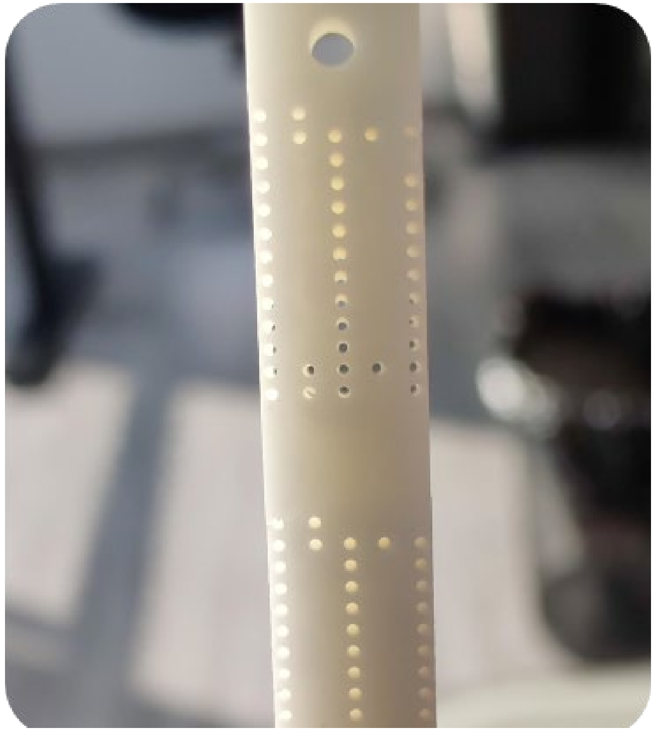
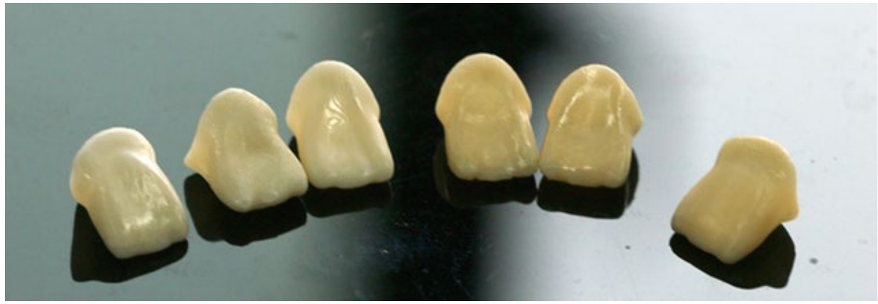
EPFL PSI Empa Materials Science and Technology

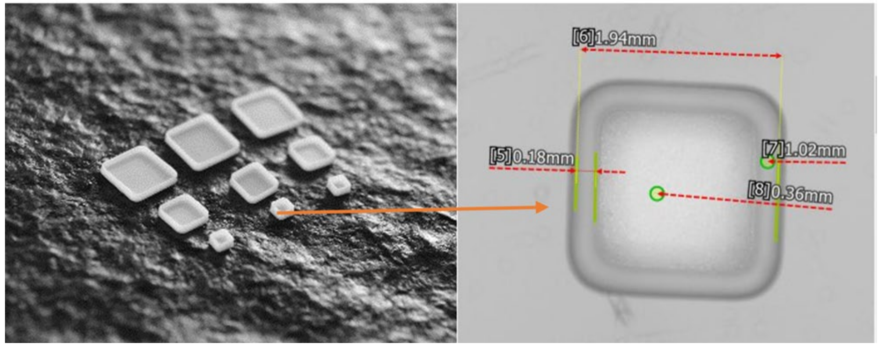
MSE 495 – Advanced Ceramics Technology

Michael Stuer (Empa) - Andrea Testino (PSI)

Week 1 – Introduction and Ceramic Processing







About myself, in one slide…

Lausanne (CH)
École Politecnique Fédérale de Lausanne (EPFL)
Powder Technology Laboratory (LTP)
&
Techpowder SA
(3y)

Milano (I)
Permanent Staff Researcher
University of Milano "Bicocca"
Dip. Material Science
(2y)

Genoa (I)
University of Genoa, Dept. Ind. Chem. (Master) (5y)
University of Genoa, Dept. Chem. Ing. (PhD) (3y)
National Research Council (CNR) (2y)

London (UK)
University College (UCL)
Dept. Chem. Ing.
(1y)

Deutschlandsberg (A)
EPCOS → TDK
Corporate Material R&D
Innovative Themes
Senior Engineer
(4y)

PSI EPFL

<u>Since 2011</u>
Swiss Federal Institute of Technology
Executive Senior Scientist (PSI)
MER (EPFL)

But let’s **START** from the **END**.

Q: What is our final target? (in ceramic manufacturing)

R: Achieve a “good” ceramic body.

Q: What is a “good” ceramic body?

R: We want good functional properties.

Q: Which functional properties we are looking for?

R: Optical, mechanical, electrical, catalytic, controlled porosity, net shape, …

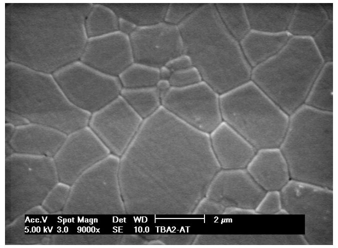
Q: How can we generate a competitive advantage (success) on the market?

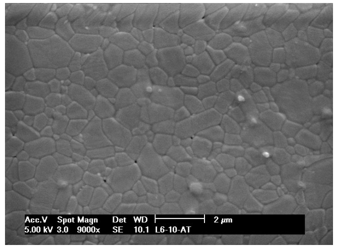
R: By producing better functional materials & processing optimization.

Let’s focus on functional properties

Q: What is defining the “functional properties” in a sintered body with defined composition?

R: Microstructure





Q: How is that microstructure in the sintered body obtained?

R: Processing of a green body. Mainly: powders quality, shaping technique, thermal history

Spray drying, pressing, casting, extrusion, AM

Drying, debinding sintering,…

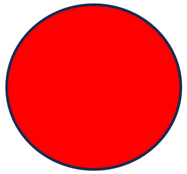
Processing

Q: What’s about powders quality?

R: Size, PSD, shape, homogeneity (or controlled composition)

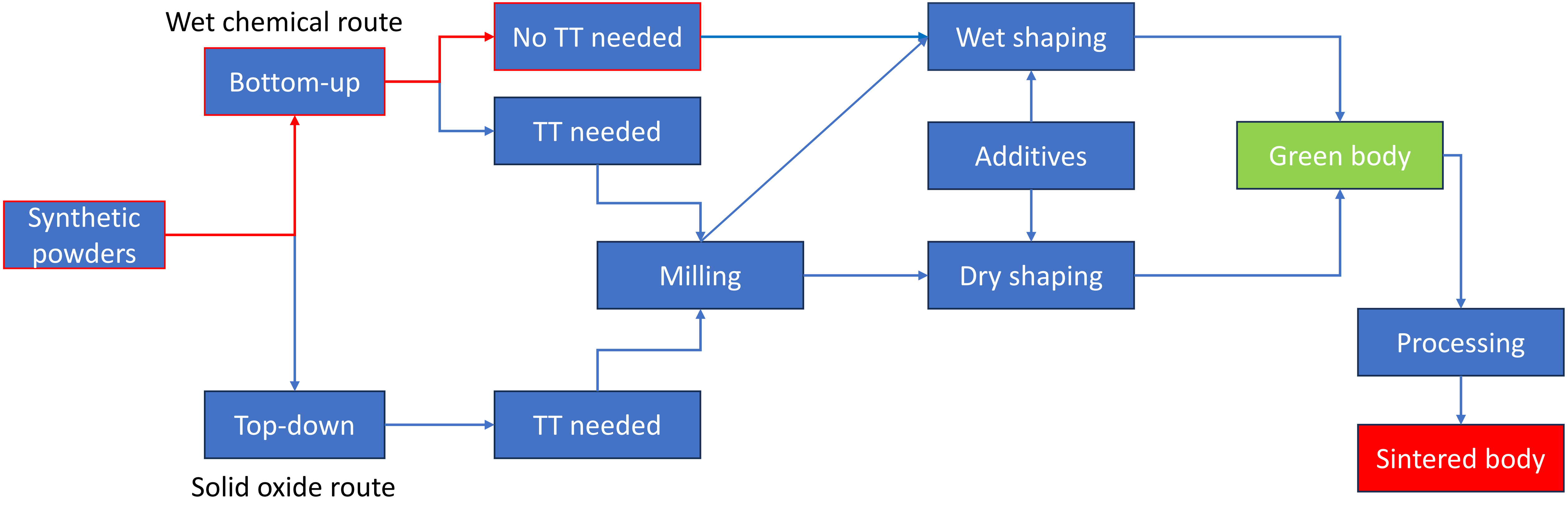
Let's focus on: powders quality

Follow this symbol for the main ceramic processing route!



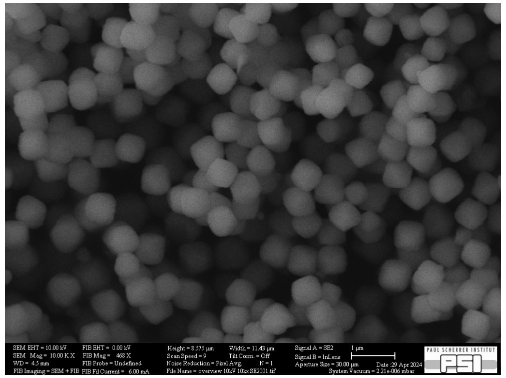
Q: How can we obtain high quality powders?

R: Synthesis



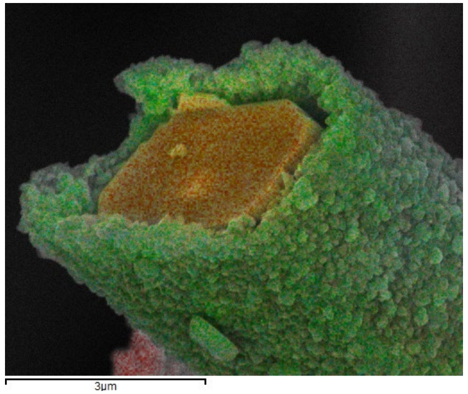
If our **END** is a good ceramic body, our **START** is high powder quality.

Powder synthesis via wet chemical route offers the possibility to produce high quality powders

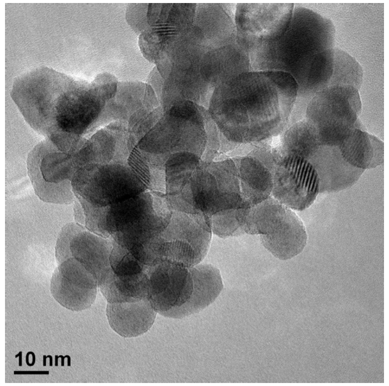


MOF 808

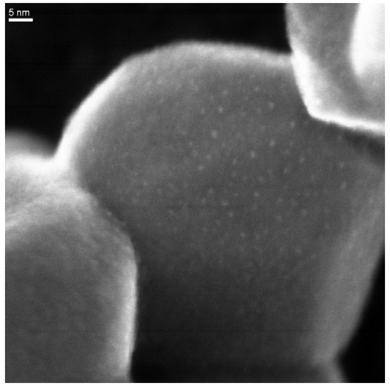
Calcium Aluminum Sulphate



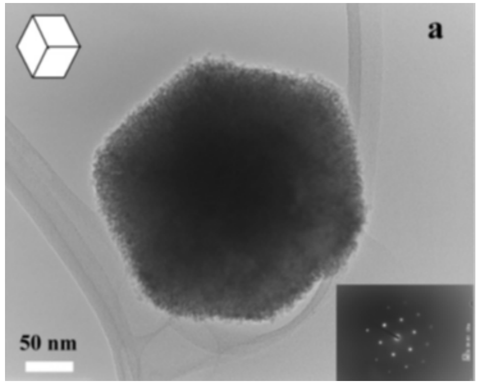
ZnS @ ZnO



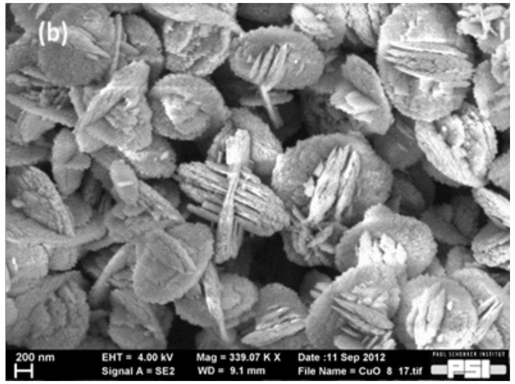
$Ce_{(x)}Zr_{(1-x)}O_2$



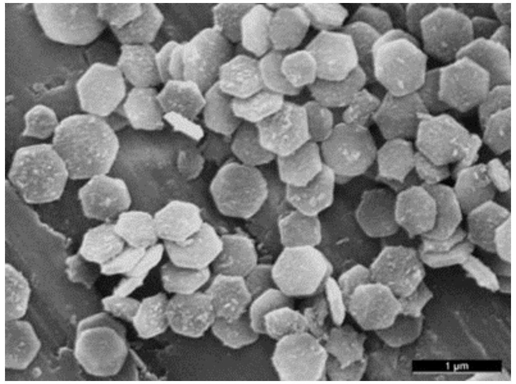
Pt @ CeO_2



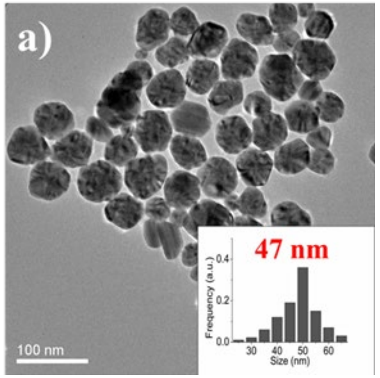
$SrTiO_3$



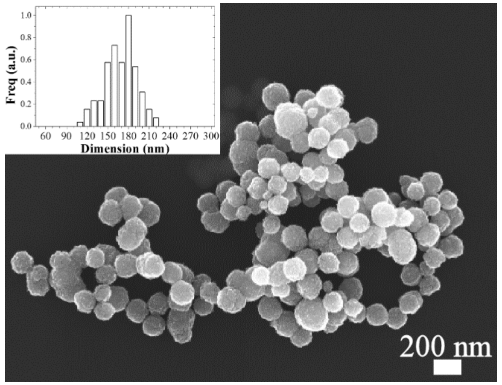
CuO



β-tricalcium phosphate



Ag



Ni

Properties of materials: atoms, bonds, packing. Basic concepts recall (*repetita iuvant)*

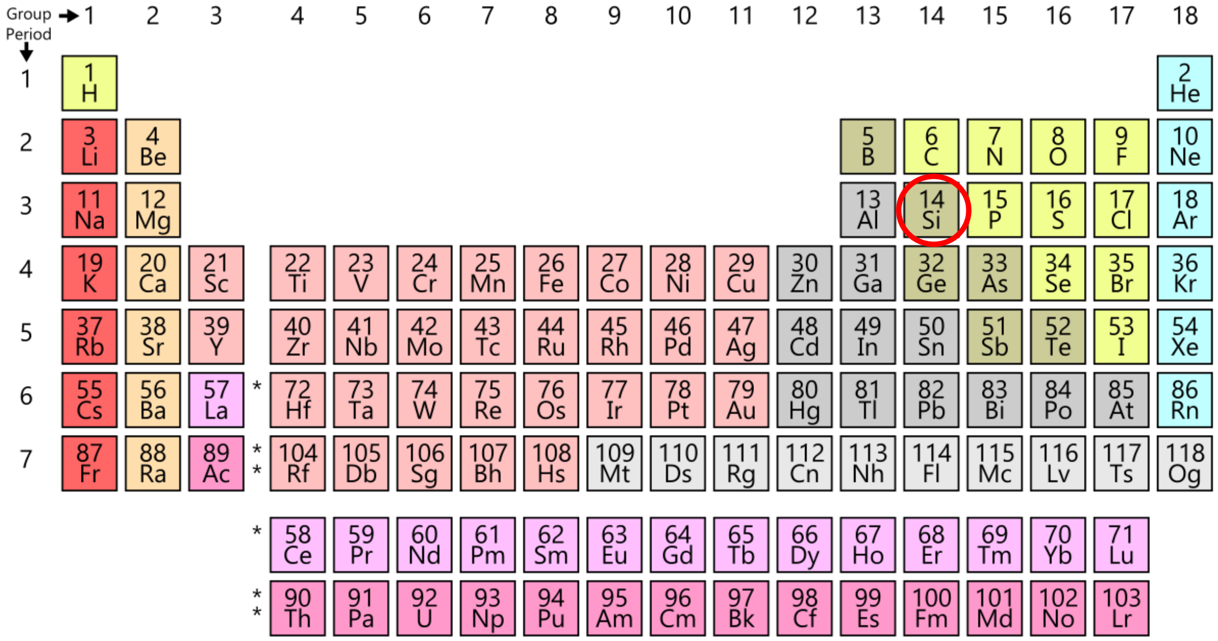
- **Ceramics**: natural or synthetic inorganic, non-metallic *polycrystalline* materials. Single crystals should not be considered ceramics. ***Ionic bonds***: metal – nonmetal (high electronegativity* difference). Cation and anion - high electrostatic force. ***Covalent bonds***: two nonmetals (similar electronegativity), shared electron pairs. In ceramic: ionic bond is predominant (due to oxygen..., metal oxides). *Properties*: high hardness, high melting points, low thermal expansion, and good chemical resistance, but brittleness. But properties depends on microstructure (grain size/shape, pores).

- **Glasses** are made of inorganic, non-metallic materials with an *amorphous* structure. Glass-ceramics: something in the middle. *Properties*: similar to ceramics in many aspects, but can be blown, drawn, laminated.

- **Metals. *Metallic bonds***: cations are surrounded by delocalized electrons. *Properties*: ductility, conductivity, etc.

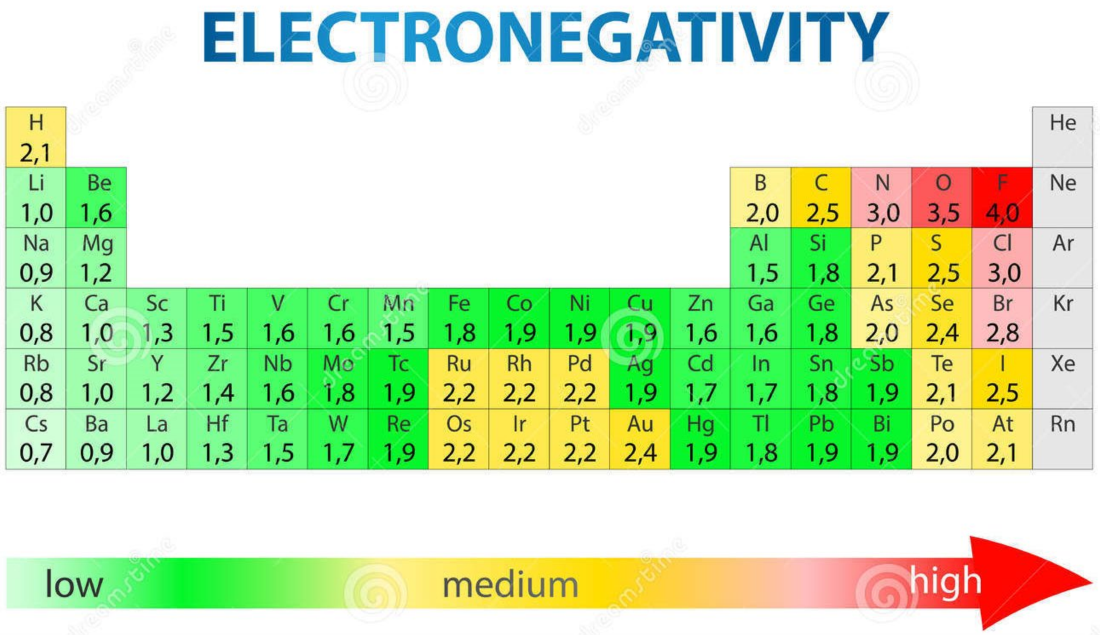
- **Polymers. *Van der Waals bonds***: weak electrostatic forces permanent or induced polarization. E.g. hydrogen bond, interaction *between* polymeric chains (C-C, C-H, etc. bonds within the polymeric chain are covalent). *Properties*: elasticity, easily to melt, low strength, etc.

*Electronegativity: is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegative at 0.7. (Oxygen: 3.5, metals: 1-2. Thus, any metal oxides…)



Chemistry and (alumino)silicates…
(90 percent of the Earth's crust)

Major group	Structure	Chemical formula	Example
Nesosilicates	isolated silicon tetrahedra	$[SiO_4]^{4-}$	olivine
Sorosilicates	double tetrahedra	$[Si_2O_7]^{6-}$	epidote, melilite group
Cyclosilicates	rings	$[Si_nO_{3n}]^{2n-}$	tourmaline group
Inosilicates	single chain	$[Si_nO_{3n}]^{2n-}$	pyroxene group
Inosilicates	double chain	$[Si_{4n}O_{11n}]^{6n-}$	amphibole group
Phyllosilicates	sheets	$[Si_{2n}O_{5n}]^{2n-}$	micas and clays
Tectosilicates	3D framework	$[Al_xSi_yO_{(2x+2y)}]^{x-}$	quartz, feldspars, zeolites



Electronegativity and
Metals / non metals

C: 2.5 N:3.0
O: 3.5 H: 2.1
Si: 1.8 Al: 1.5

Introduction

- Raw materials, as supplied by powder producers, are often partially modified for ceramic manufacturing.
- The two main families of powders are Synthetic and Natural

- Synthetic are chemically modified products - expensive
- Natural come from the earth - sometimes with washing, grinding, classification
- Clays, quartz …… - cheap material
- Several manufacturing methods for synthetic
- More expensive powders does not imply a more expensive product: it depends on the whole manufacturing process:
  - design
  - forming
  - sintering
  - machining
  - polishing
  - market size
  - added value

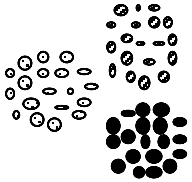
Silicon Carbide - synthetic

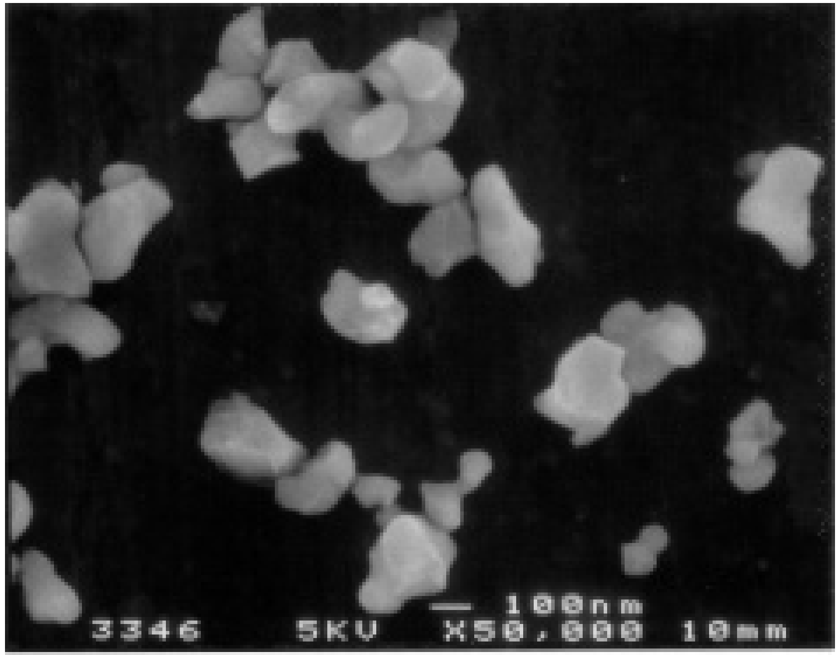
Refined quartz sand - 99.5% SiO_2

<1mm

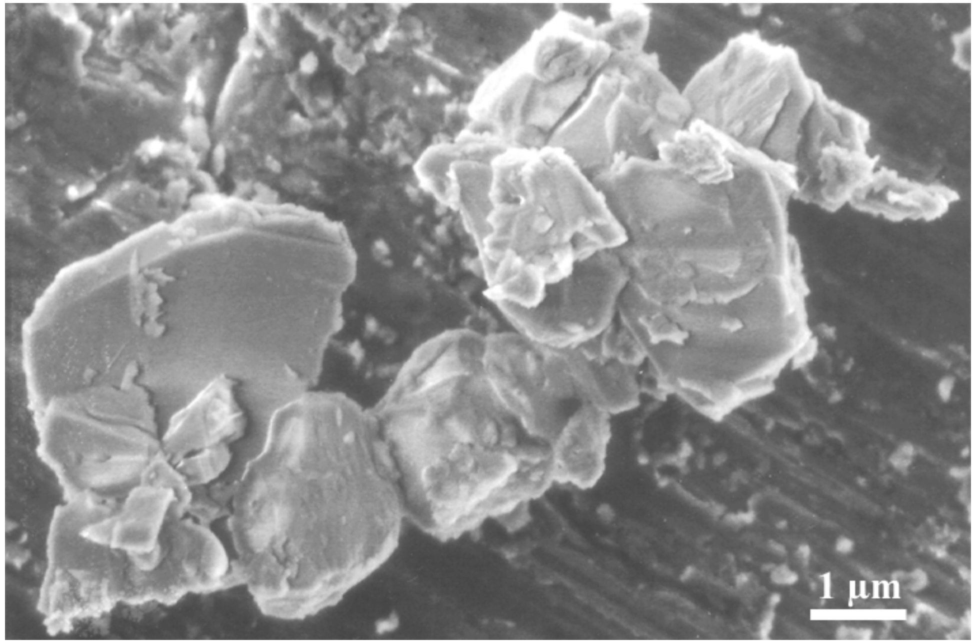
Ceramic Processing - Powders

Raw materials: synthetic or natural



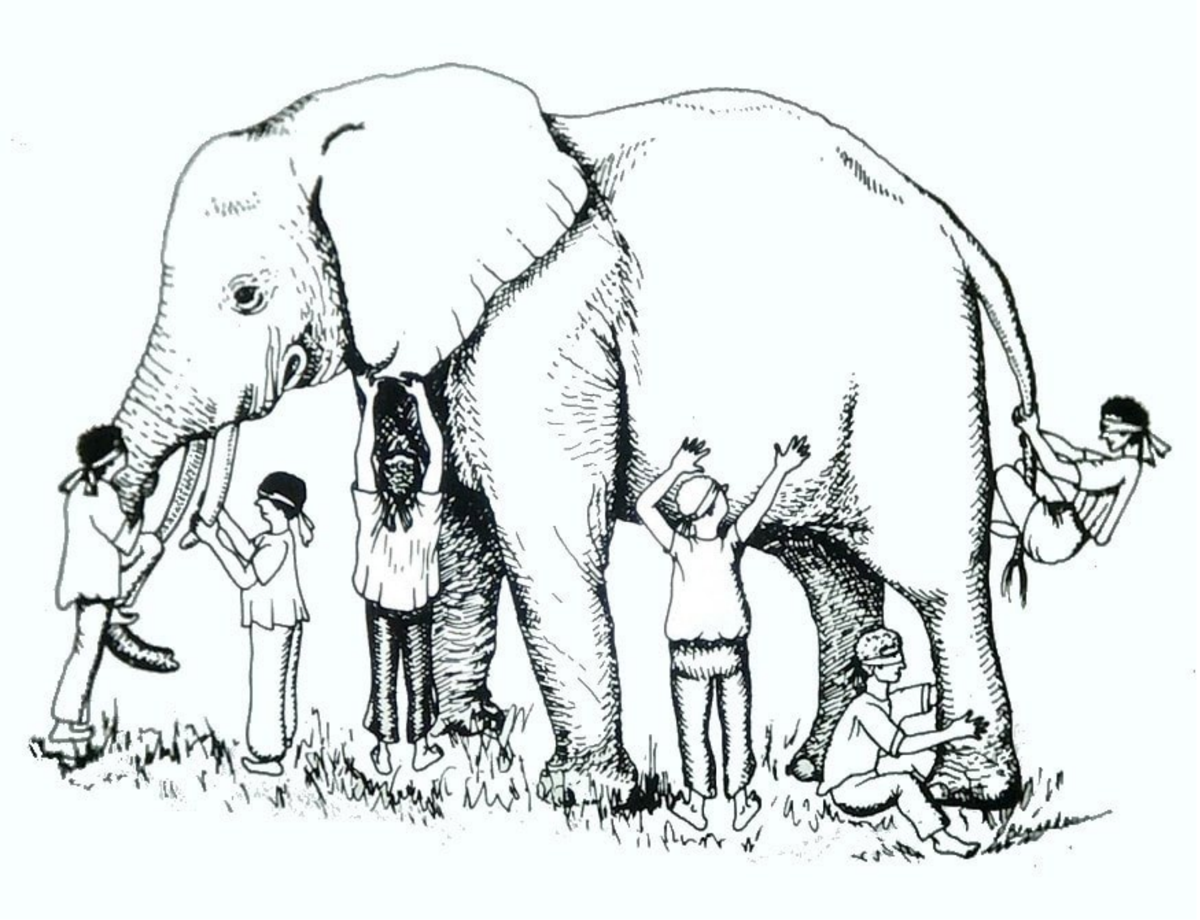


(a) alumina powder – technical ceramic – synthetic powder



(b) feldspar powder – traditional ceramics – natural powder

The Blind Scientists and the Elephant



1: grabs the elephant by the tail and puts forward the hypothesis that **the elephant is like a rope**.

2: touches the elephant's leg and puts forward the hypothesis that **the elephant is like a tree**.

3: touches the side of the elephant and puts forward the hypothesis that **the elephant is like a wall**.

4: touches the ears of the elephant and puts forward the hypothesis that the **elephant is like a fan**.

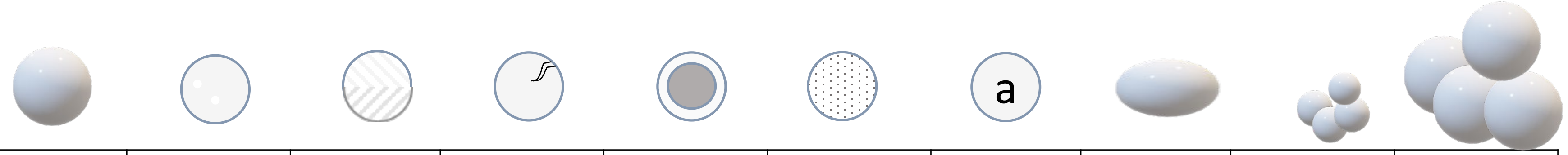
5: grabs the tusk of the elephant and puts forward the hypothesis that **the elephant is like a spear**.

6: feels the moving trunk of the elephant and puts forward the hypothesis that the **elephant is like a snake**.

Do not be blind...

This is a story found in Hindu and Buddhist texts dating back more than 3,000 years. It has been used in religious and philosophical contexts to illustrate how we often think we know the truth, even though we have just grasped only part of it. The most famous version in English is the poem entitled "The Blind Men and the Elephant" written by the poet John Godfrey Saxe.

Example: multi-technique characterization

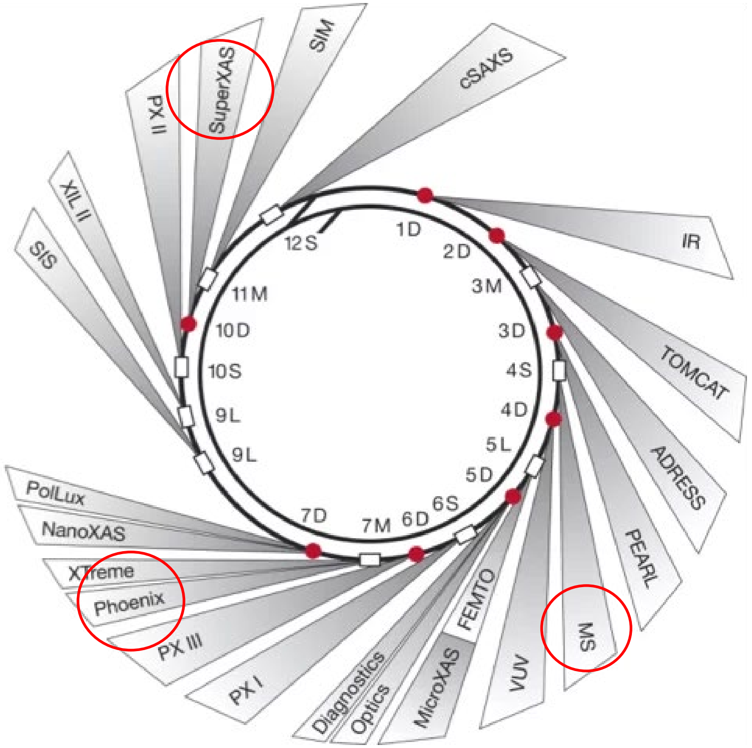


		Single crystal spherical particle	Internal close pores	Multi-domain	Open pores	Core-shell	Clusters segregation	(Partially) Amorphous	Different shape	Small aggregate	Aggregated particles
$/$$	Diffraction (X, n)	REFERENCE	☹	☺	☹	☺	😐	☺	☹	☺	☹
$$	SSA – PoreSD		☹	☹	☺	☹	☹	☺	☹	☺	☹
$	Density		☺	☹	☹	☹	☹	☺	☹	☹	☹
$	PSD		☹	☹	☹	☹	☹	☹	😐	☹	☺
$	Micrography (LR)		☹	☹	☹	☹	☹	☹	☺	☺	☺
$$$	Micrography (HR)		☺	☺	☺	☺	☺	☺	😐	😐	😐
$/$$	Chem. Comp (ICP)		☹	☹	☹	☹	☹	☹	☹	☹	☹
$$$	Chem. Comp (Local)		☺	☹	☺	☺	😐	☹	☹	☹	☹
$/$$	Spectroscopy		☹	☹	☹	😐	☺	😐	☹	☹	☹

Synchrotron light characterization Basic overview and few examples on XRD and XAS

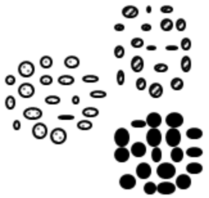
SLS at PSI

Beamline Map: 16 beamlines are in user operation.

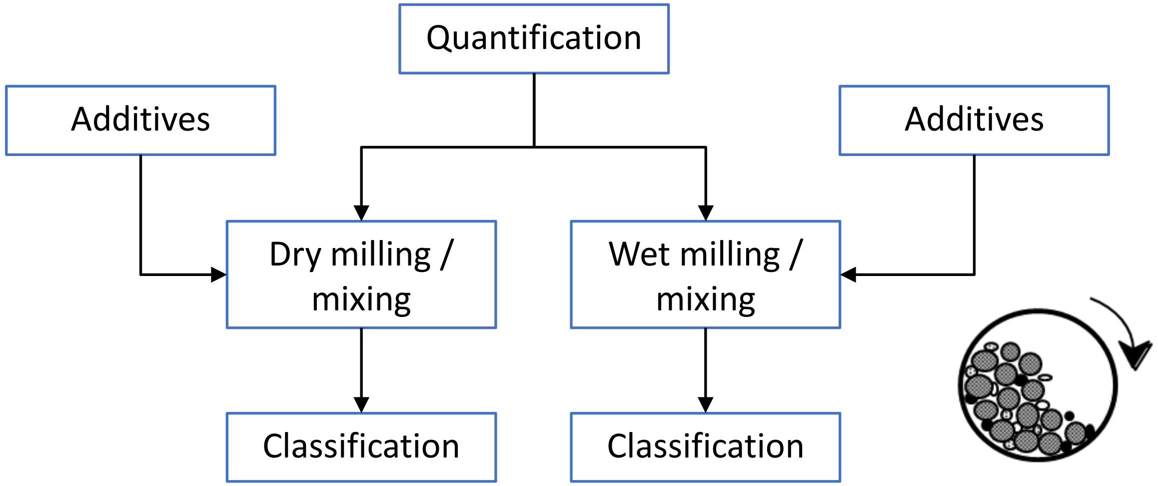


Manufacture of Ceramics – Powders

Raw Materials

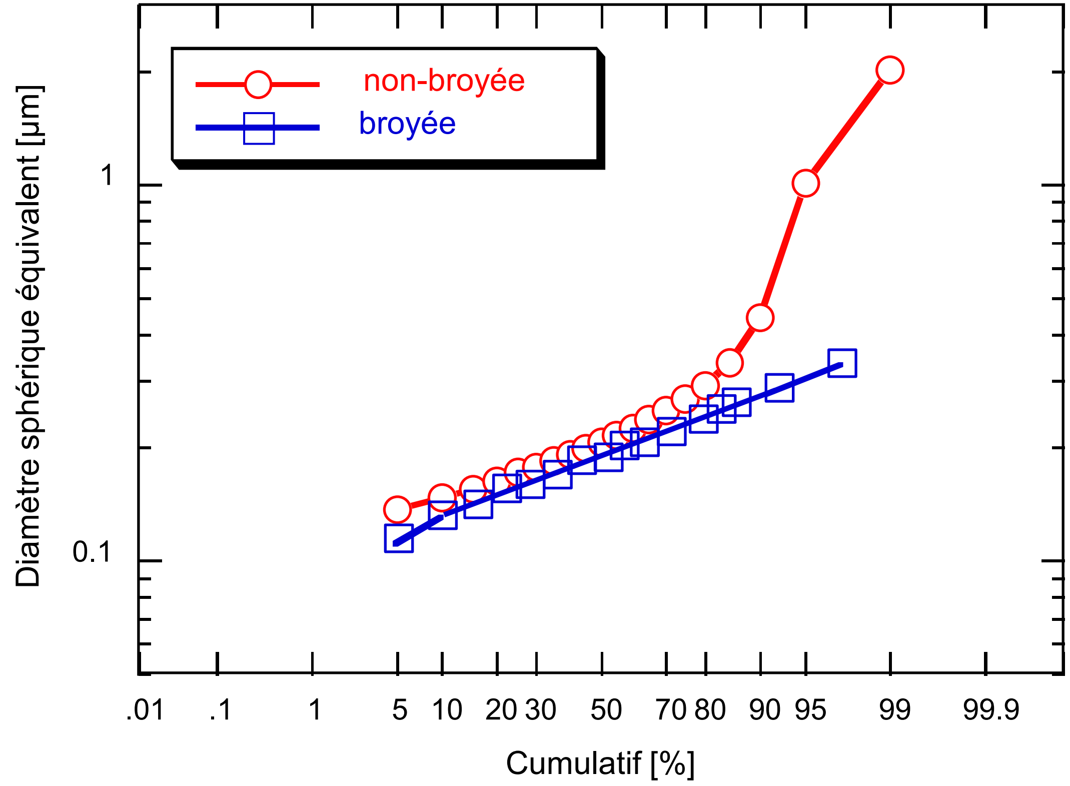


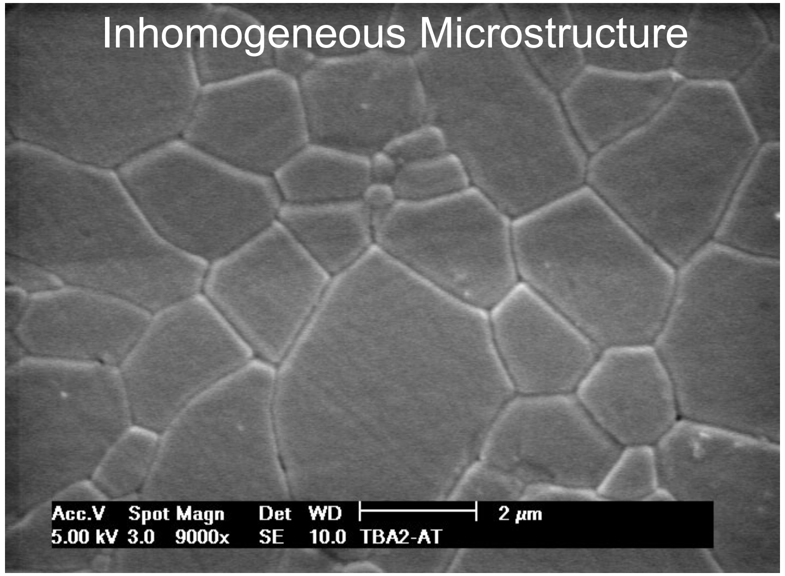
- High chemical purity;
- High reactivity: particle size in the μm (≈ 1 μm) range and a SSA of about 5-10 m^2/g;
- High homogeneity from both physical and chemical viewpoint;
- Constant quality of the raw materials (reproducibility is essential!)

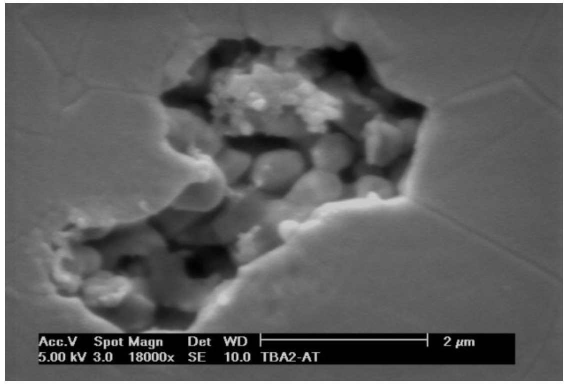


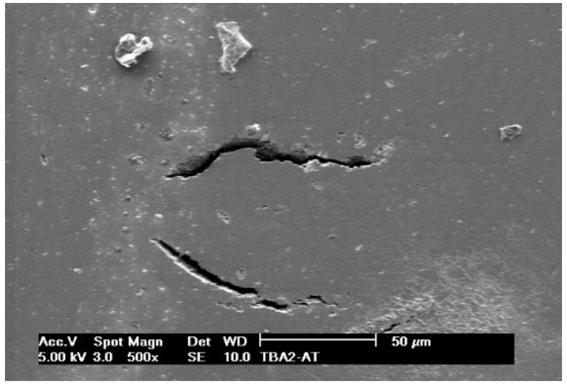
Alpha alumina - effect of agglomerates

- Particle size distribution shows small tail of agglomerates - leads to defects in microcstructure and low sintered densities (94%)







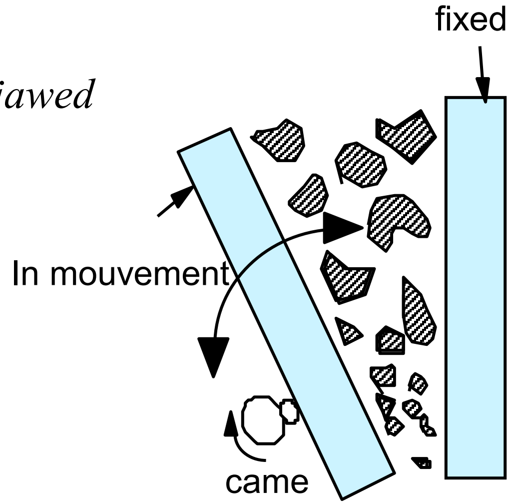


Defects due to feedstock inhomogeneity

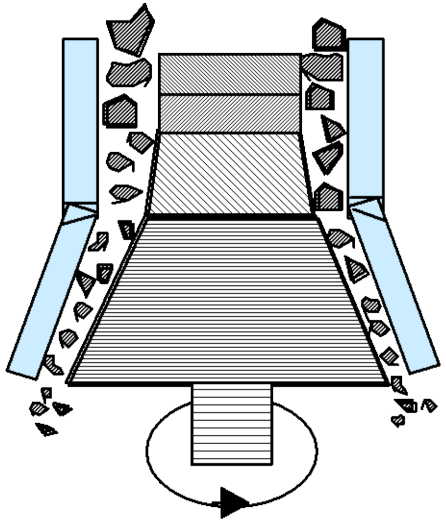
Aggregate: chemical bonds
Agglomerate: physical bonds

Comminution: Crushers

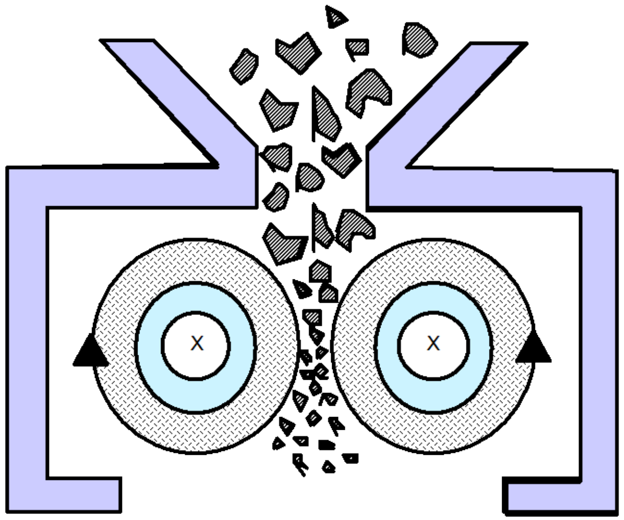
(at) *jawed*



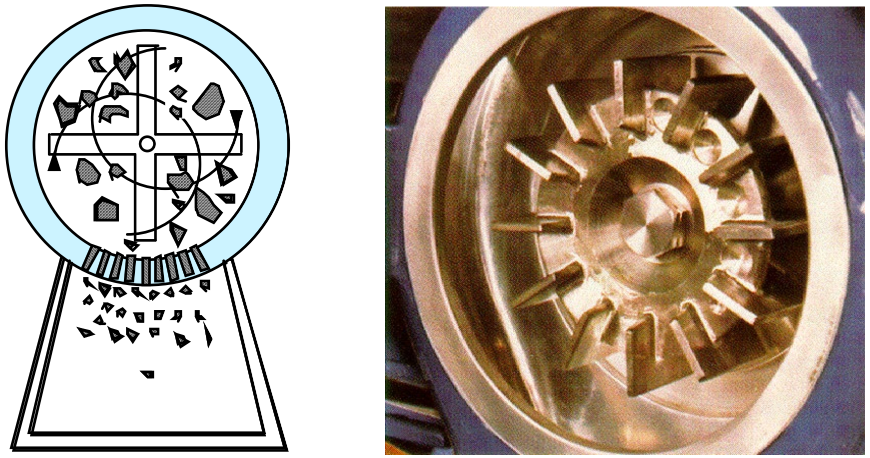
(b) *rotary*



(vs) *roller*

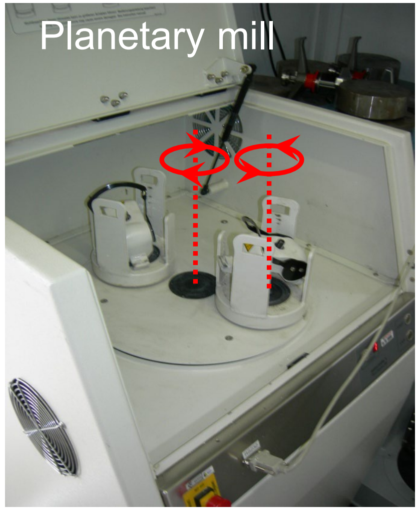


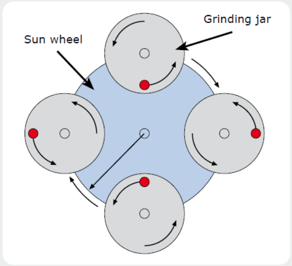
(d) hammer



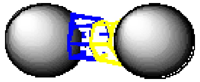
Planetary ball milling

❖ Decrease particle size to obtain higher homogeneity and increased reactivity for further processing. Also attractive for the preparation of complex compositions.

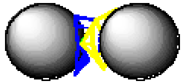




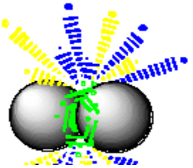
elastic deformation



plastic deformation



fracture, amorphisation, chemical reactions



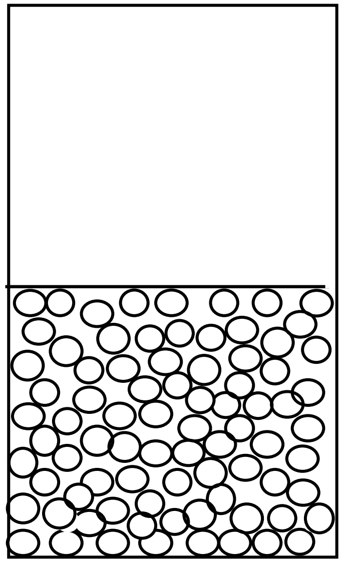
with P, T sensors

Planetary Ball Mills	General remarks	Grinding jar	Grinding balls	Feed size	Sample amount	Grinding time	Revolution speed*	Final fineness
Catalysts		250 ml ZrO_2	15 x 20 mm ZrO_2	1 - 20 mm	130 ml	2 min	450 rpm	63 µm
Cement clinker	5 - 10 drops of methanol	125 ml ZrO_2	6 x 20 mm ZrO_2	2 - 5 mm	50 g	5 min	450 rpm	100 µm
Coal		500 ml ZrO_2	25 x 20 mm ZrO_2	10 mm	150 g	4 min	400 rpm	200 µm
Glass	pre-grinding with 15 x 20 mm balls	250 ml ZrO_2	60 x 10 mm ZrO_2	5 - 10 mm	120 g	90 min	420 rpm	20 µm
Metal oxides	wet grinding	250 ml ZrO_2	500 g x 3 mm ZrO_2	< 300 µm	100 g + 50 ml IPA	1 - 2 h	450 rpm	< 1 µm
Sand		500 ml ZrO_2	25 x 20 mm ZrO_2	1 - 3 mm	200 g	6 min	500 rpm	63 µm
Sewage sludge	pre-grinding with 7 x 20 mm balls	125 ml ZrO_2	50 x 10 mm ZrO_2	10 - 20 mm	20 g	30 min	400 rpm	63 µm
Soil		250 ml Stainless steel	15 x 20 mm Stainless steel	10 mm (agglomerates)	120 g	10 min	400 rpm	100 µm
Straw		125 ml ZrO_2	8 x 20 mm ZrO_2	0 - 2 mm	10 g	30 min	400 rpm	160 µm

This chart serves only for orientation puposes.
*In a Planetary Ball Mill PM 100
ZrO_2: Zirconium oxide

Milling and fine milling - beads

- The jar volume is usually about 50% full with the milling beads.
- The added milling powder is just enough to cover the surface of the beads and fill in the gaps, i.e. approximately 25% of the jar volume.
- The size of the beads used ranges from approximately 1cm to 10cm.
- Its size must be approximately 25 times the size of the material to be ground for milling to be effective.
- A mixture of sizes can be used to increase the number of collisions, keeping a few large beads to produce large impact forces (in some cases, not in general. Large beads strongly increase contamination due to abrasion of small beads).



Milling and fine milling - materials

- Several materials are used for milling ceramics:

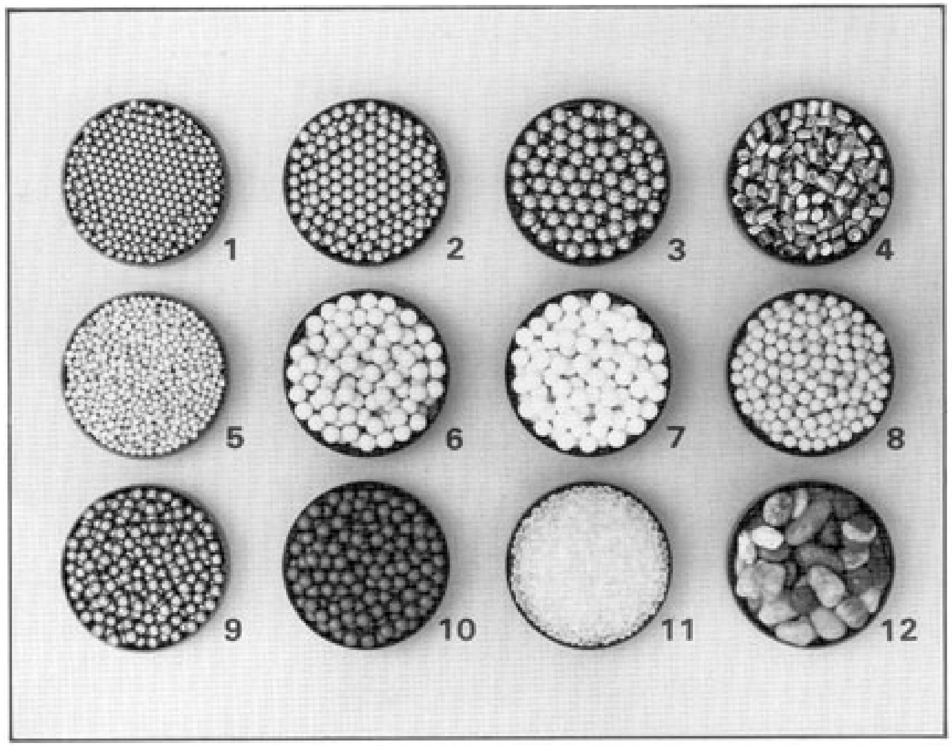
GRINDING MEDIA

Union Process carries a full line of all types and sizes of the highest quality grinding media available to meet your particular needs.

Some examples shown at right are:

1. 1/8″ stainless steel
2. 3/16″ chrome steel
3. 1/4″ case hardened carbon steel
4. 3/16″ stainless steel diagonals
5. 1/8″ mullite
6. 1/4″ ceramic
7. 1/4″ high alumina 87%, 96%, 99%
8. 3/16″ zirconium oxide
9. 3/16″ tungsten carbide
10. 3/16″ silicon nitride
11. 1/8″ glass
12. Flintstones

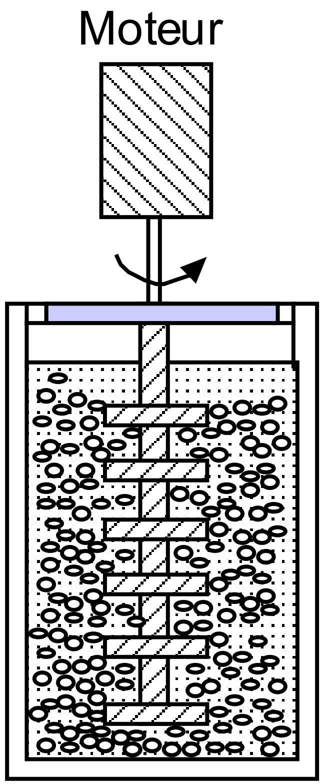
For additional information regarding composition and sizing recommendations, contact Union Process.

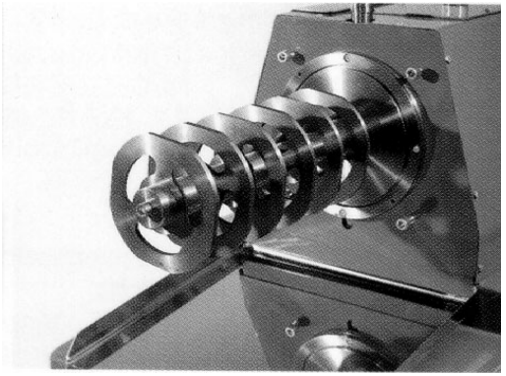


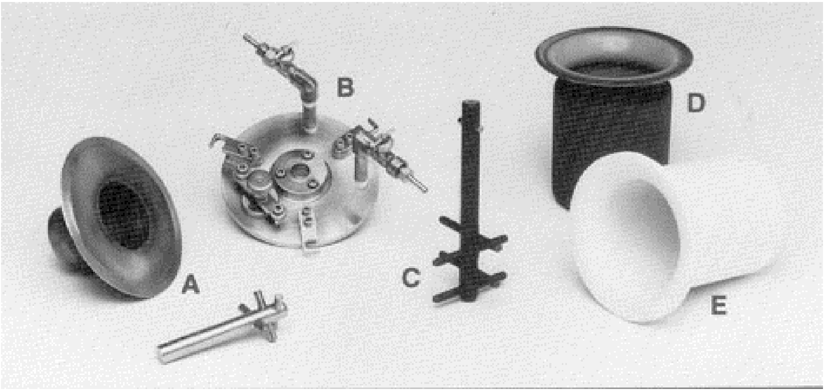
12. Flint or Flintstone (Fr: silex, It: selce) is a sedimentary cryptocrystalline (crypto: hidden) form of the mineral quartz.

Agitated bead mills – Attrition mills

2

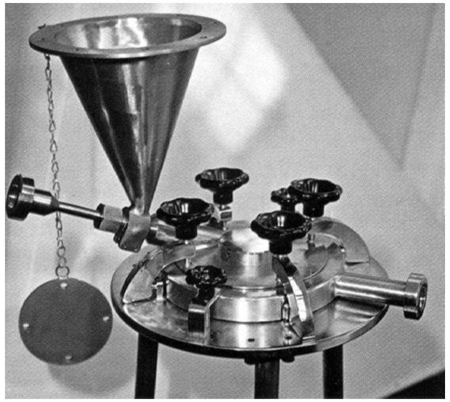


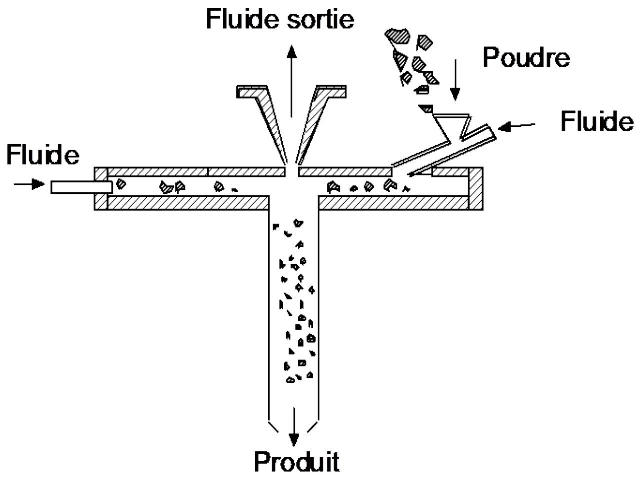


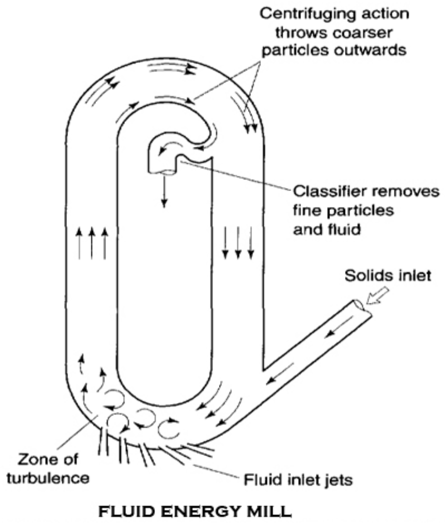


- High turbulence produces high compressive and shear stresses - high collision frequencies and fast milling kinetics.
- Significant stress is produced by the friction of particles between the beads, causing attrition - as much as by the compressive and shear stresses resulting from direct collisions.

Fluid Energy Mills

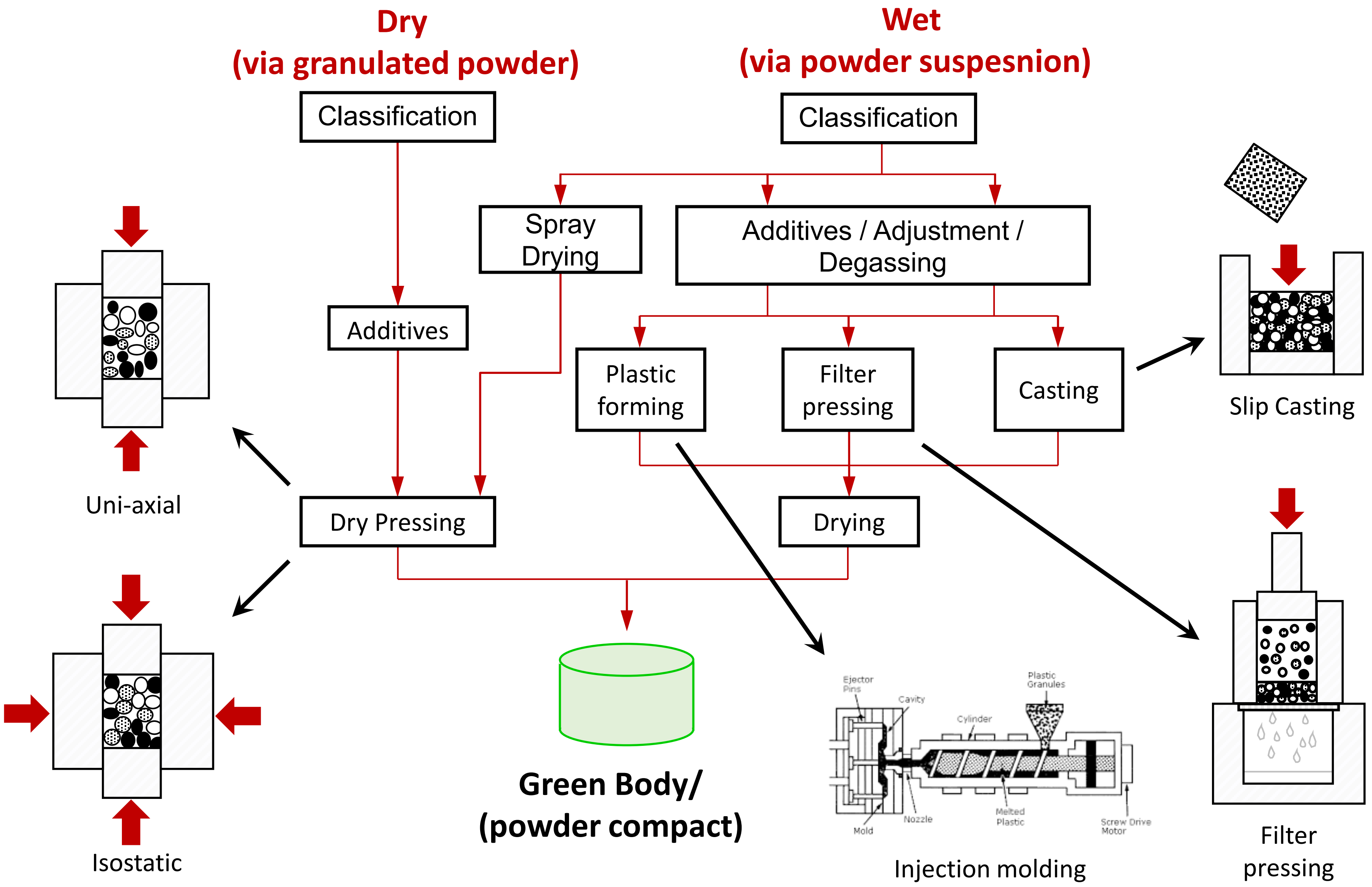






- Often used for high purity products (Baikowski 99.995% gamma alumina - synthetic rubies),
- Virtually all of the collision energy is used to break up the particles
  - the crusher coating must resist abrasion by the product, but
  - wear is generally low.
- These mills are often and easily combined with turbo-classifiers and
- The desired product can therefore be withdrawn and
- Only the excessively large fraction returns to the milling chamber with the incoming flow of product to be ground.
- Also known as “micronizer” and used in pharma industry

Manufacture of Ceramics - Ceramic Processing

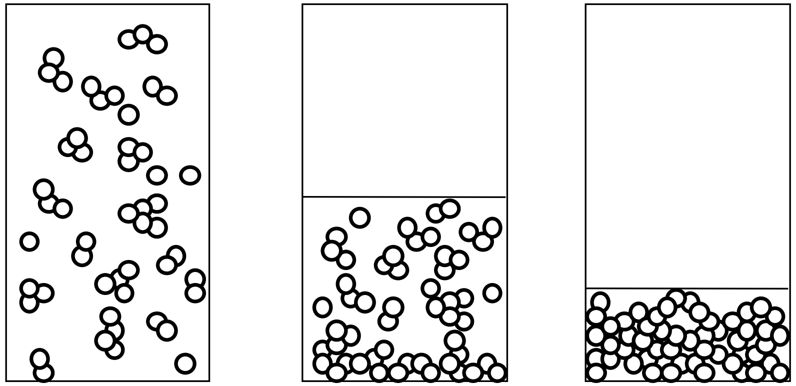


Powder Suspensions – Interparticle forces

- Suspension

1. Surface wetting
2. De-agglomeration
3. Stabilization against re-agglomeration
4. Modification / rheology control (e.g. additives)

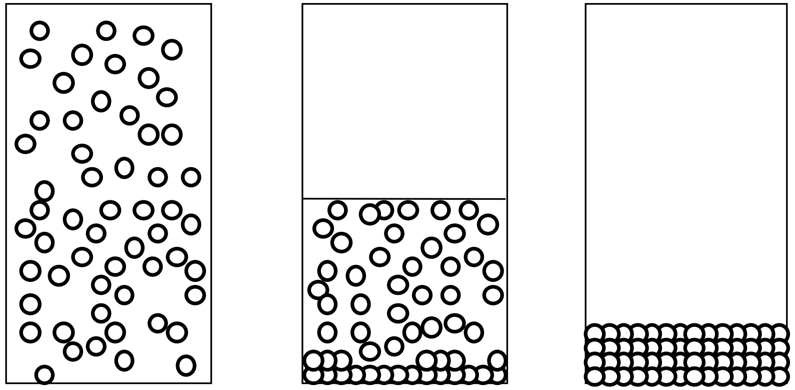
Poorly dispersed - rapid network formation - low green density (30%)



Well dispersed-

slow network formation

- high green density (70%)



FF Lange, J. Am. Ceram.Soc., 72 (1) 3-15 (1989).

Interparticle Forces – Colloidal stability: Week 4

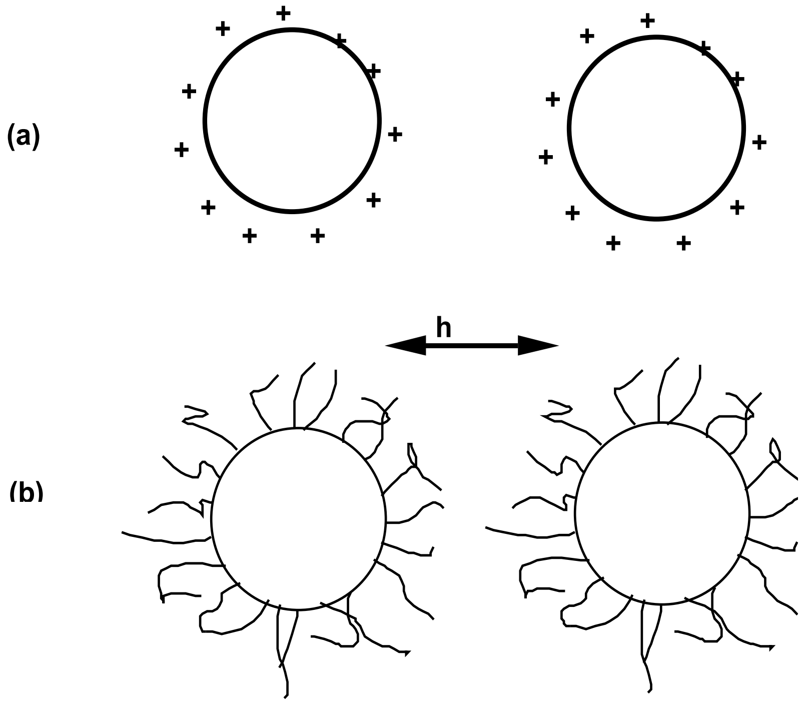
- Attractive

Van der Waals forces

- Repulsive

(a) electrostatic,

(b) soluble polymers - steric polymer adsorption

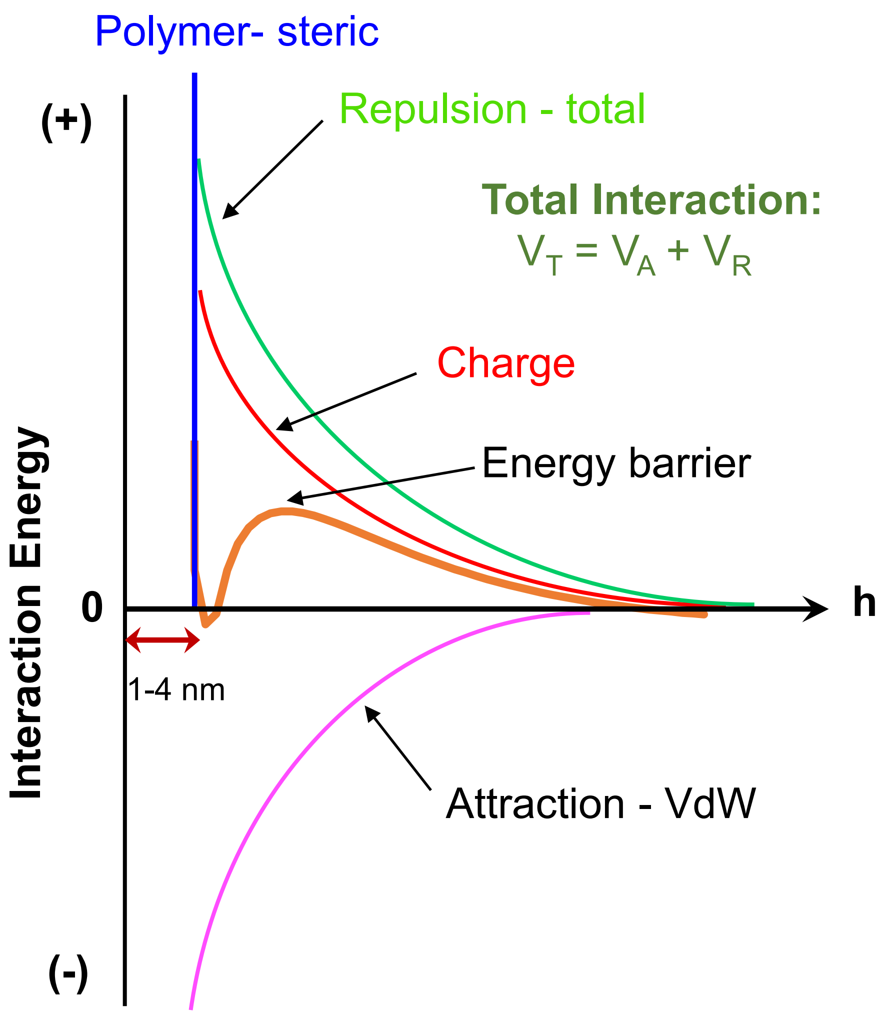


(distance h between particles)

.R.G. Horn, J.Am.Ceram.Soc., 73(5) 1117-35 (1990).

Overall Interaction Energy

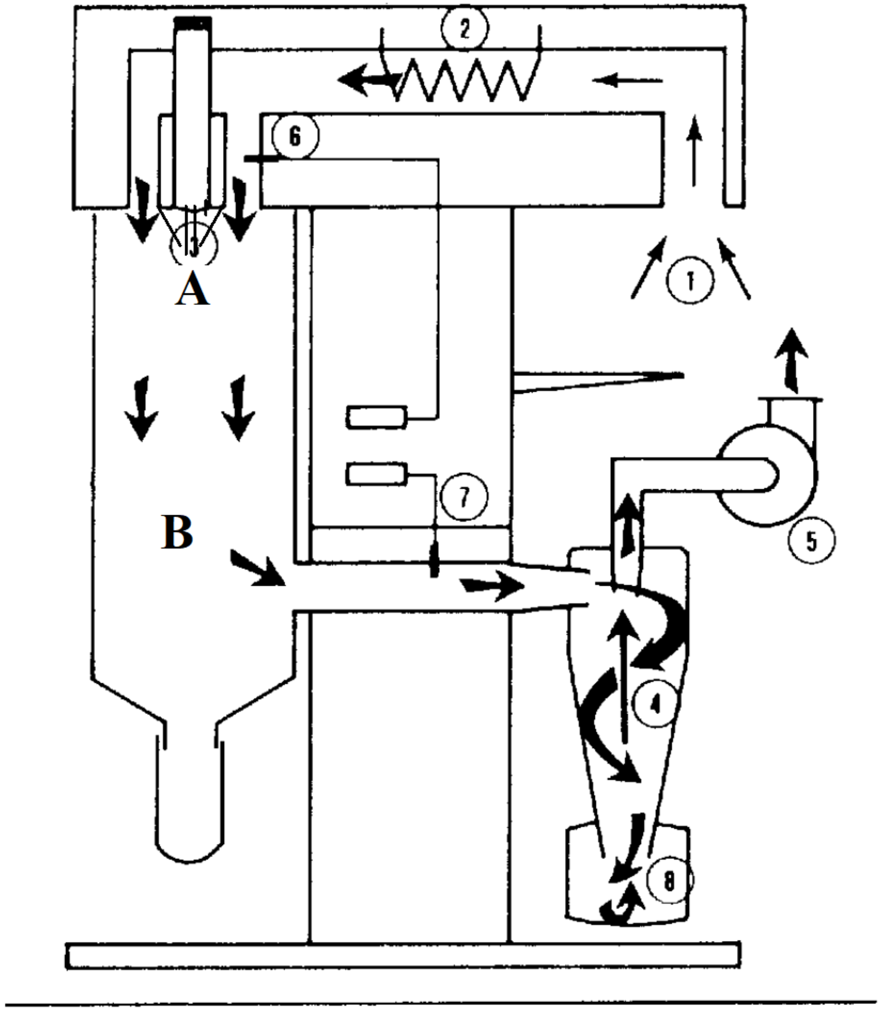
- Total Energy :
  algebraic sum….
  $V_T = V_A + V_R$
- Influences:
  - Rheology (flow of suspension)
  - Particle packing
  - Green body density
- Which in turn influences:
  - Sintering
  - Microstructure and
  - Properties

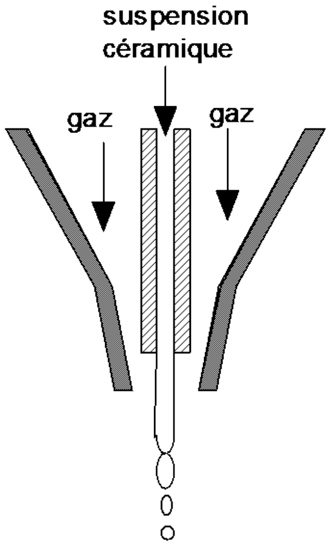


Aggregate: chemical bonds
Agglomerate: physical bonds

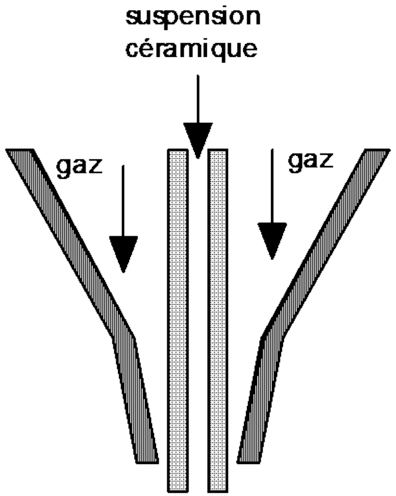
L. Bergström, C.H. Schilling, I.A. Aksay, J.Am.Ceram.Soc., 75(12) 3305-14 (1992).

Atomisation – Spray Drying



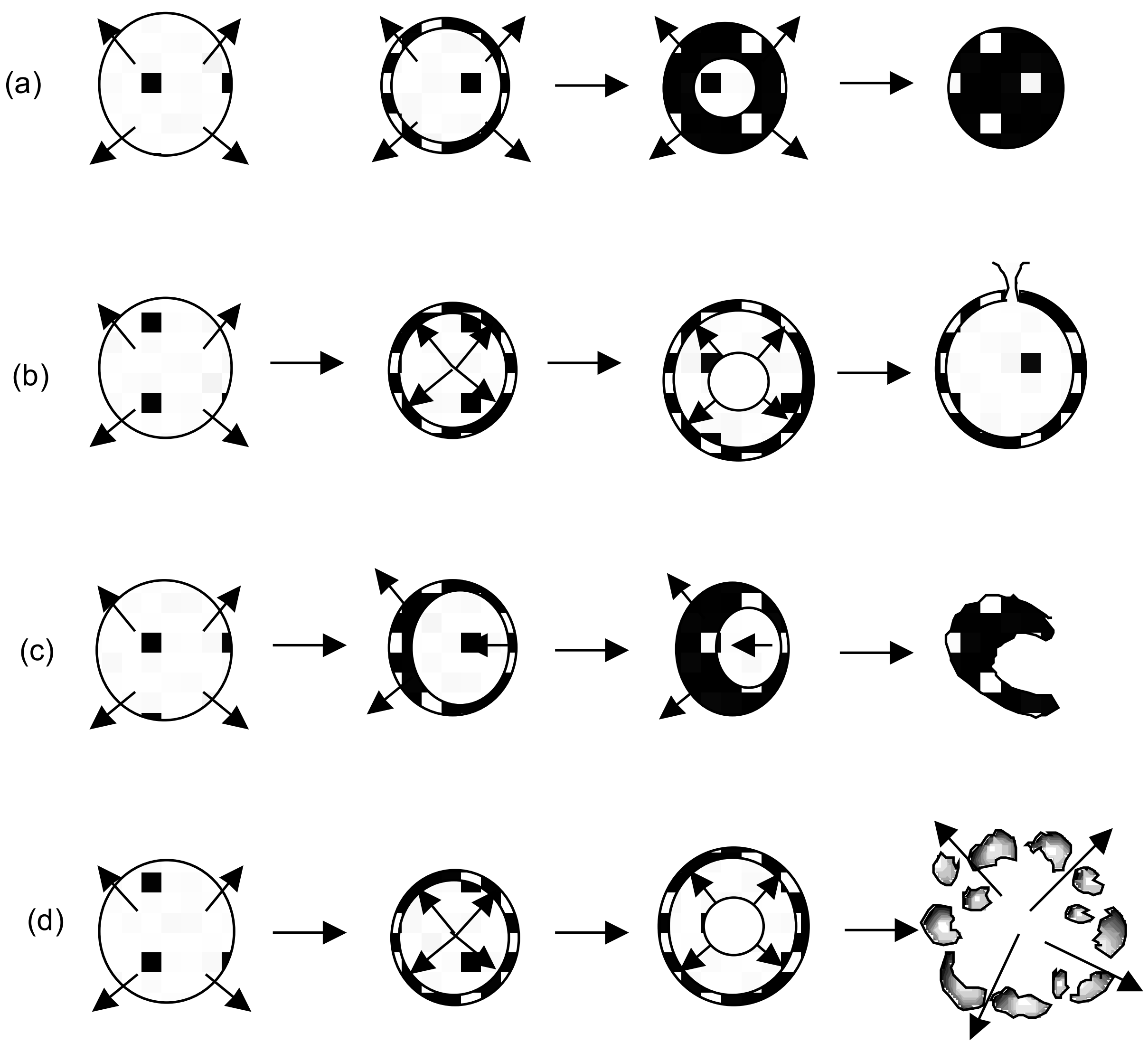


(c) internal mixing nozzle



(d) external mixing nozzle

Drying of a suspension droplet



(a) dense granule
(desired)

(b) hollow granule
(not desired)

(c) collapsed granule
(not desired)

(d) granule explodes
into fragments
(not desired)

Granules - defects

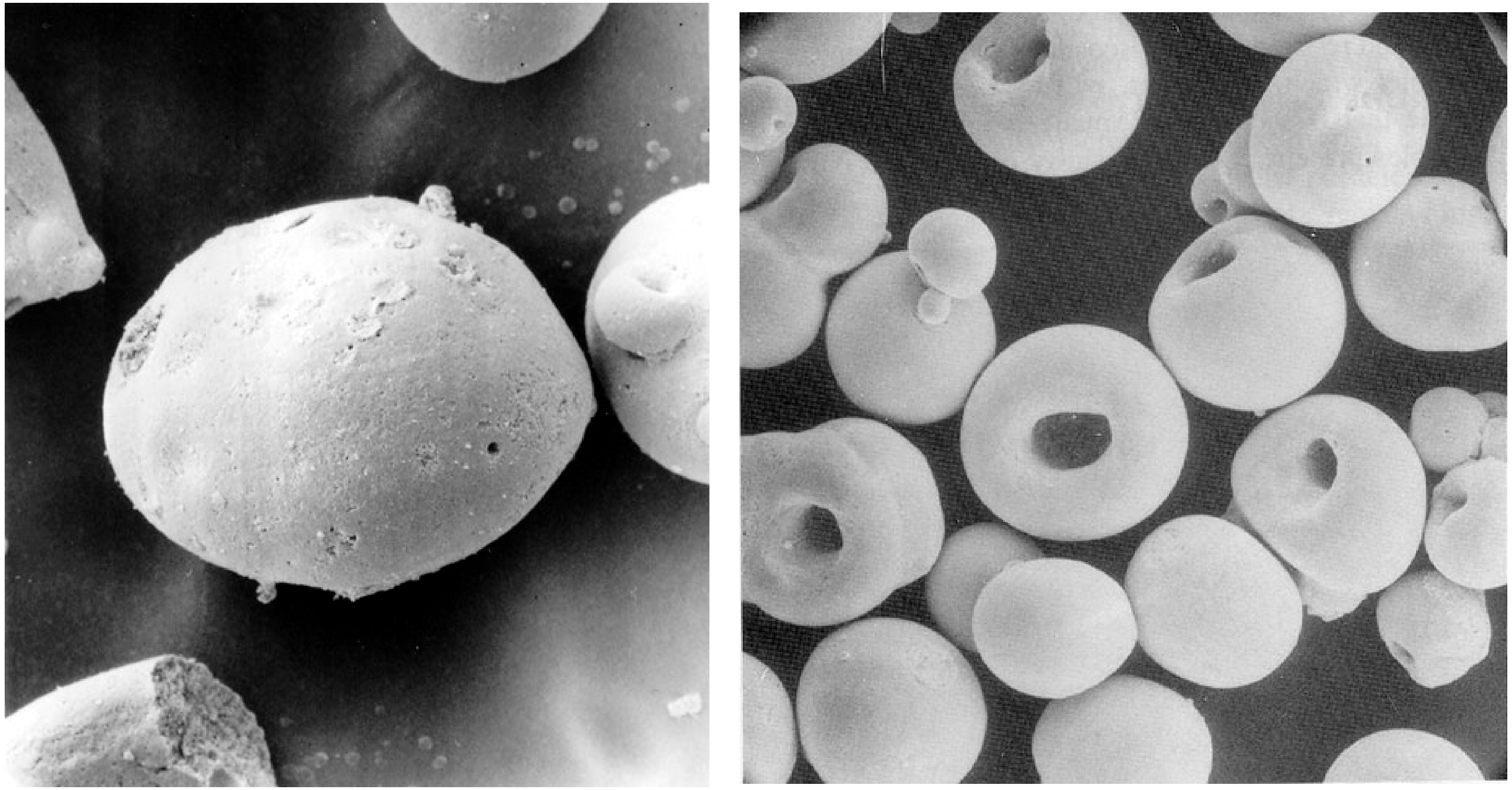
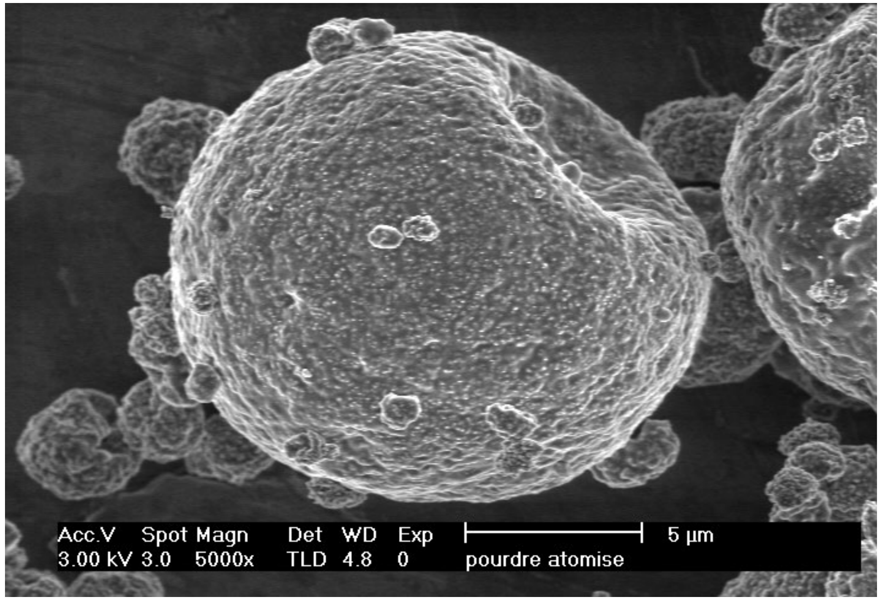


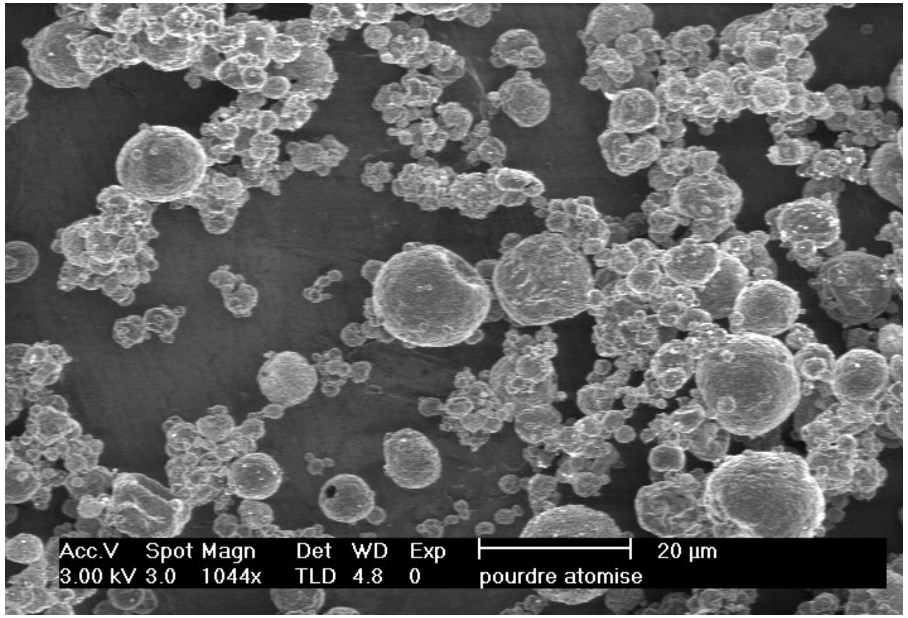
Figure 3.4.34. *Typical commercial granules (100µm) showing (a) granules with homogeneous density (b) hollow spheres with depression.*

Primary particles - 1 μm !!

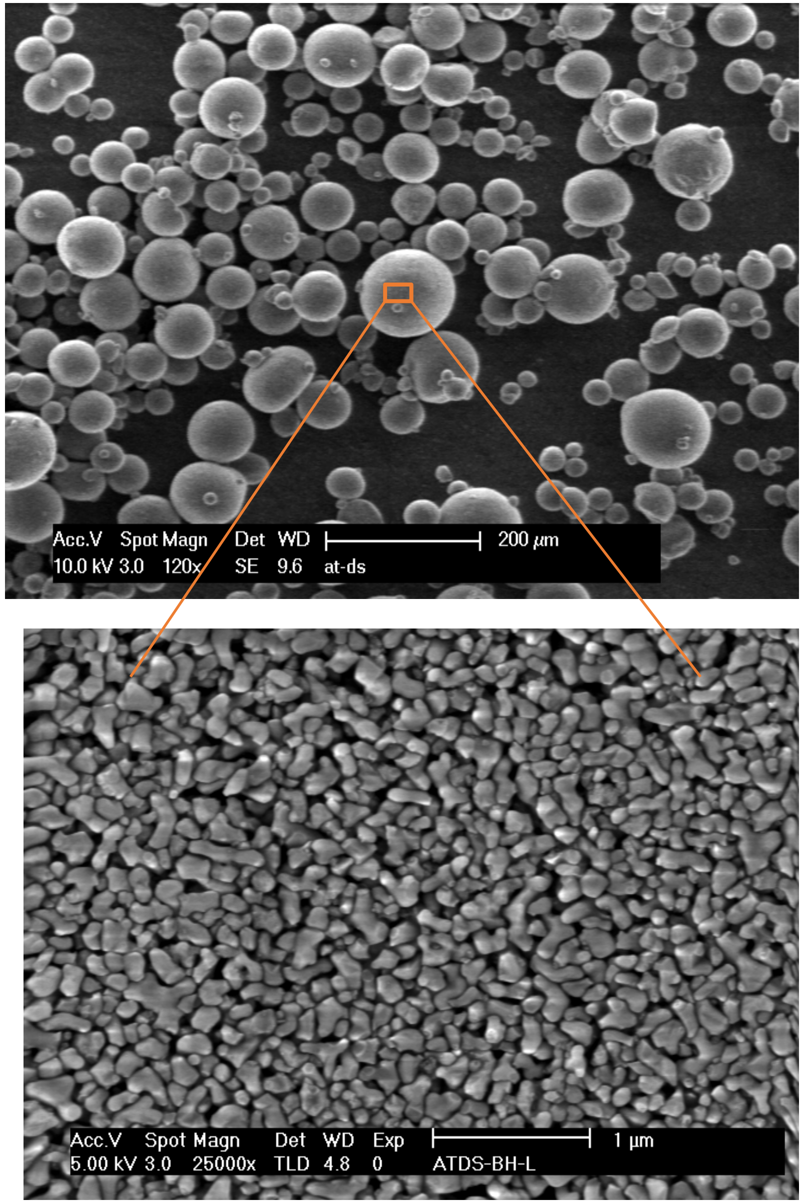
Granules from atomization

- Laboratory scale - Al_2O_3



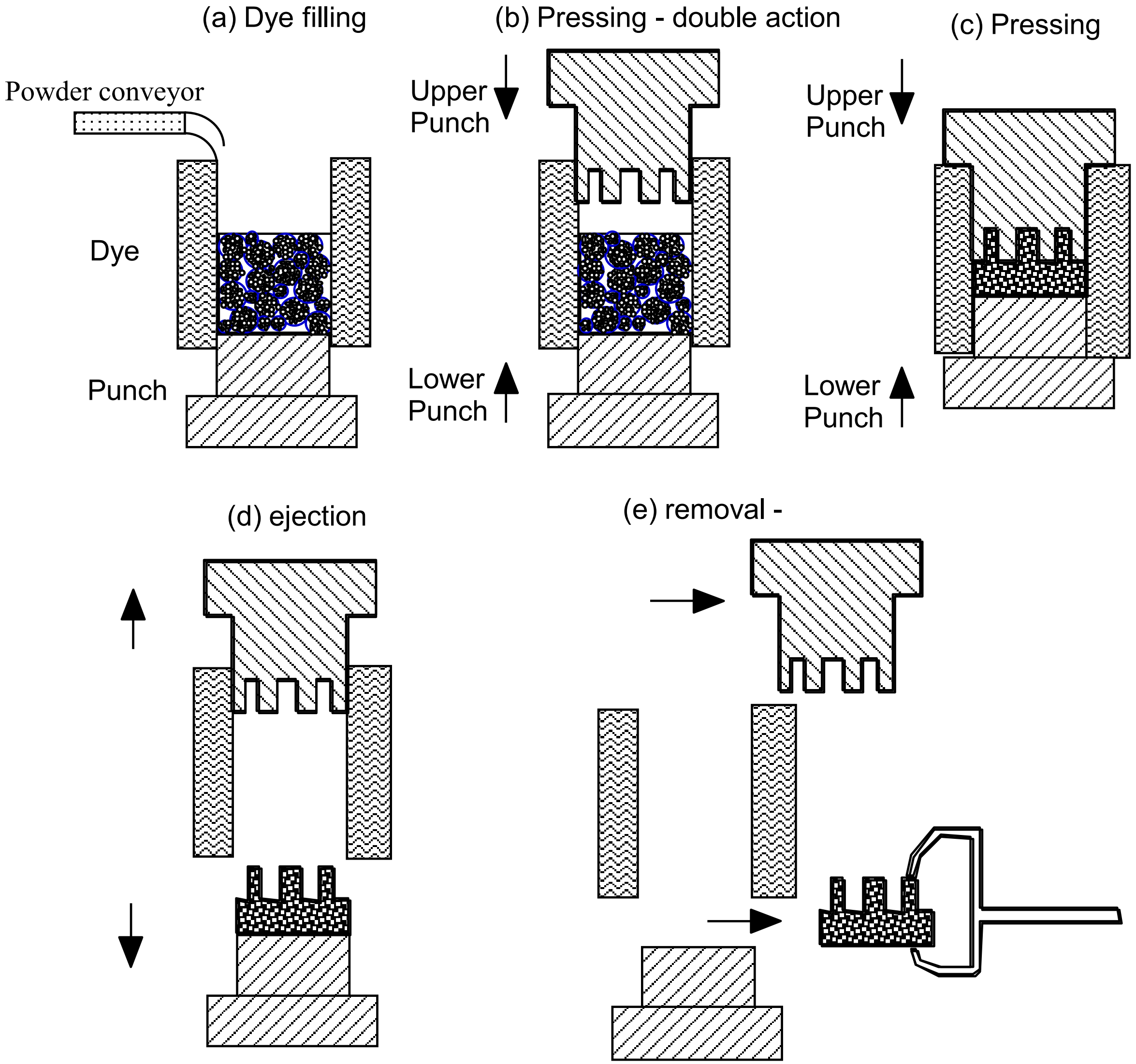


- Industrial Scale Al_2O_3



Uniaxial Dry Pressing - Automatic

- Can be used for samples with relatively simple geometry at least in 2D
- Limited to mm thicknesses
- High rate up to 1000 pieces per hour!

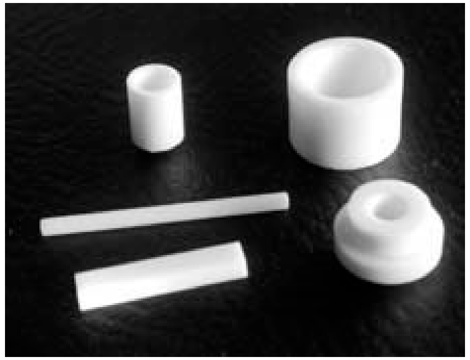


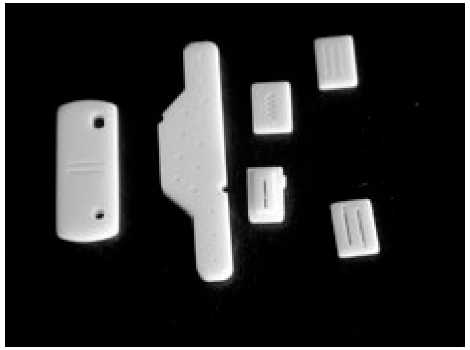
Limitations
- Elongated shapes
- Complex shapes too
- Large pieces cm….

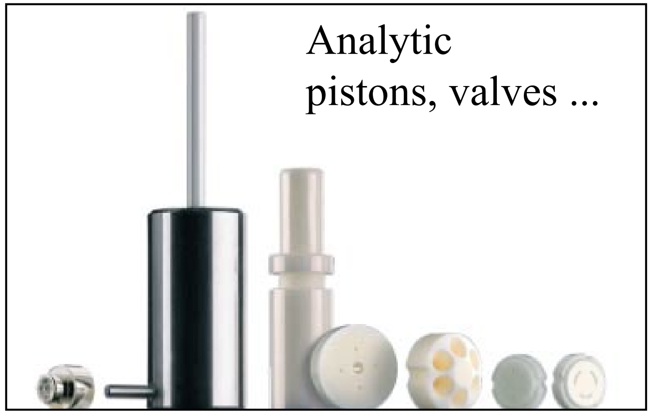
eg ceramic knife… https: //www.azom.com/materials-video-details.aspx? VidID = 386

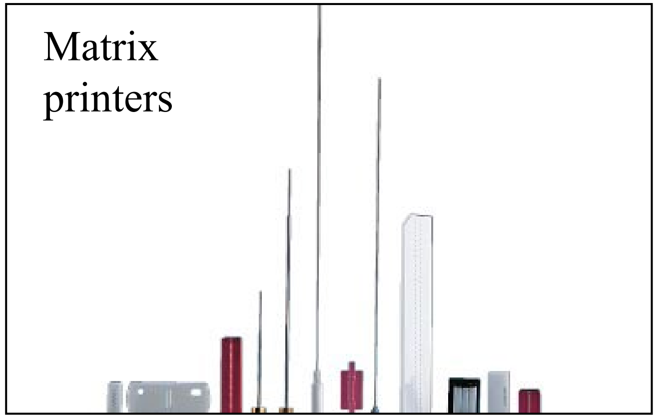
Uniaxial pressing - automatic - examples of Ceramaret SA Bole - CH

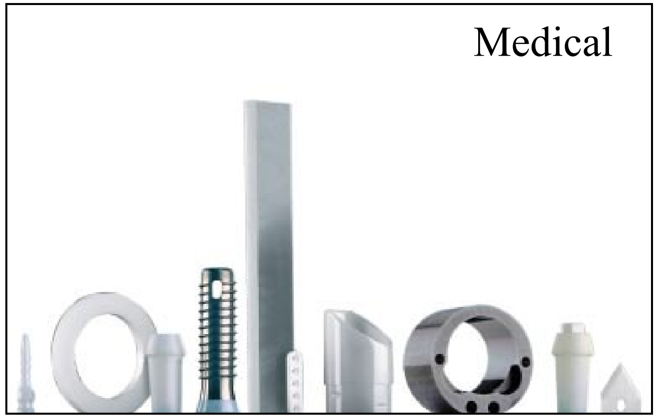
- 1-2 micron precision as pressed without post-machining - only debinding, sintering and polishing







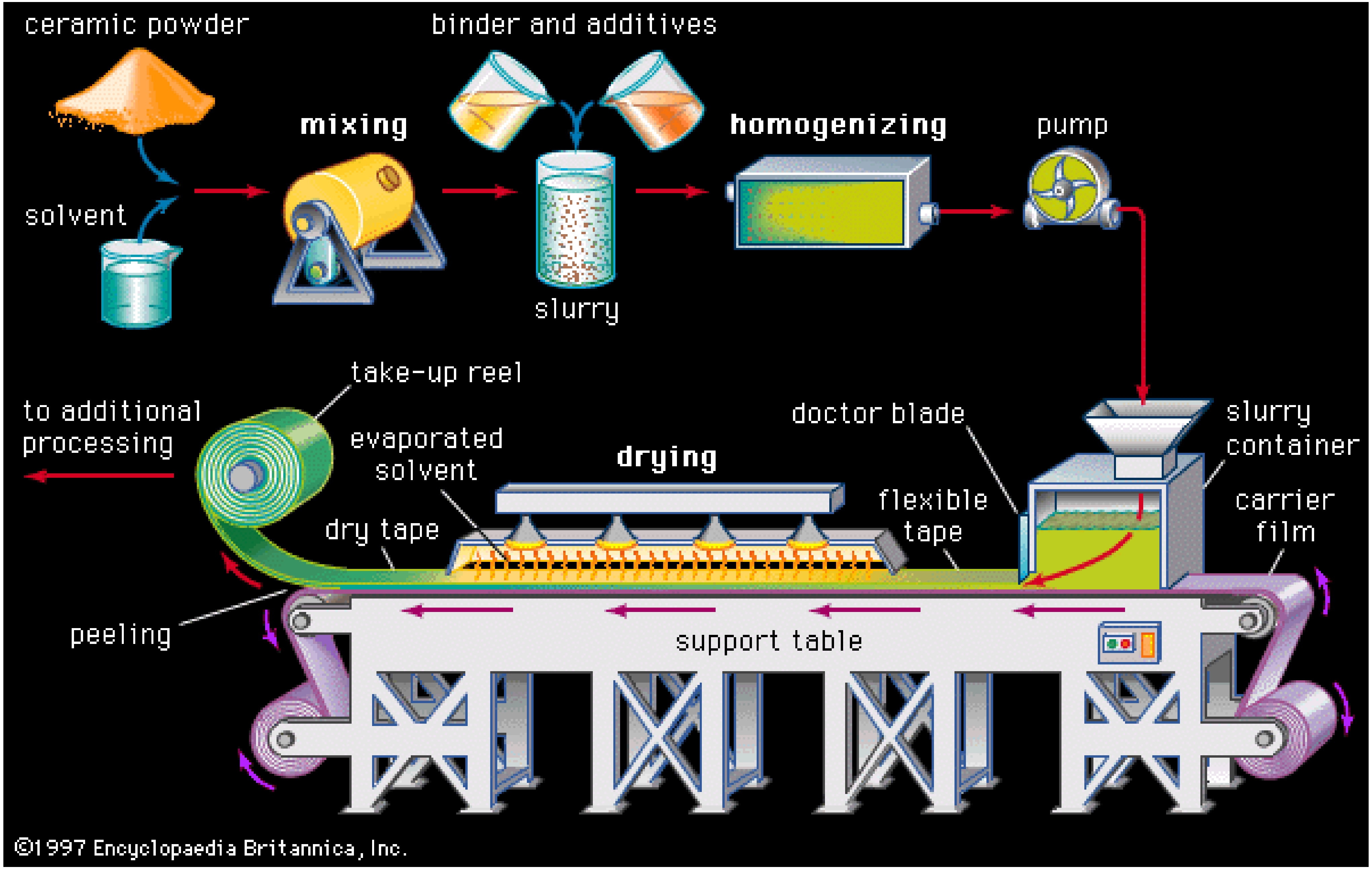




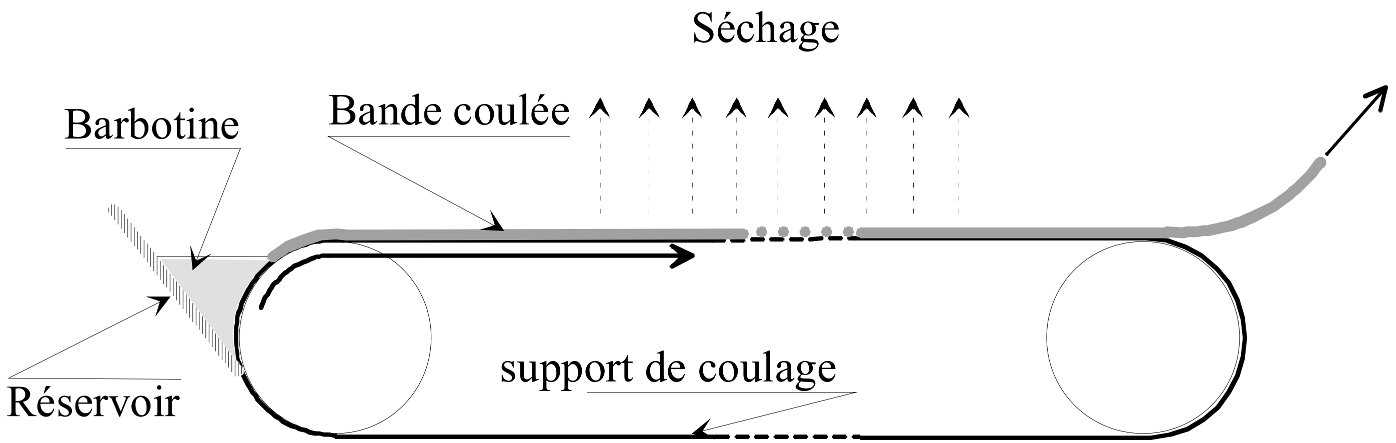
- By compacting the powders to obtain parts close to the final dimensions, Ceramaret decreases the number of expensive secondary operations.
- This approach significantly reduces production costs. The savings are all the more significant as the manufacturing is repetitive, even for a high number of parts to be produced.
- **Tungsten Carbide Forming Tools** guarantee maximum precision and longevity
- For shaping ceramic powders, Ceramaret has fully automated mechanical presses, single and double acting, cold and hot isostatic presses (CIP and HIP).

http://www.ceramaret.ch/index.php

Tape Casting – "thick" ceramic films

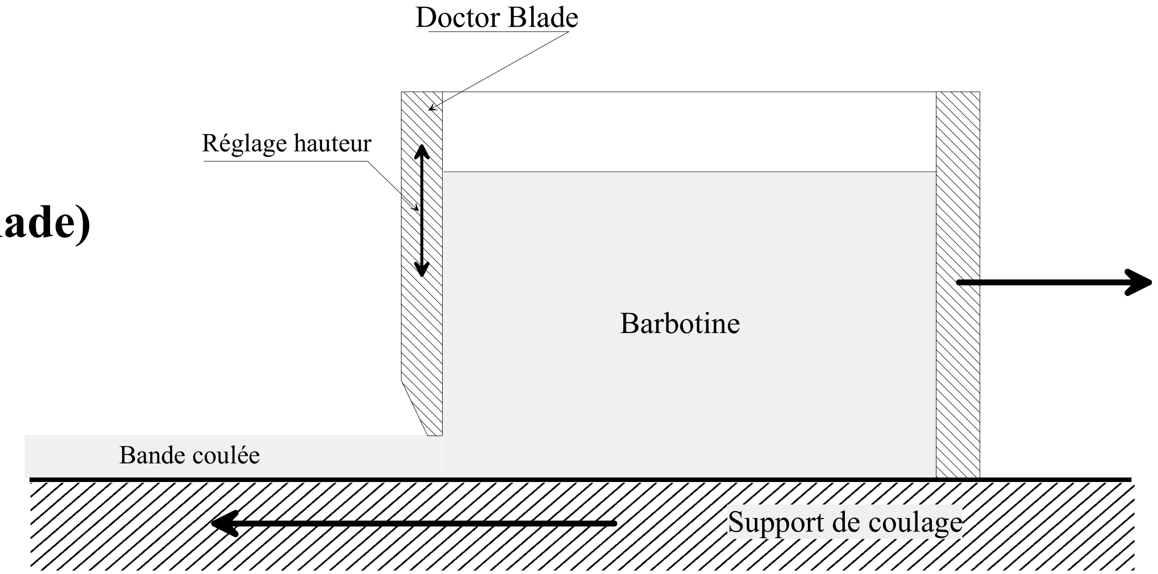


Tape Casting – “thick” ceramic films

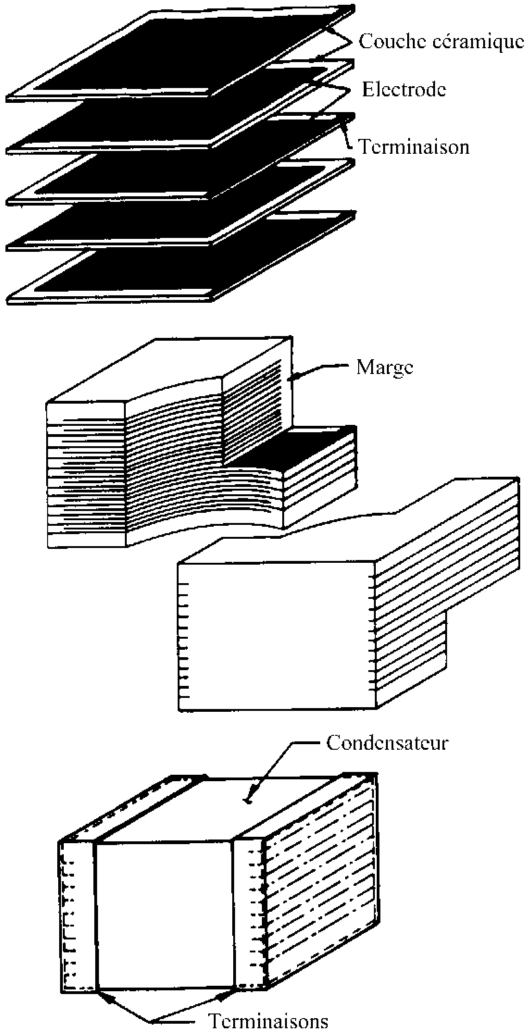


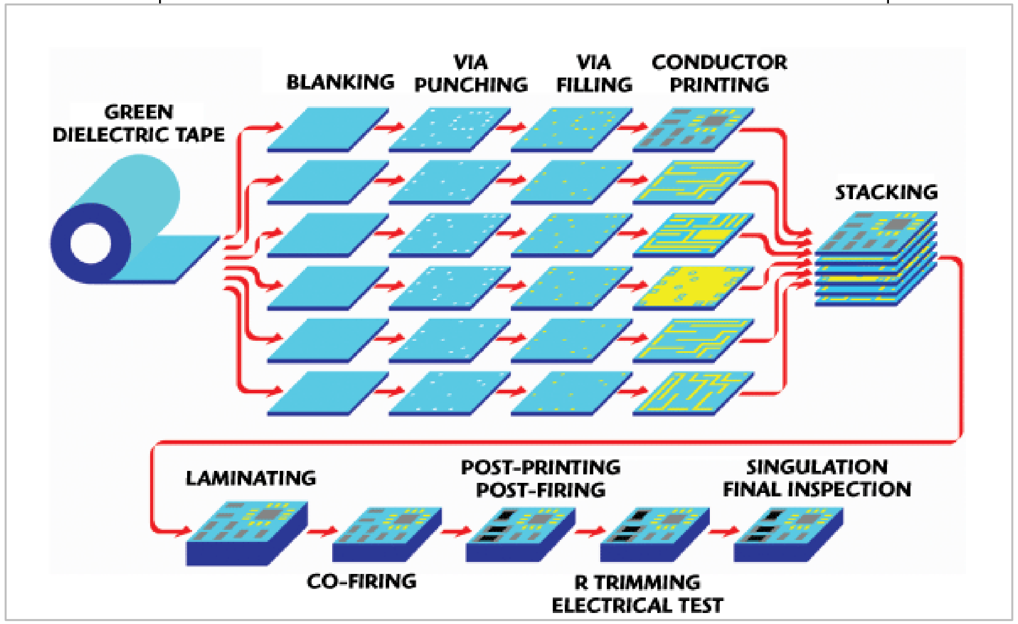
Training

Calendering or (doctor blade)



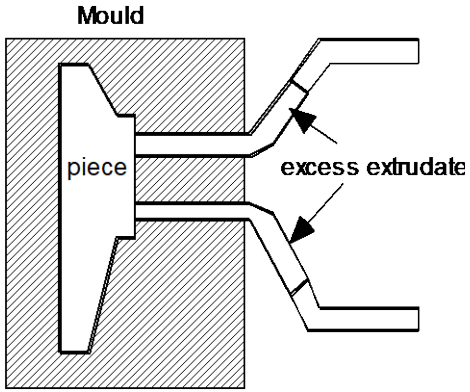
Multi-layer capacitors – $BaTiO_3$

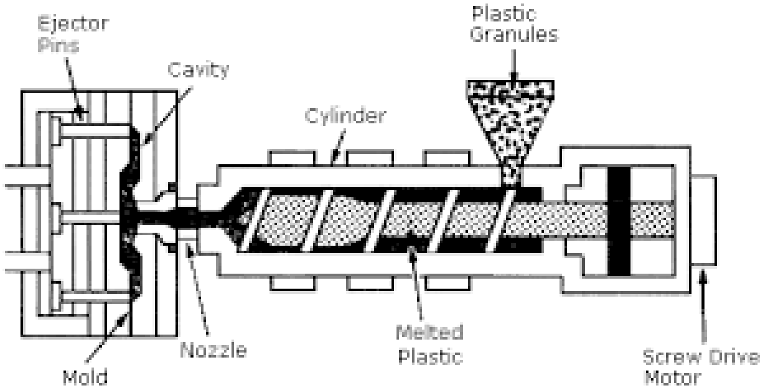




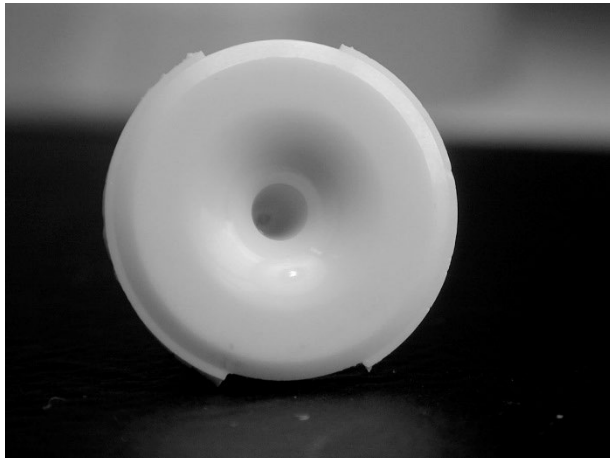
Injection moulding - SPT Roth SA, Lyss

- Small precision parts - very complex shapes
- Powder - polymer mixture (20% weight 50% volume of polymer) heated to around 200 °C
- Limitations - expensive - part sizes limited to cm
- De-binding - slow 2-3 days… or 2-4 h with new technology BASF HNO_3 at 120 °C





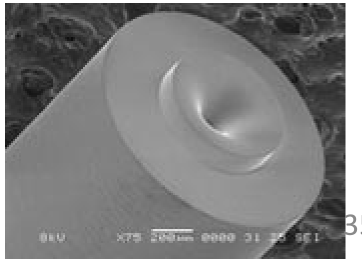
https://www.osha.gov/dts/osta/otm/otm_iii/otm_iii_1.html



SPT Roth SA- Ceramic injection molding (CIM) of small complex & precise components in micron tolerances. Materials include Alumina, Zirconia, Zirconia-toughened Alumina and polycrystalline Ruby.
Limitation of cut max cm...expensive….

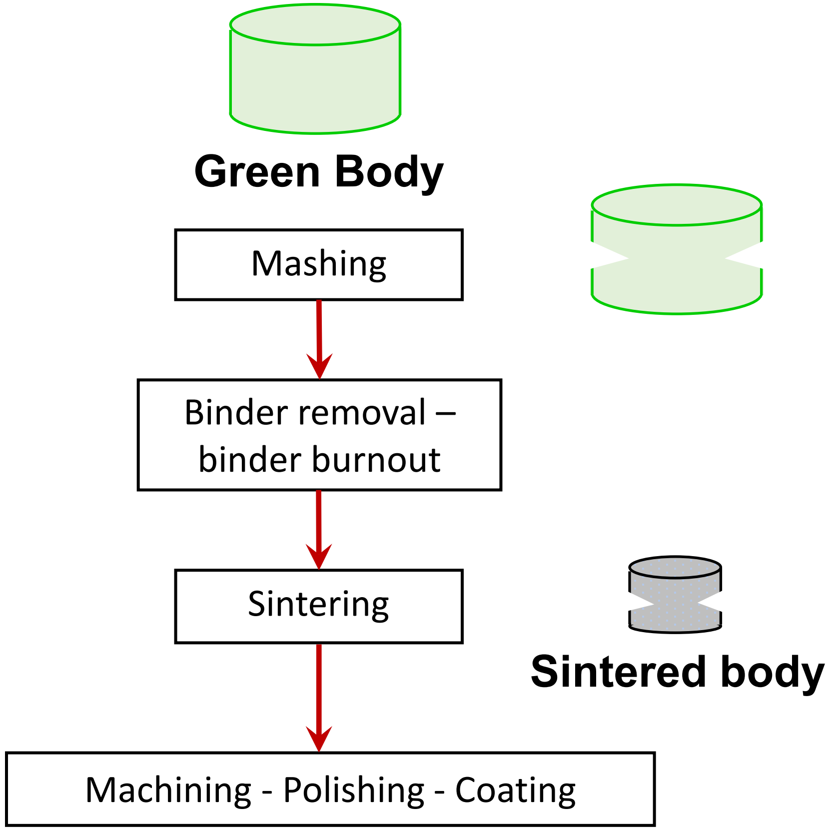
- Medical tools & implants
- Dental applications
- Industrial and Electronic components
- Nozzles with hole diameter less than 15μm
- http://www.smallprecisiontools.com/

Nozzles- nozzles

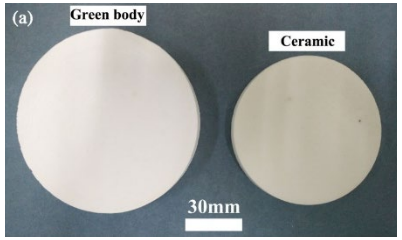


Manufacture of Ceramics - Ceramic Processing - Firing

- Sintering (firing) and Finishing



Source: ceramicartsdaily.org

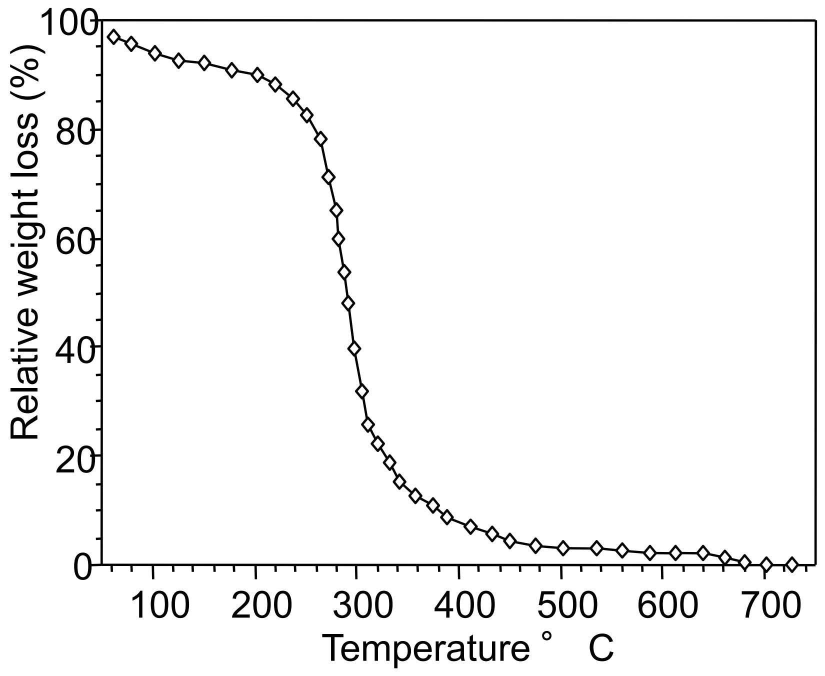


Gan et al. DOI:10.1002/app.48889

© CeramTec

Binder Removal – Binder Burnout

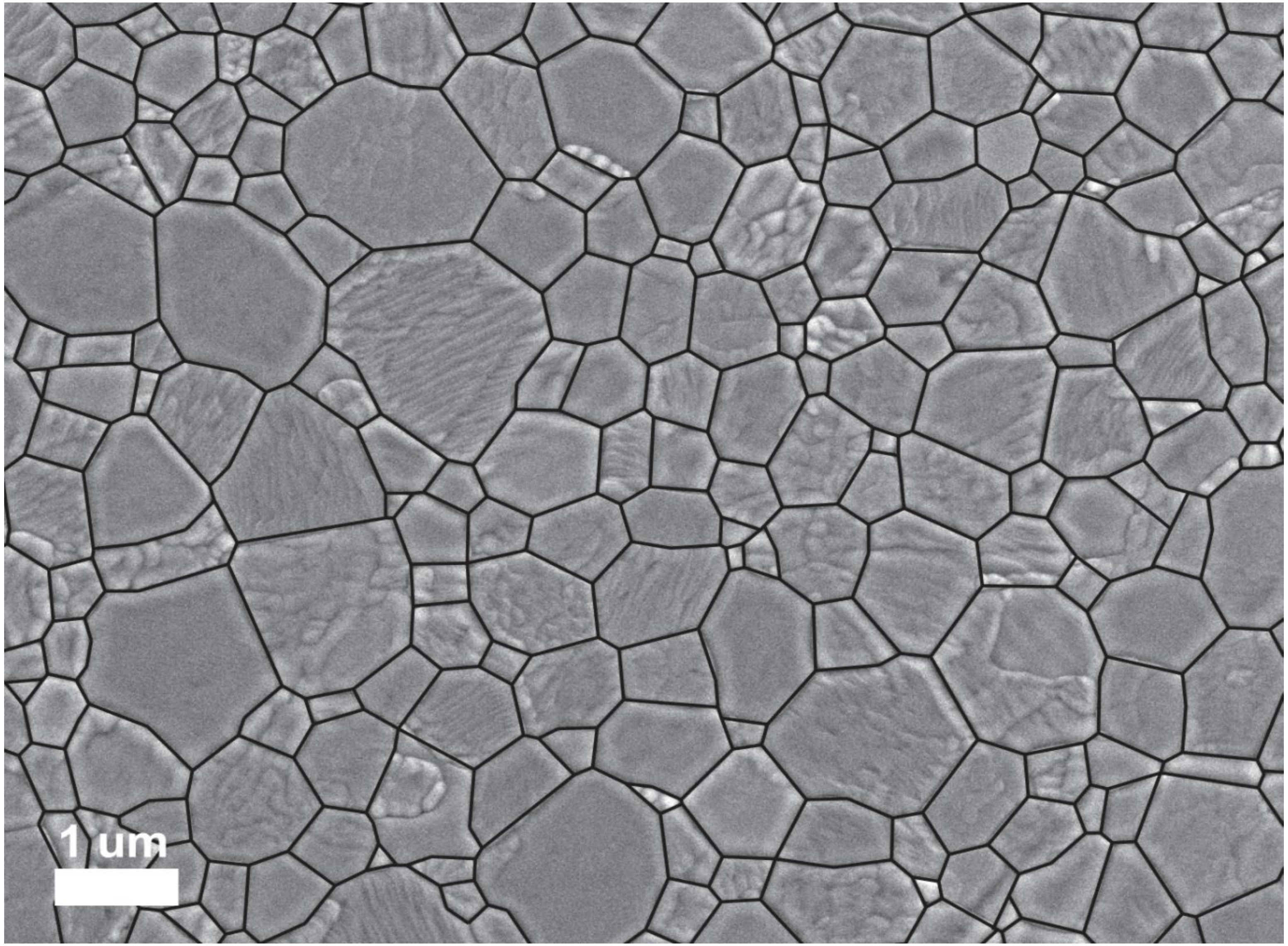
- Additives (organic) must be removed before sintering.
- The most common method is by decomposition and pyrolysis in air at around 500 °C - slow heating rates of 0.5-1 °/ min are essential.
- Mechanisms – include evaporation, oxidation and decomposition
- The phenomenon to be avoided is the crosslinking of carbon bonds, which can give carbon residues which are difficult to remove.
- If the removal of the binder is incomplete the carbon residues can react with oxygen in the ceramic forming CO/CO_2
- the ceramic may swell and even crack due to the pressure of the gases produced at sintering temperatures (> 1000 °C)



Typical decomposition weight loss curves for slip cast barium titanate green body with PAA as dispersant.

Other methods, by capillary flow (waxes) and by solvent (normal or supercritical fluids (CO_2)) dissolve the binders – sometime more than one binder is used – one removed by solvent, and one removed by pyrolysis

Microstructure - Alumina (Al_2O_3)



Two main families of synthetic powders / ceramics

- oxides (Al_2O_3, ZrO_2… ..)
- Ionic bonds…..

- non-oxides (SiC, TiN, Si_3N_4……)
- Covalent bonds….

e.g. Alumina, Al_2O_3

e.g. Silicon Nitride, Si_3N_4 (Kyocera)

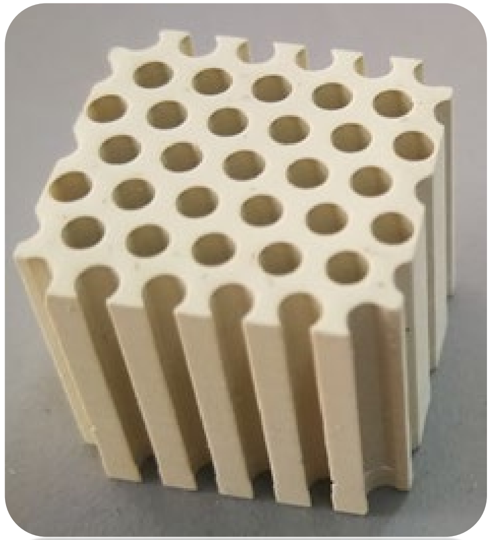
* Les Traité des Matériaux, Volume 16 « Les Céramiques »

Additive manufacturing: an enabling technology

CeramPlus 饶稷科技

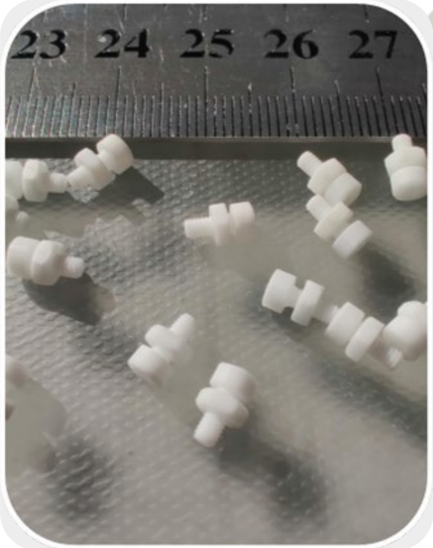
Oxides, Nitrides, Carbides

Zirconia
2Y,3Y, 4Y, 5Y, 8Y
RD> 99%
500-1200MPa
WB >8



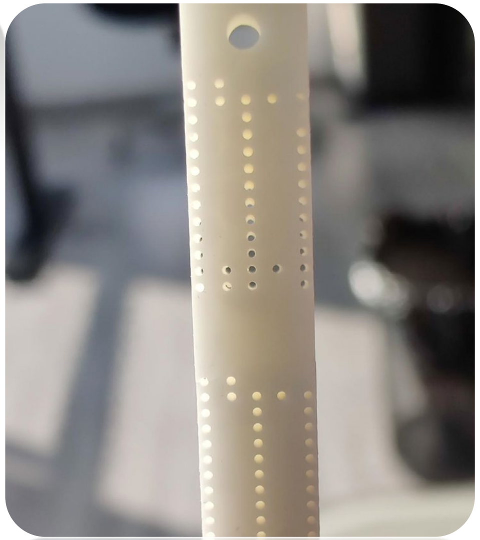
SiC
(pressureless)
Density > 3.18g/cm^3
400MPa

Al_2O_3
Purity 95-99.99%
3.8-3.93g/cm^3
350-650MPa



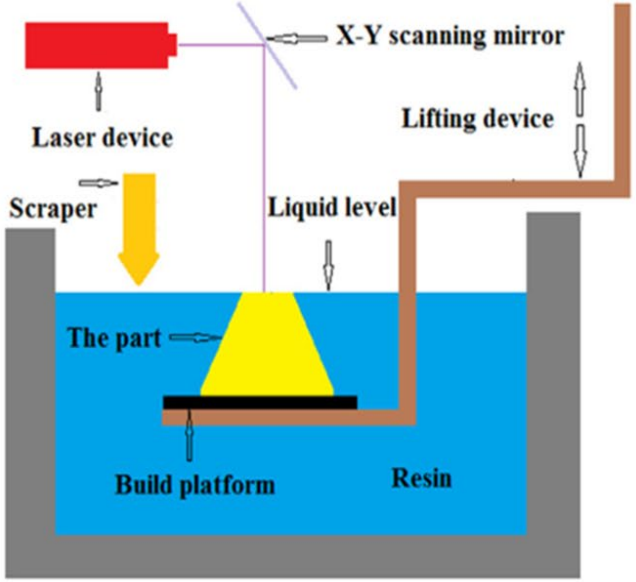
Si_3N_4&Sialon
RD >99%
600-900MPa
WB >8

HAP
RD >95%
100MPa (bending)



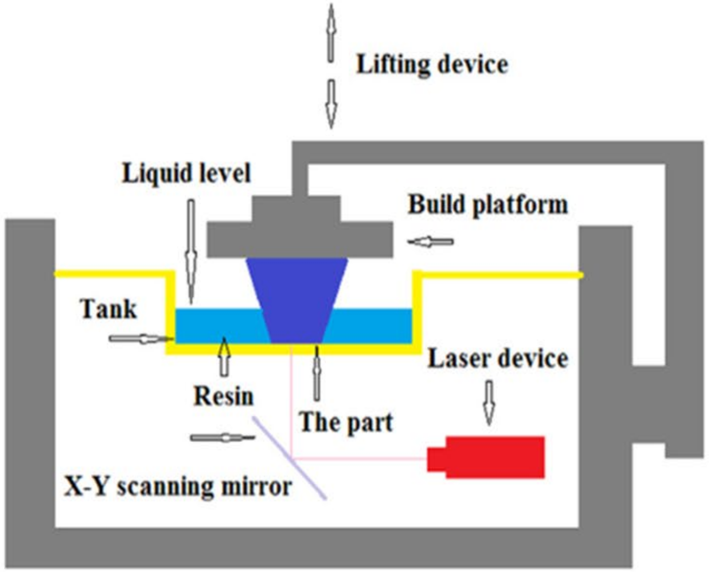
Different work-modes

CeramPlus 饶稷科技



Top-down

3DCeram (SLA), CeramPlus (DLP)



Lift-up

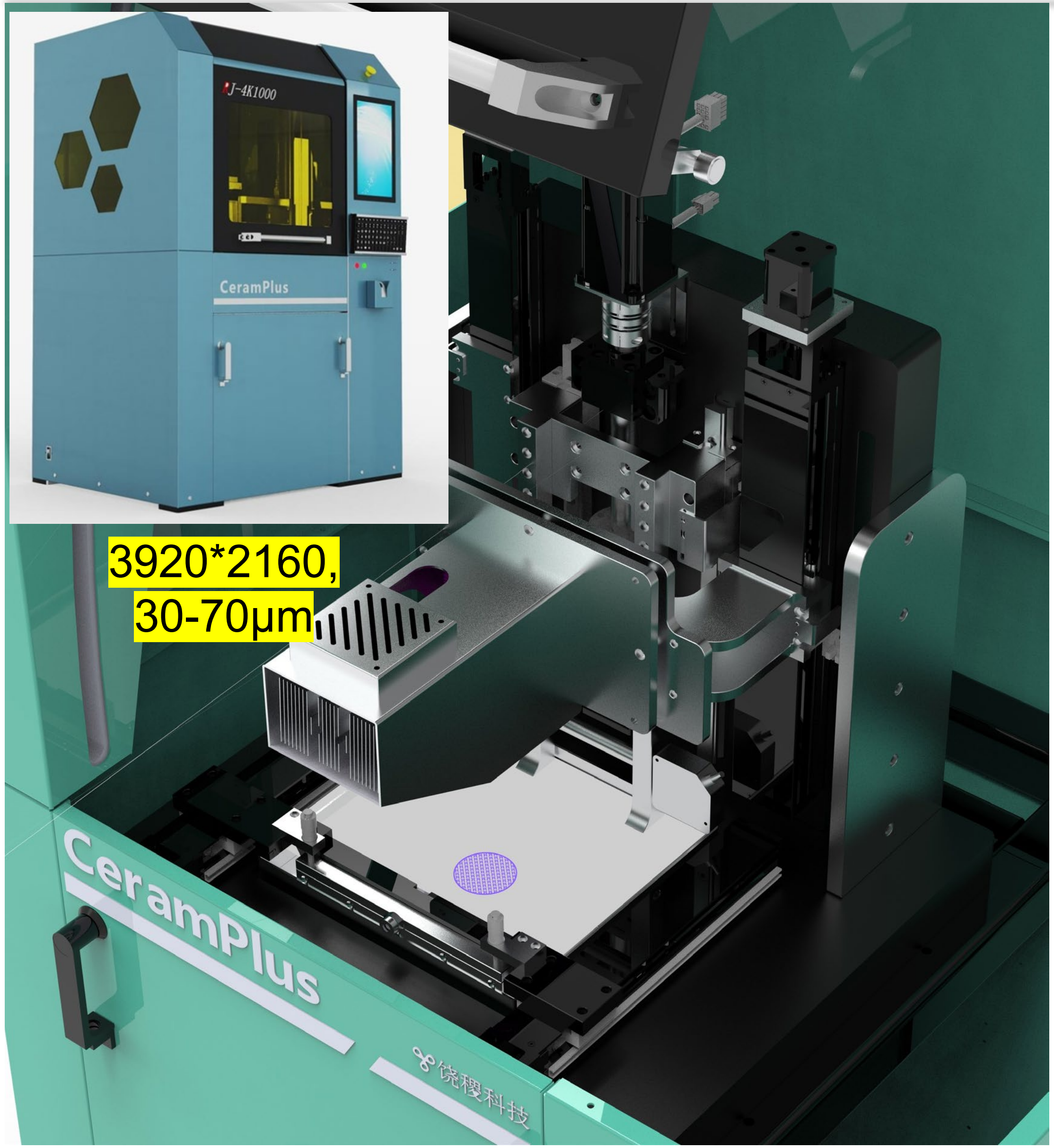
LithoZ, Admatec

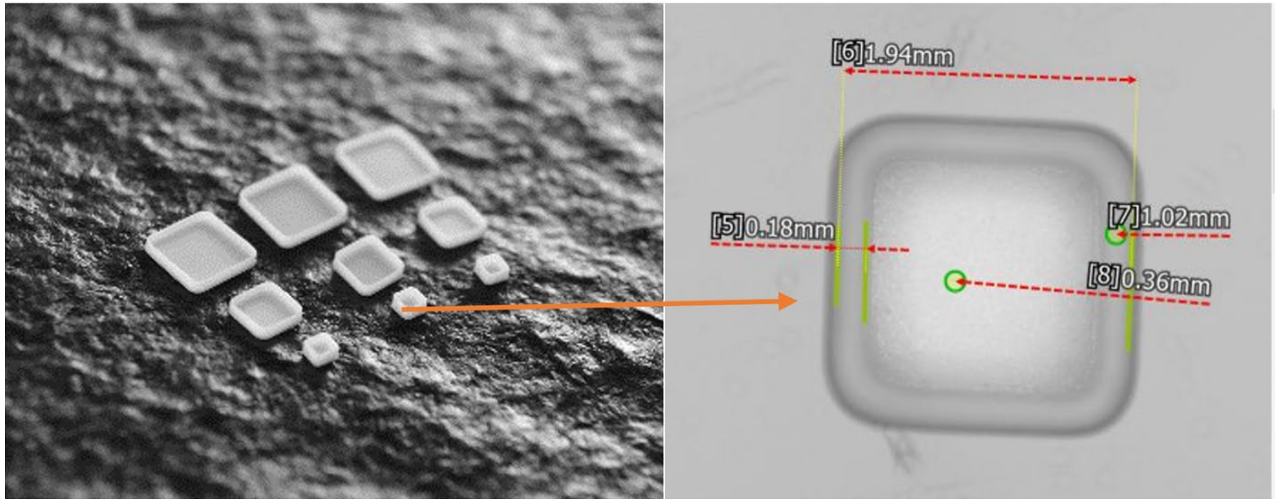
Key benefits of DLP configuration:

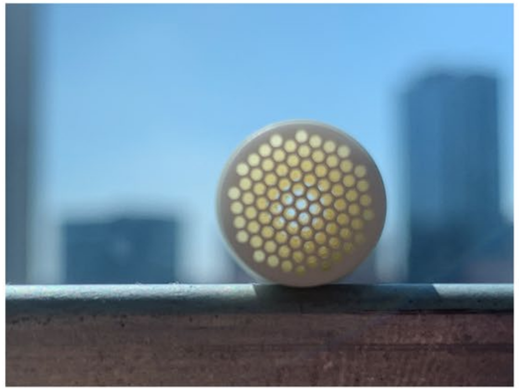
1. Low residual stress during printing,
2. better for non-stop 24hrs production, easy to handle and no risk of falling-down
3. Better adaptability to more ceramic resins options
4. Easier for large printing area

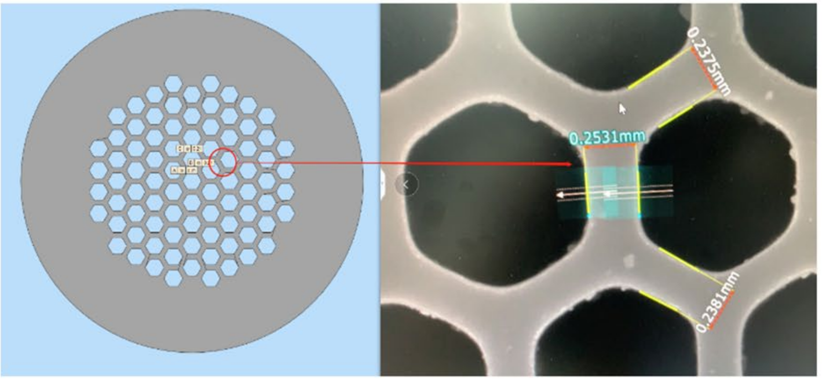
SLA: stereolithography
DLP: digital light processing

Top-down DLP printers and capabilities



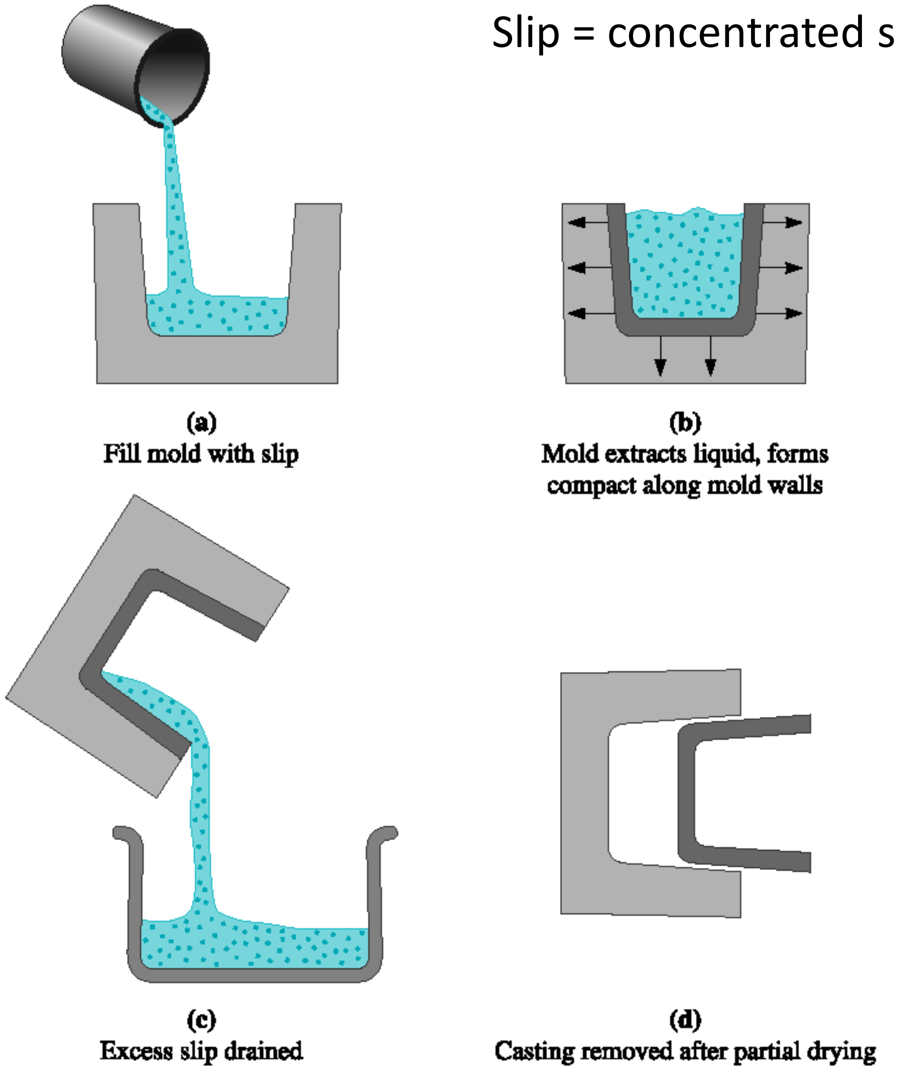






Slip casting – large complex shapes

Slip = concentrated suspension



https://www.victorianplumbing.co.uk/premier-carlton-ceramic-wc-pan-cistern-with-seat

Slip casting: https://youtu.be/FZzOTX9Ihqs

Traditional Application

- Porcelain – wash basin etc
- Complicated and large shape
- Slip casting 45% vol powder - 80 minutes each mould
- Pressure casting - 2 minutes!! 40 times faster
- Modern semi-automatic
- 1 week for mixing, homogenizing and milling the slip (concentrated suspension)
- Slip Casting with alumina up to
- 68% green density

LAUFEN - Switzerland

Porcelain: quartz, kaolin, feldspar

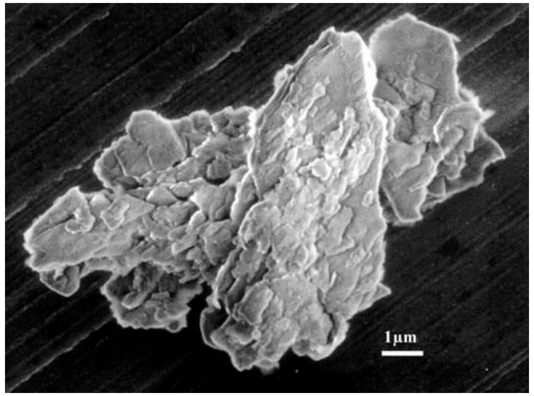
Porcelain

Porcelain: from old Italian word “porcellana”

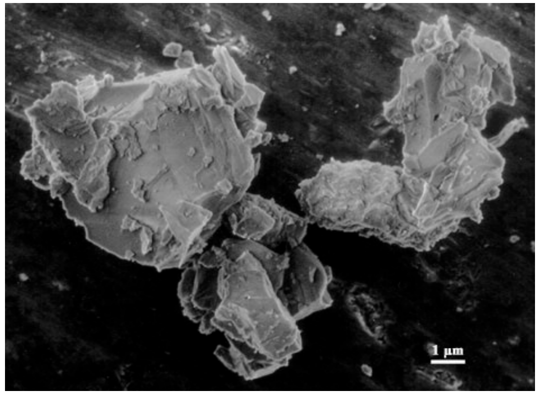
since resemblance the shell surface.

Cowrie shell

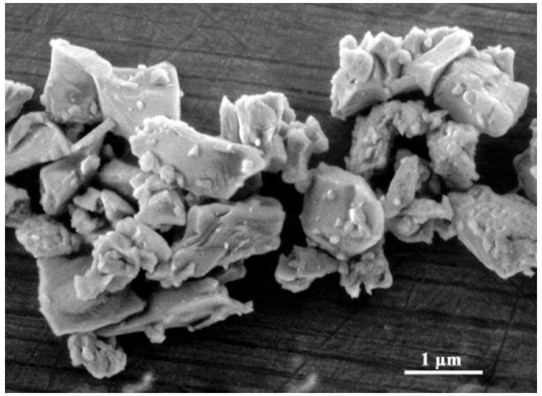
Kaolin
(50-55%)



Feldspar
(25%)
glassy phase,
decrease firing temperature (flux)

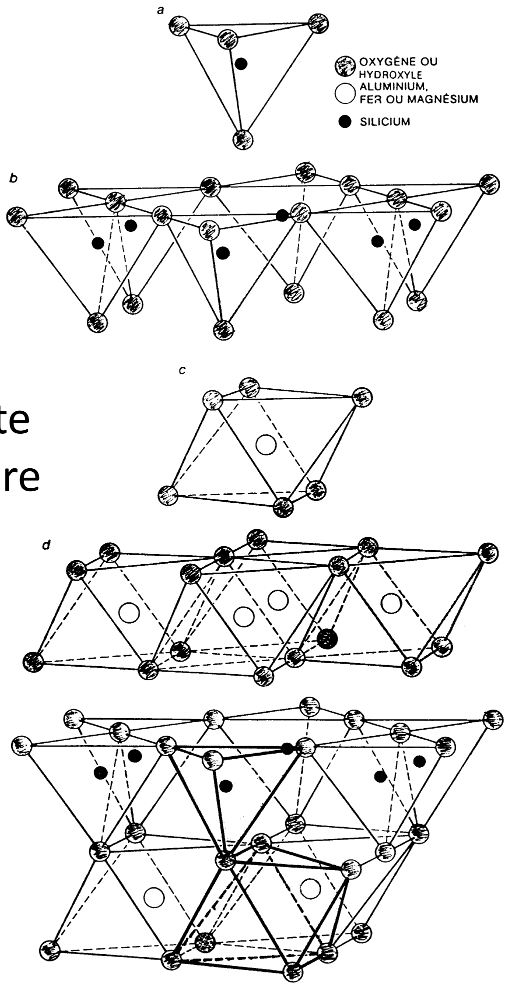


Quartz
(20-25%)
thermal and dimensional stability



Porcelain
(hard)

Kaolin
Alumino-silicate layered structure



Kaolin
Thin sheets

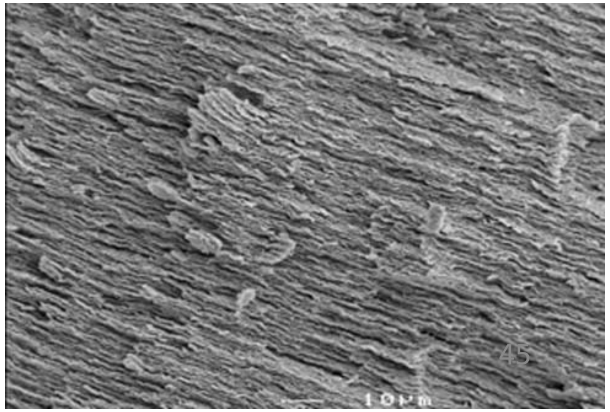


TABLE 4. ILLUSTRATIVE CERAMIC BODY FORMULATIONS

product	composition (% mass) kaolin	ball clay	feldspathic flux	silica	firing temp/°C biscuit	glost
hard porcelain	50–55	0	15–25	20–30	900	1400
soft porcelain	40	10	20–30	20–30	1230	1100
bone china†	25	0	25	0	1270	1120
vitreous sanitaryware‡	28	24	18	30	1200	—
earthenware	25	25	10–20	30–40	1170	1060
lime earthenware white tiles§	25	25	0	40	1080	980

† Also contains 50 % by mass bone ash.
‡ Nepheline syenite is the normally preferred flux.
§ Also contains 10 % by mass calcium carbonate.

alkali- aluminosiliacate

glaze firing or second firing

W.B. Jepson, " Kaolins: their properites and use"
Phil. Trans. R. Soc. Lond. A 311, 411-432 (1984)

earthenware

soft/hard porcelain
(different firing T,
weaker / toughness)

Bone china
strongest porcelain

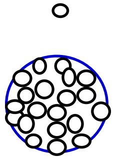
Dry pressing – small simple geometries: shaping Week 7

- Pressing of spray dried granules

effects of powder parameters on green compact density

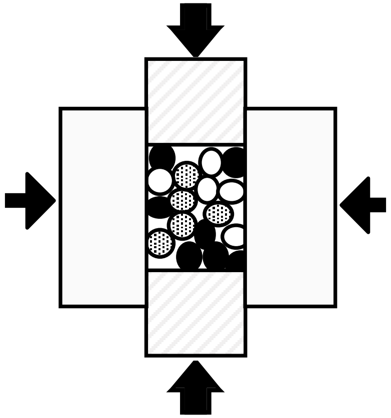
- Compaction 3 stages
  - Rearrangement
  - Deformation of granules
  - Fracture of granules

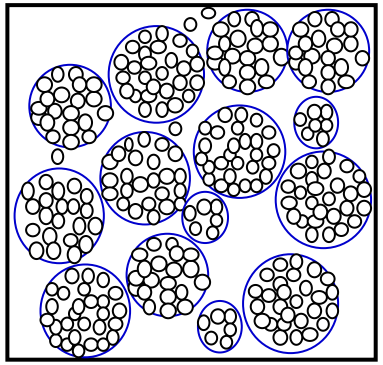
  (rarely reached in practice)

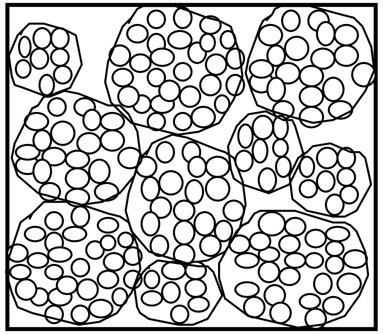


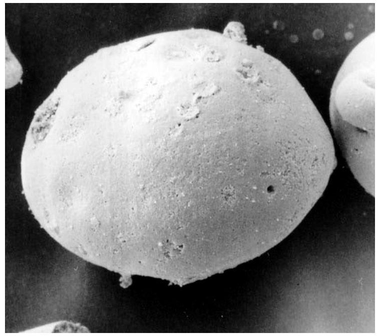
Primary particle (1µm)

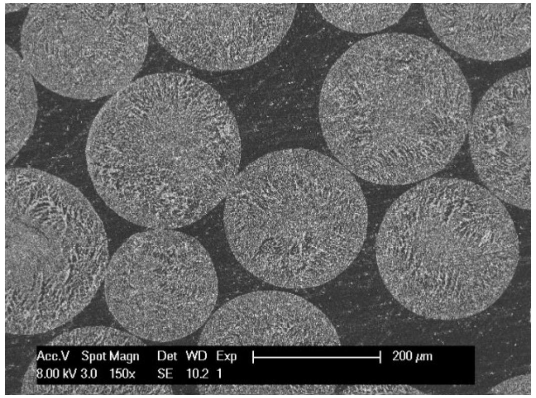
Granulated for pressing (50-300µm)

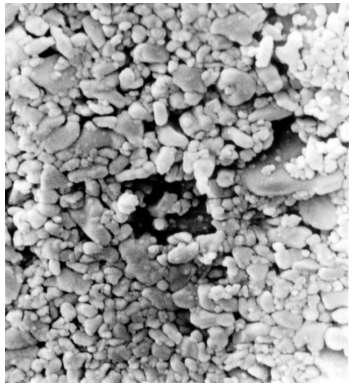








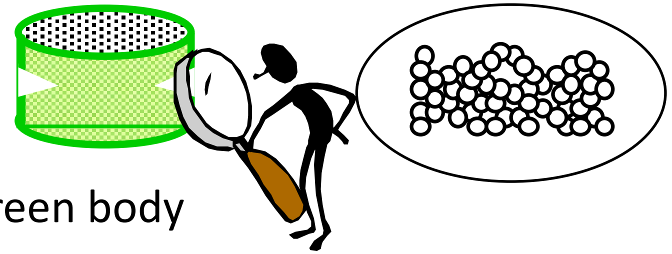




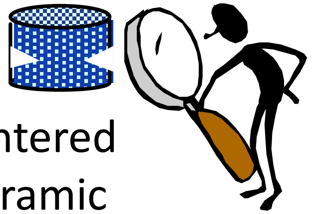
VIDEO - e.g. ceramic knife: https://youtu.be/cb0Hr_kAYvc

Sintering and Control of Microstructures: Week 8, 11

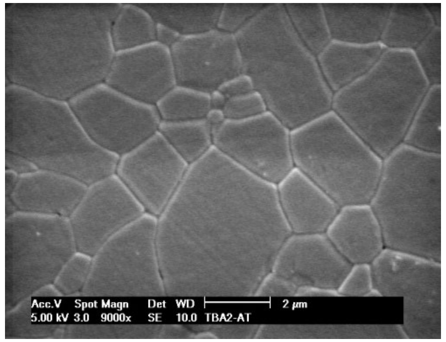
In the second part of the course, from shaping to sintering:



Green body



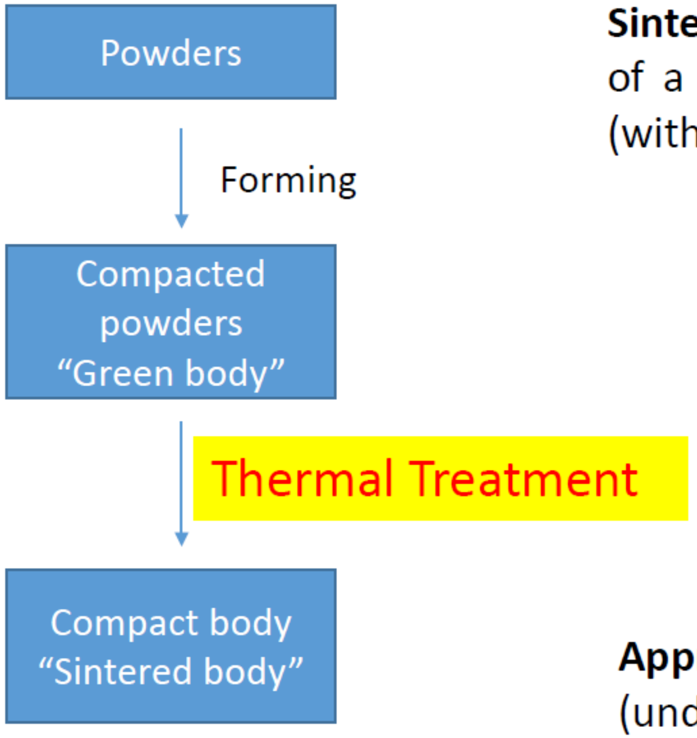
Sintered ceramic



Main Supporting Text

M.N. Rahaman-Ceramic processing and sintering. Taylor & Francis. Second edition (2003). Chapters 7-10

Sintering Fundamentals



Sintering: thermal treatment which allows the transformation of a compacted powder body (green body) into a solid body (without fusion).

Key objectives: understand how the process variables influence the microstructure evolution.

Approach: experimental trials (trial-and-error) or theoretical basis (understanding of the elementary mechanisms which are governing the consolidation process).

Driving force: decrease in the free energy of the system! Influenced by:

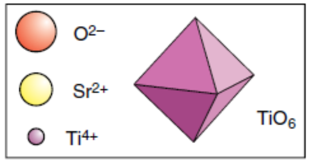
Curvature of the particle (overall surface)
External applied pressure (external applied fields)
Chemical reactions (within the solid or with a gas phase)

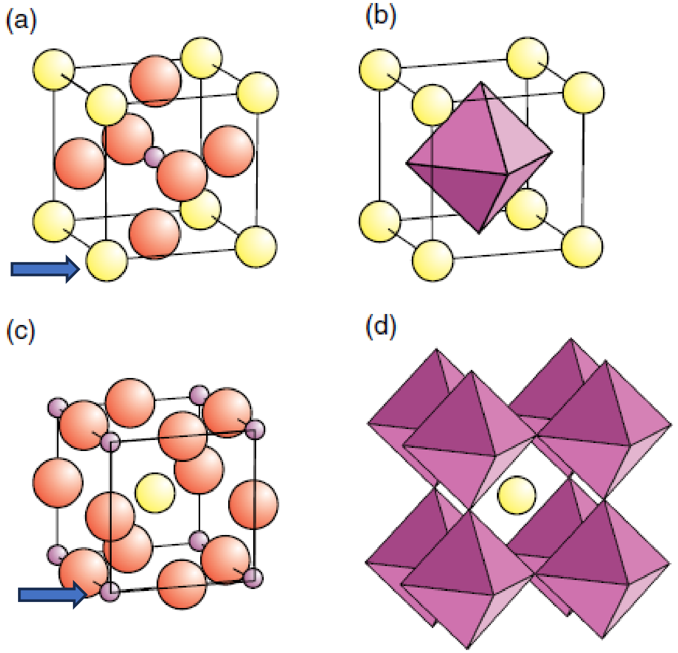
Types of sintering

- Generally, there are three **types** sintering:
- ***in solid phase***: all constituents remain in solid state throughout sintering. Densification involves a grain shape change. The transport of matter mainly occurs by diffusion in solid phase and at grain boundaries.
- Temperatures between 0.5 and 0.8 cf melting temperature
- e.g. Al_2O_3 - T_f 2072 ° C - sintering 1500 ° C
- ***in liquid phase***: forming of a viscous liquid (generally eutectic with a low melting point) which more or less completely fills the pore spaces of the initial compact. (ex: porcelains). Densification occurs mainly by dissolution and re-precipitation, allowing rapid material transport.
- ***reactive***: two or more constituents react during sintering. Densification is done by re-precipitation of the new compound.

Perovskites ABX_3 – Week 5

$SrTiO_3$





Origin on Sr^{2+}

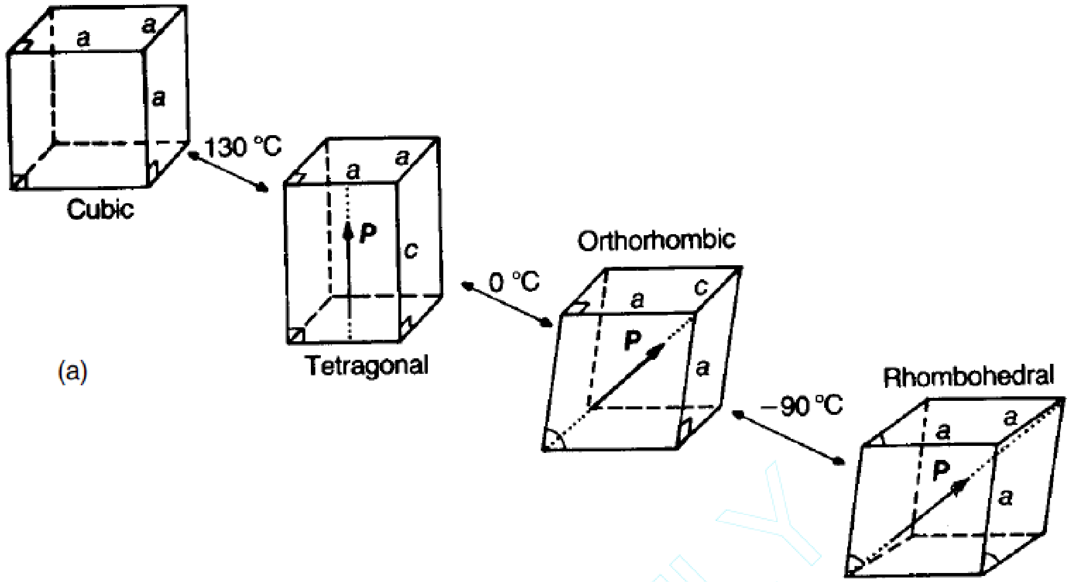
Sr: 1 (*a*) 0,0,0;
Ti: 1 (*b*) ½,½,½;
O: 3 (*c*) ½,½,0; ½,0,½; 0,½,½;

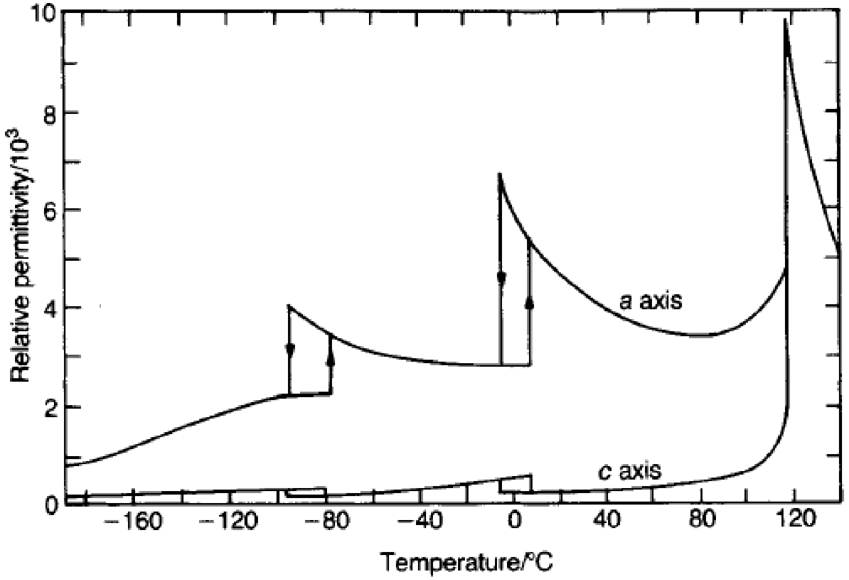
Origin on Ti^{4+}

Ti:1(*a*)0,0,0;
Sr:1(*b*)½,½,½;
O:3(*d*)½,0,0; 0,½,0; 0,0,½;

Sr^{2+} is coordinated with 12 O^{2-}
Ti^{4+} is coordinated with 6 O^{2-}

$BaTiO_3$





Spinel AB_2X_4 : Week 6

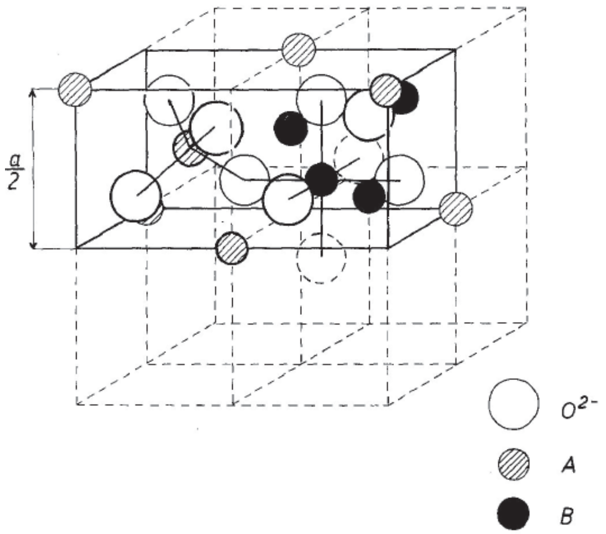


Fig. 1. Primitive cell of the spinel structure.

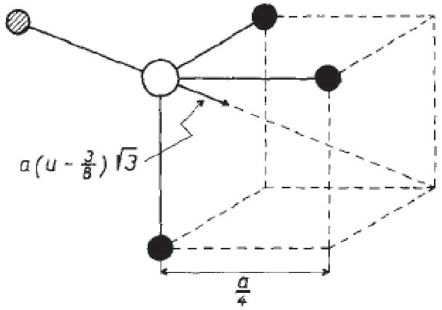


Fig. 2. Environment of the anion in spinel.

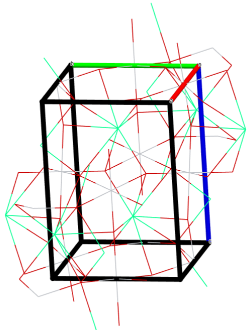
X is generally O^{2-}, but it can be replaced by chalcogenic bivalent anion (S^{2-}, Se^{2-}, Te^{2-}) , and also partially substituted with halogens (-1). A and B are metals with oxidation state that match the electroneutrality requirements, e.g., $MgAl_2O_3$.
Oxides are generally insulators. A is a tetrahedral site, while B is an octahedral site. The unit cell is composed by 32 anions, 8 cations A-type and 16 cations B-type.

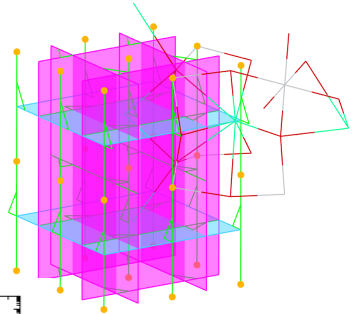
A small displacement, defined by a single parameter μ, of the anions form their ideal position is allowed along the corresponding body diagonal, which enable a better matching of the anion position radii of A and B cations. $\mu = 3/8$ corresponds to the ideal close-packed anion lattice.
MM'_2X_4

Normal spinel: all M in tetrahedral (A) and all M' in octahedral (B) position. **Inverse spinel**: ½ of M' in tetrahedral site (A) and ½ in octahedral (B) sites with M. Intermediate cases exist: the degree of inversion is a fundamental parameter, which is synthesis and processing dependent.

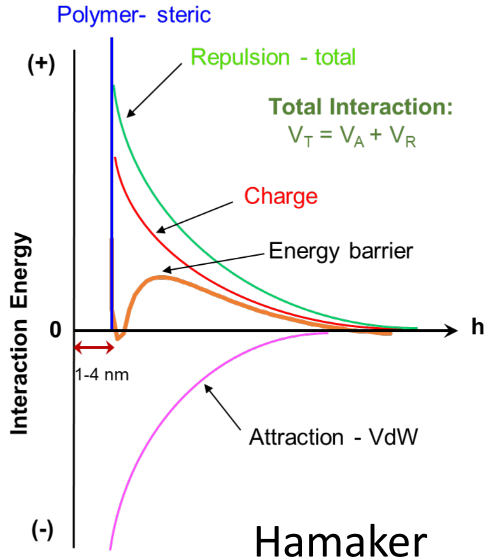
Computational tools: preview

1. Colloidal stability: Hamaker software
2. Aqueous thermodynamic: OLI studio
3. Kinetics modelling and population balance: introduction and examples
4. XDR and crystal structure: GSAS, Mercury

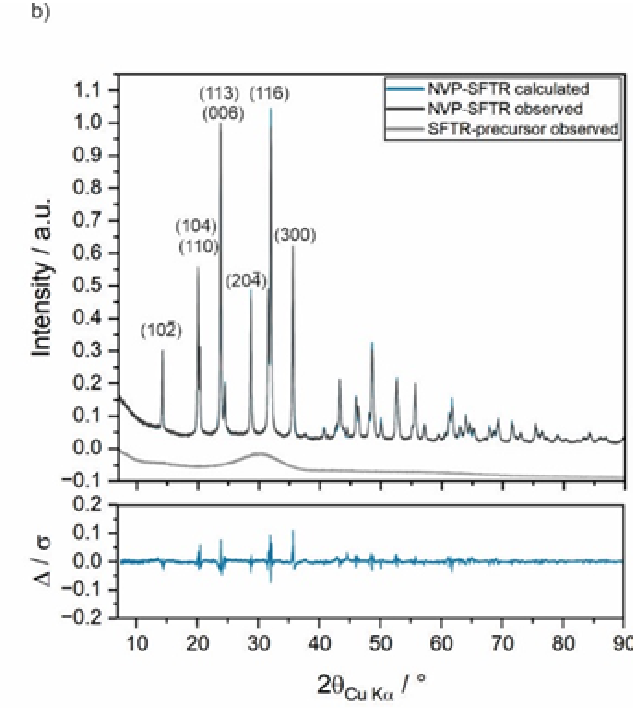




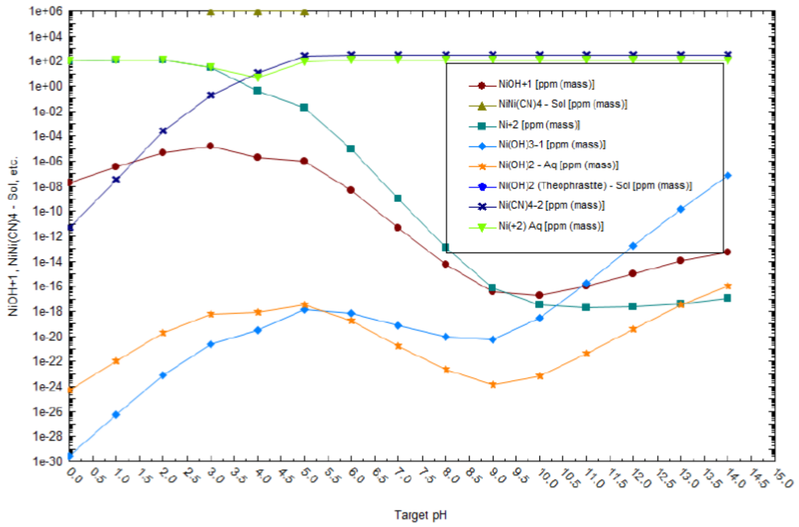
Mercury



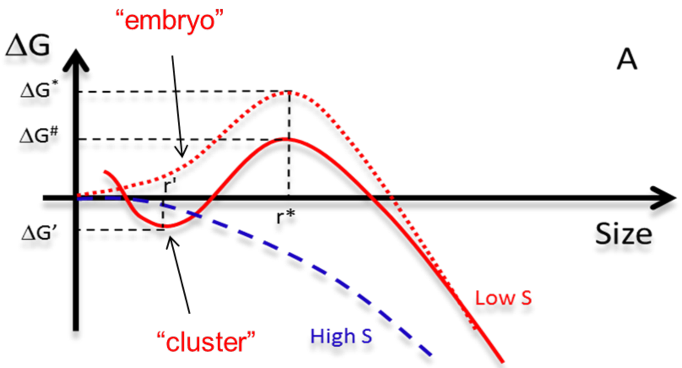
Hamaker



GSAS – Rietveld refinement (brief overview)



OLI studio



Kinetic modelling