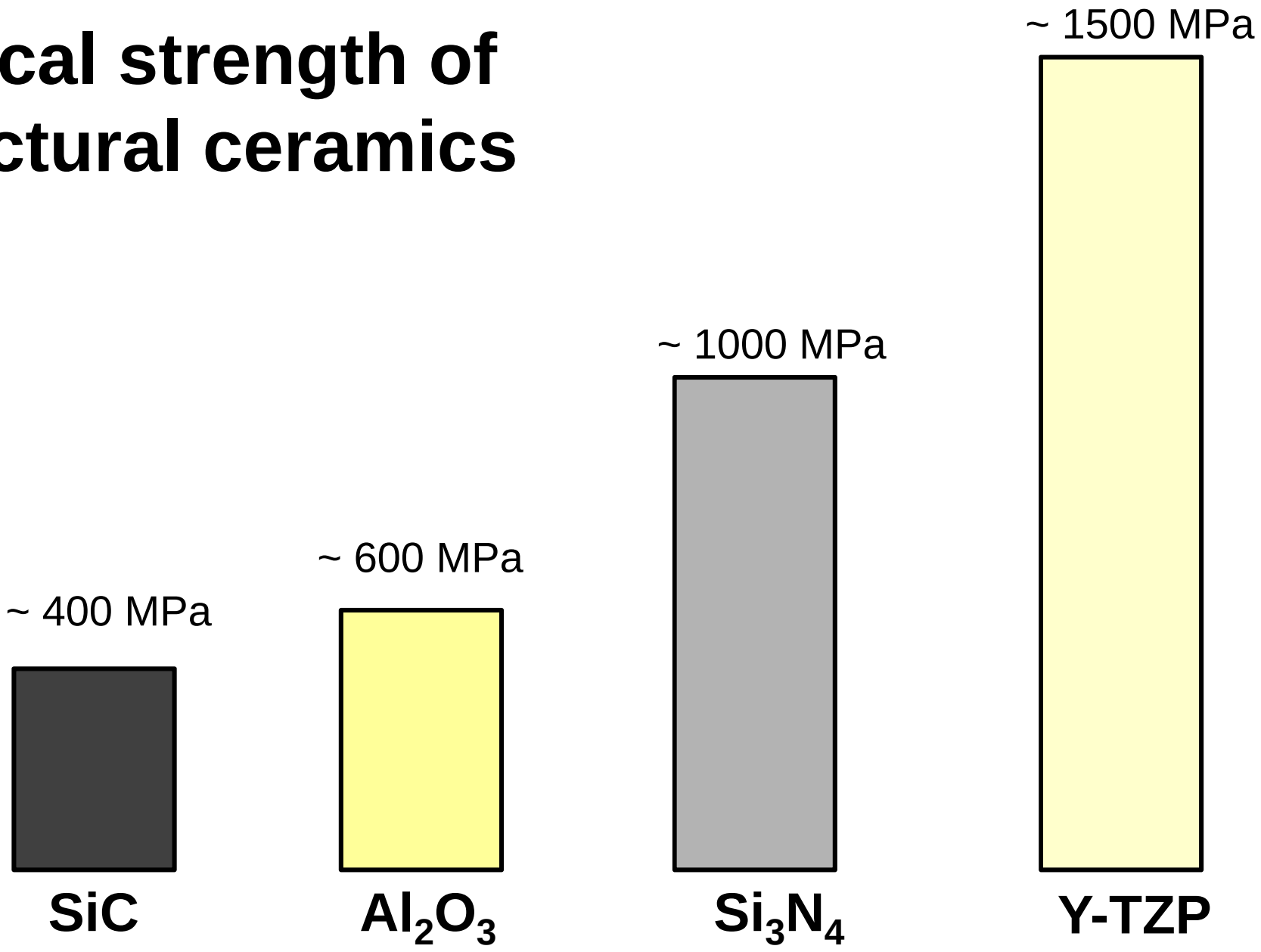
Typical strength of structural ceramics



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Dental Applications: Blanks

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Dental Applications: Implants

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Medical Tools: Drills

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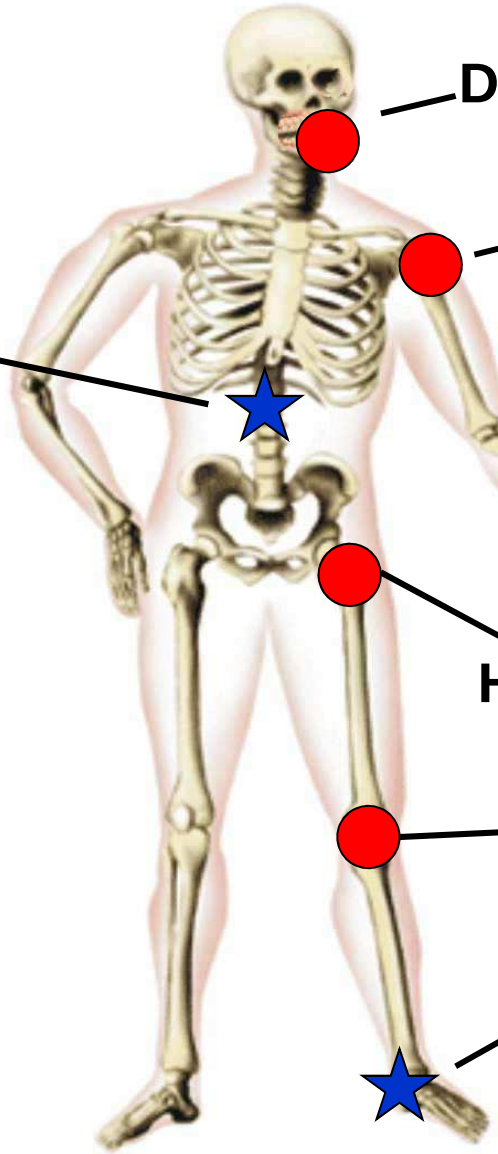
Applications for high strength ceramics



Dental – mass production – aesthetics !

Shoulder – clinical study

Spine –
Customers inquiry

Finger – Customers inquiry

Hip joint – mass production

Knee joint – increasing customers inquiry
Difficult design – niche product

Foot joint – currently no activities

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Products for Endoprosthetics

Alumina

Zirconia Toughened Alumina

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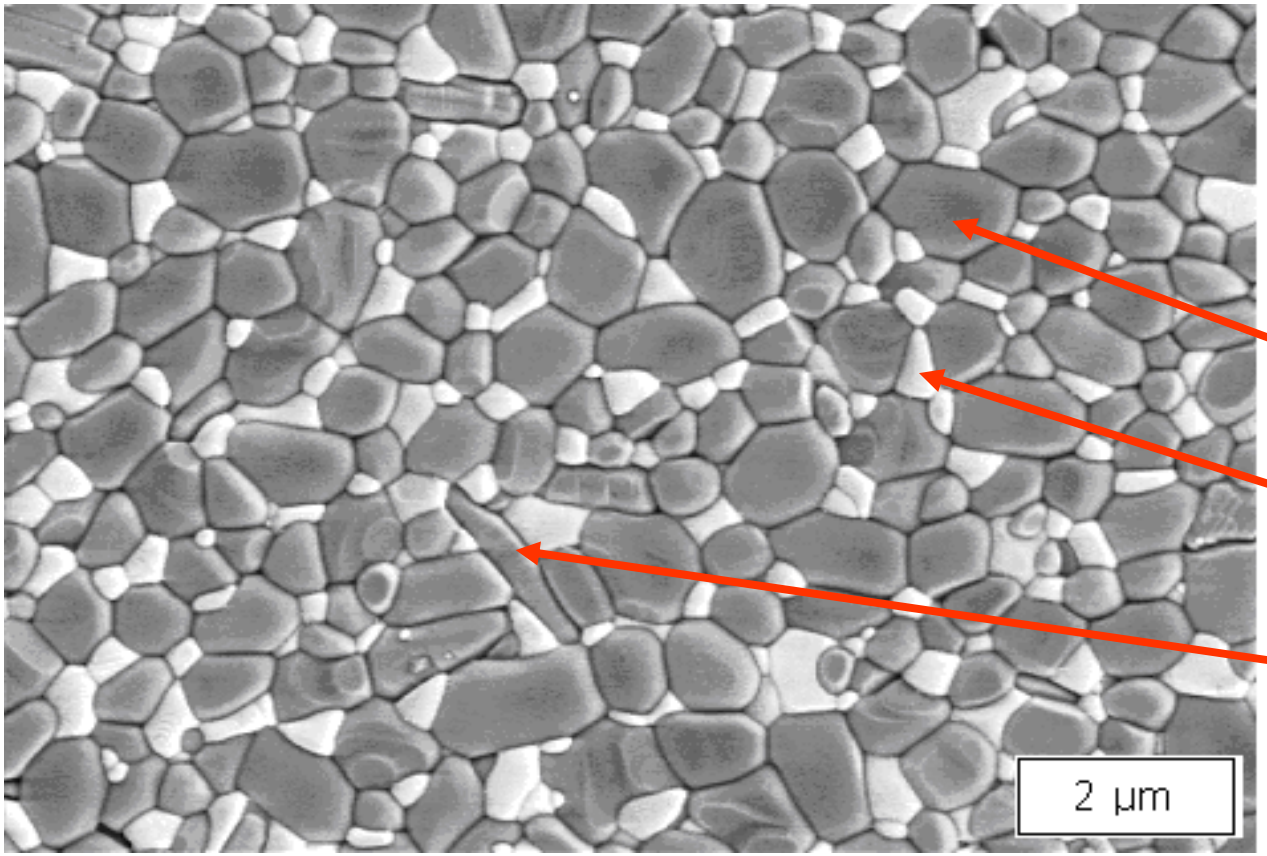
ZTA composite material BIOLOX®*delta*

Alumina based material incl. 17 vol% Zirkonoxid

Double strength and toughness compared to Al_2O_3



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Quality control

Quality of a powder batch:

- In-line: BET, grain size, pressing properties, …
- Powder batch release: density, microstructure, chemical analysis, strength, hardness, fracture toughness

Component control:

- On reference parts: density, microstructure, roughness
- 100% Dimension control
- 100% Prooftest
- 100% Crack inspection
- 100% Visual inspection

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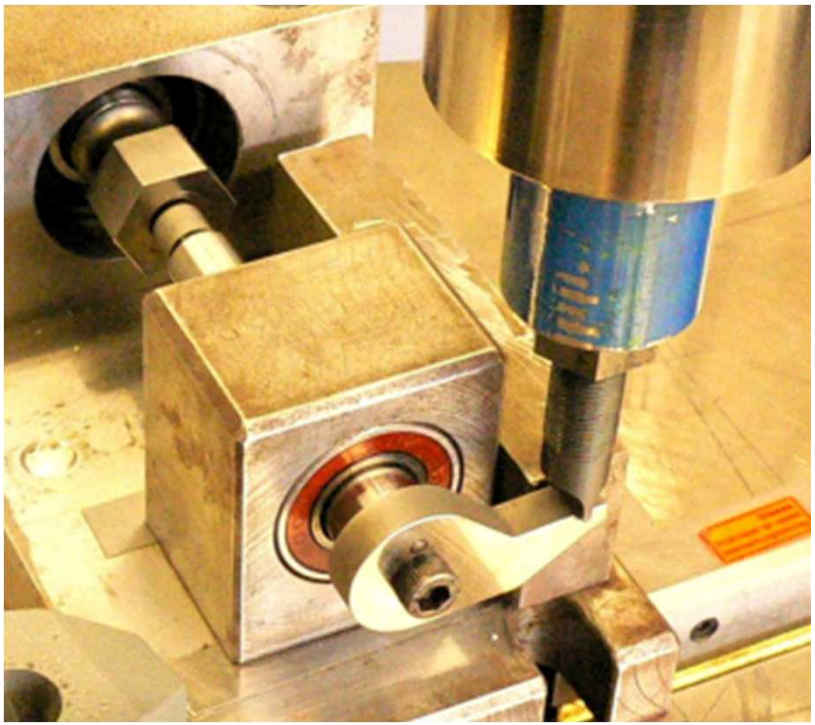
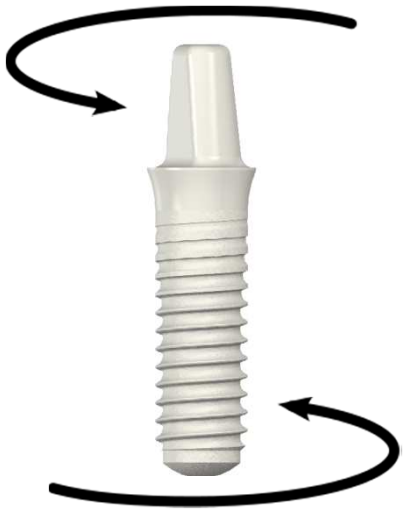
Principle of prooftest

1. FE-analysis of critical stress situation (in-vivo or operative)
2. Selection of a safety margin (2 – 3)
3. Mechanical stress application = maximum stress × safety margin
4. Destructive selection of „weak components“

Example:
Operative torsion load on a dental implant





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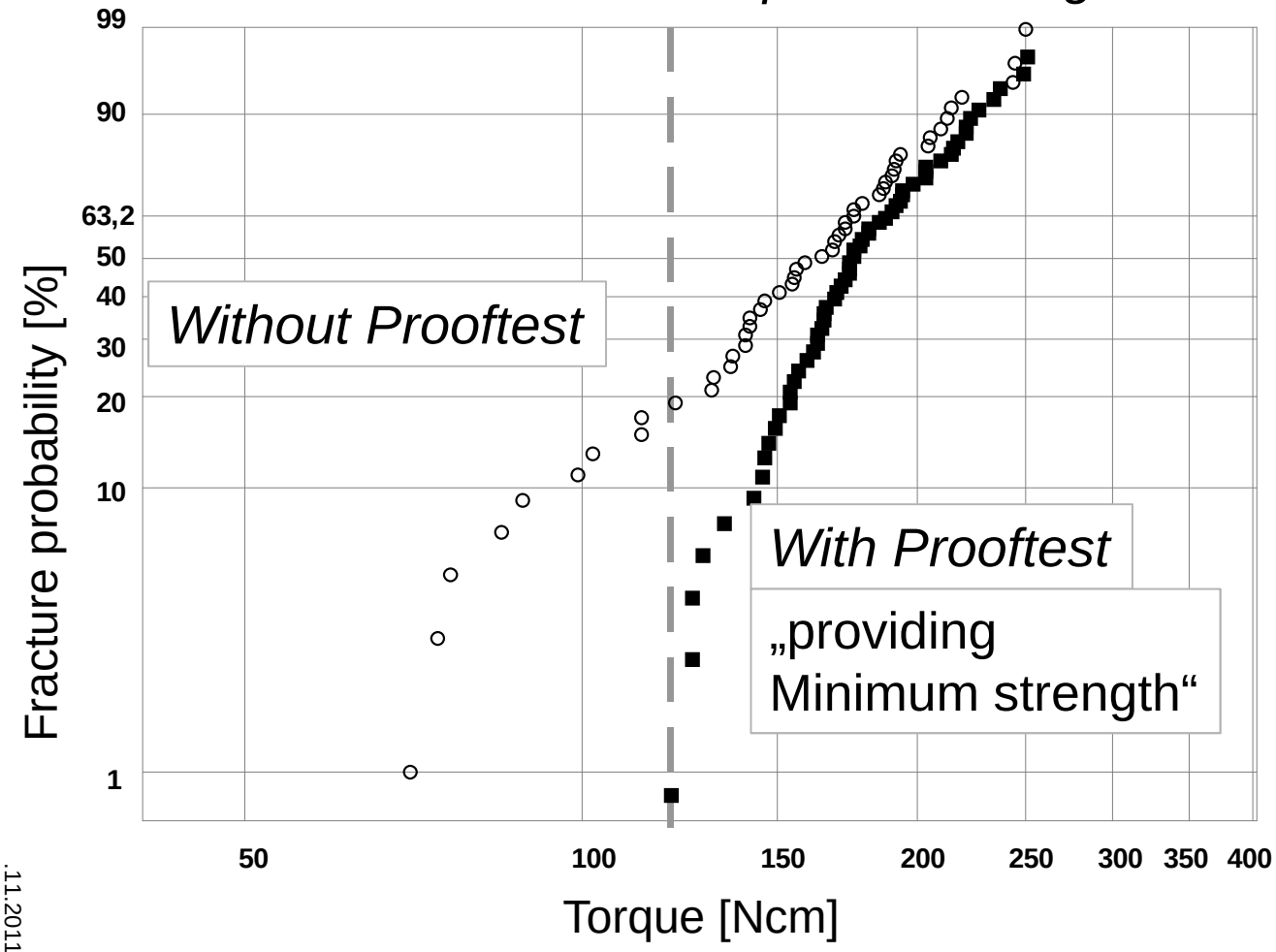
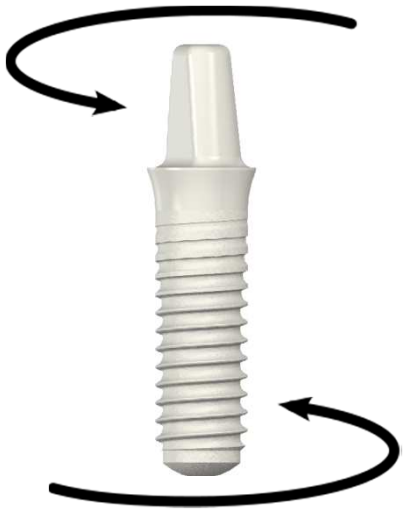
Principle of prooftest

Example:
Operative torsion load on a dental implant

Weibull-distribution of component strength





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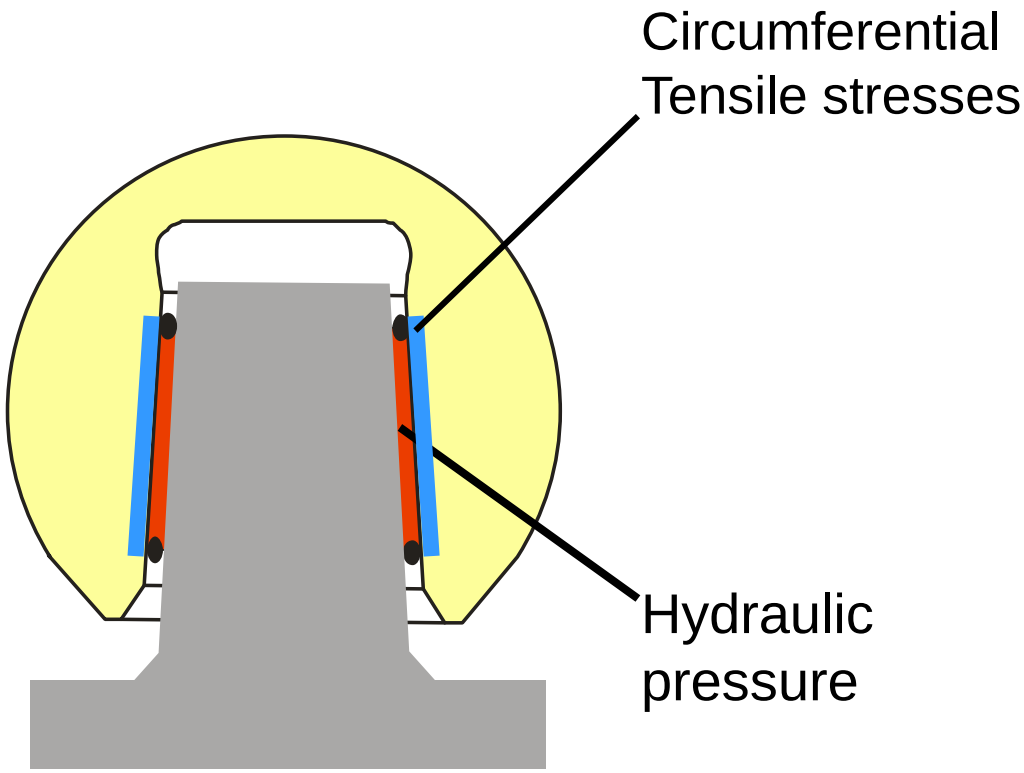
Prooftest on a ball head

Artificial hip joint
Modular system
Mechanical assemblage



Prooftest for ball head

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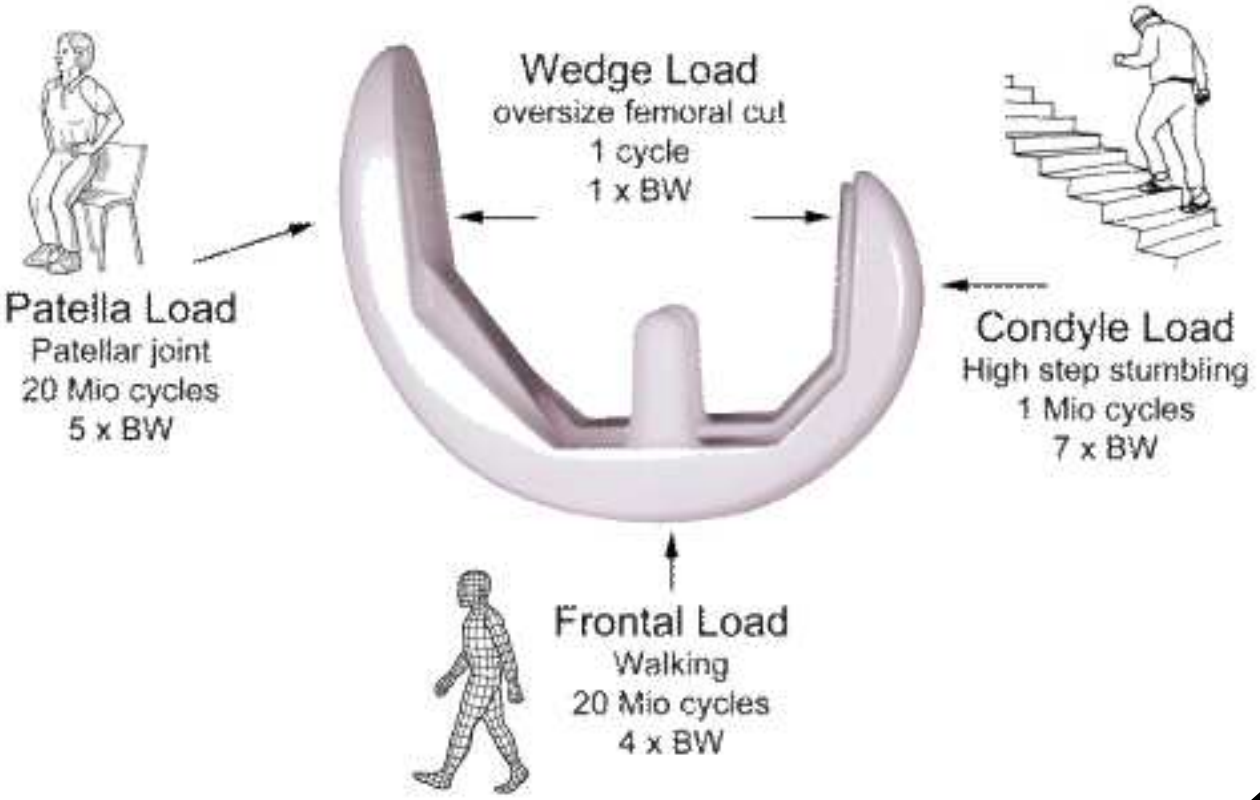
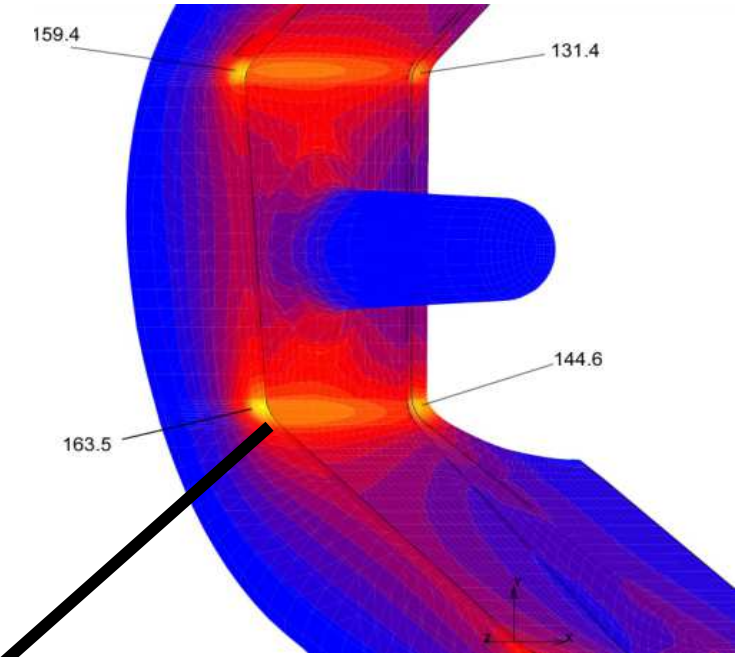
Example:

Loading szenario of a femoral knee component





Maximum load up to
9-time body weight (BW)

Stress maximum
at critical stress situation in vivo

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KOBELCO
Thank you
For attention