

EPFL



Ceramic and Colloidal Processing

MSE 326 - Week 1

1. Introduction

A. Testino (PSI-EPFL)



hip prosthesis

Ceramics courses - SMX 3rd year

3rd year - semester 5 - ENGLISH

- Elaboration of ceramics and colloids & exercises: 3 credits
- Elaboration of ceramics and colloids – exercise and invited guests

• 3rd year - semester 6 - ENGLISH

- Crystalline material: Structures and Properties – (Stolichnov) MSE-306

• Master course: Advanced ceramic technologies MSE - 495

Learning Methods

- feeling and watching – virtual demonstration
- thinking and watching - classical lectures
- thinking and doing - problems - exercises

Supporting Material

- Lectures pdf on MOODLE – Monday before course (at the latest)
- Course mainly based on French book
- **Les Céramiques**, J. Barton, P. Bowen, C. Carry & J.M. Haussonne, Les Traités des Matériaux, Volume 16, PPUR, 2005

TRAITÉ DES MATÉRIAUX

16 
**CÉRAMIQUES
ET VERRES**

Jean-Marie Haussonne James L. Barton
Paul Bowen Claude Paul Carry

PRESSIONS POLYTECHNIQUES ET UNIVERSITAIRES ROMANDES

English Books:

1. **Ceramic Processing and Sintering** - M. N. Rahaman Taylor & Francis, London, 2003 (available as e-book EPFL library)
2. **Fundamentals of Ceramic Powder Processing and Synthesis**, T.A. Ring – Academic Press, 1996 (available as e-book EPFL library)
3. **Principles of Ceramic Processing**, JSReed , Wiley, 1995 (available as e-book EPFL library)
4. **The Colloidal Domain** – DF Evans & H. Wennerström, Wiley, 1999.

Different nomenclature in books...Take care...but same as in scientific literature

Ceramics come in all shapes and sizes

- ❖ Variety of applications/properties - dictates powder & forming method
- ❖ Powder can be natural e.g. clays etc or synthetic e.g. precipitation



Hip joints

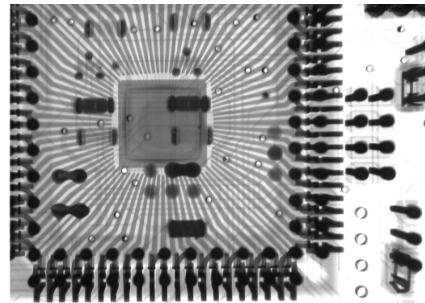
Building materials



Automotive -
spark plugs



Tableware

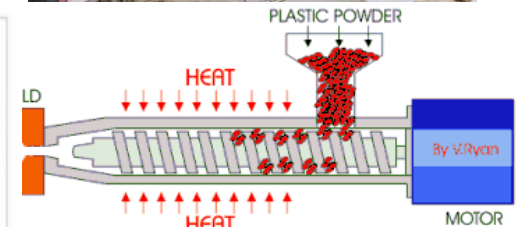


Electronic circuits - the mobile phone (> 700 ceramic capacitors*) - cars...

*<https://www.youtube.com/watch?v=dVTWq8s7y4E>

Ceramic processing - Forming

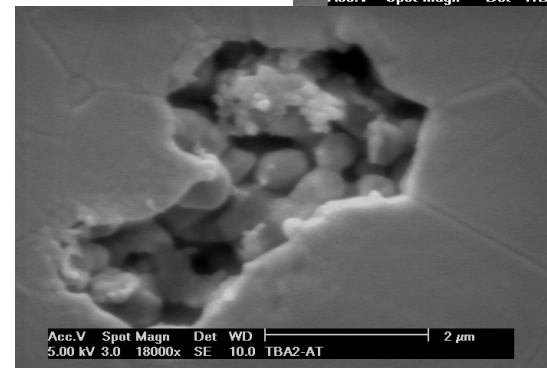
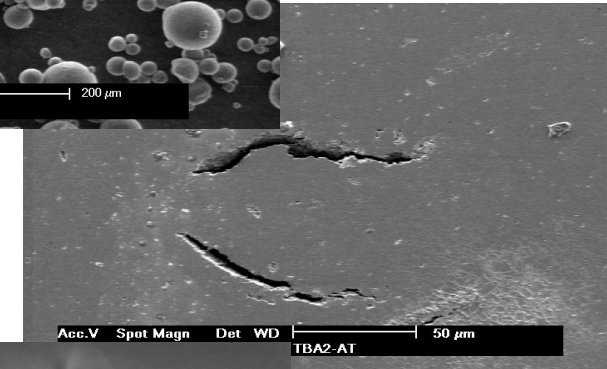
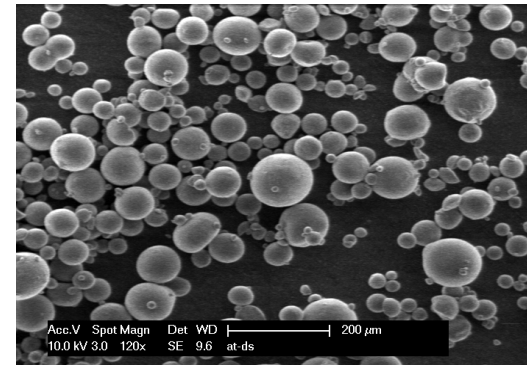
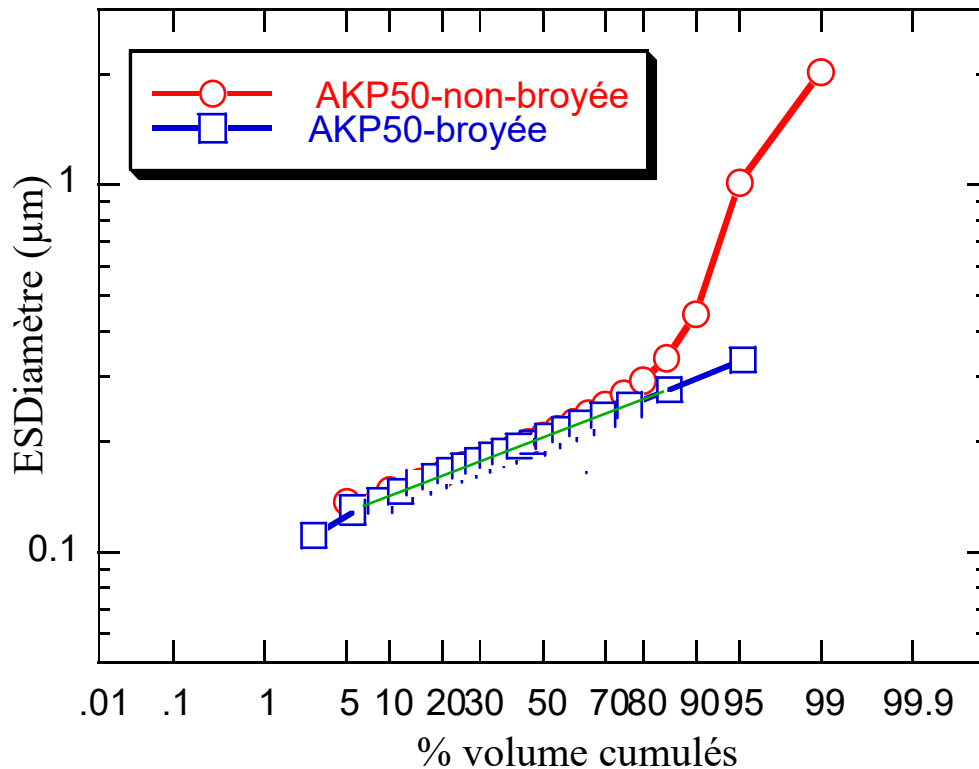
- ❖ Ceramic forming - example
- ❖ Powder - mixed with liquid - water
 - Potter's wheel or tape casting
 - organic-polymers - injection molding for complex forms
 - Fire or sinter to form a ceramic
- Properties depends on
 - density (porosity)
 - microstructures
- Controlled by powder surfaces
- - become grain boundaries after sintering
- Design microstructures



V. Ryan © 2002

Why quality powders? Al₂O₃ -alumina– effect of agglomerates

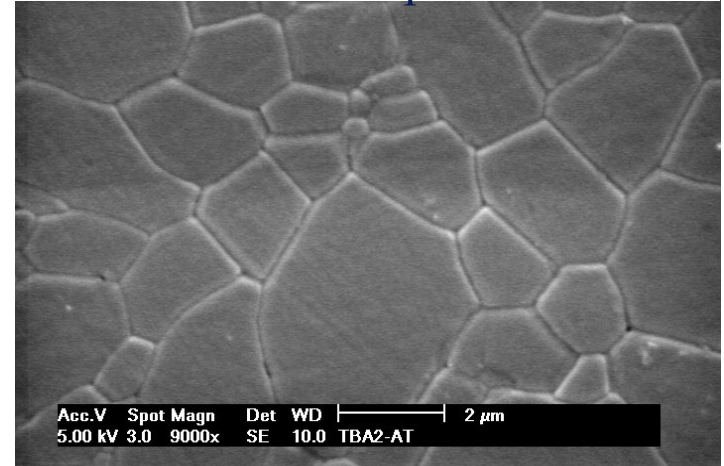
- Particle size distribution shows small tail of agglomerates – leads to defects in microstructure and low sintered densities (94%)



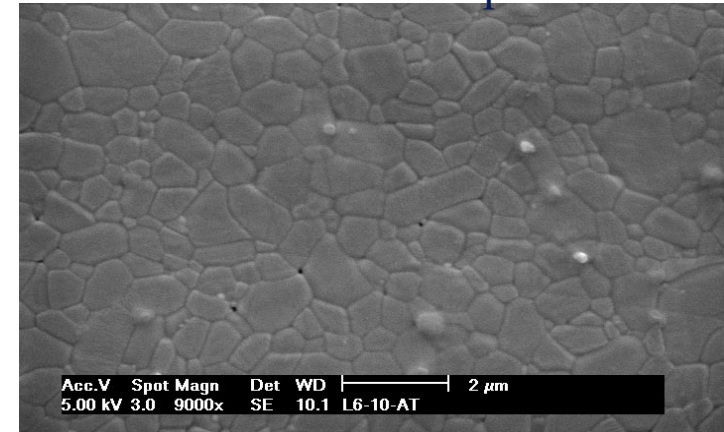
Powder influences microstructure - properties

- ❖ Transport properties -
 - Electrical, Mechanical, Optical
 - Influenced by
- ❖ Grain size and
- ❖ Grain boundary composition
- ❖ Processing - high quality powder*
 - High compact density
 - Narrow pore size distribution
 - Close pores as late in sintering cycle as possible
 - Better microstructure (homogeneous)
 - Understand surfaces and interfaces
 - microstructure control

As received - slip cast - 94%



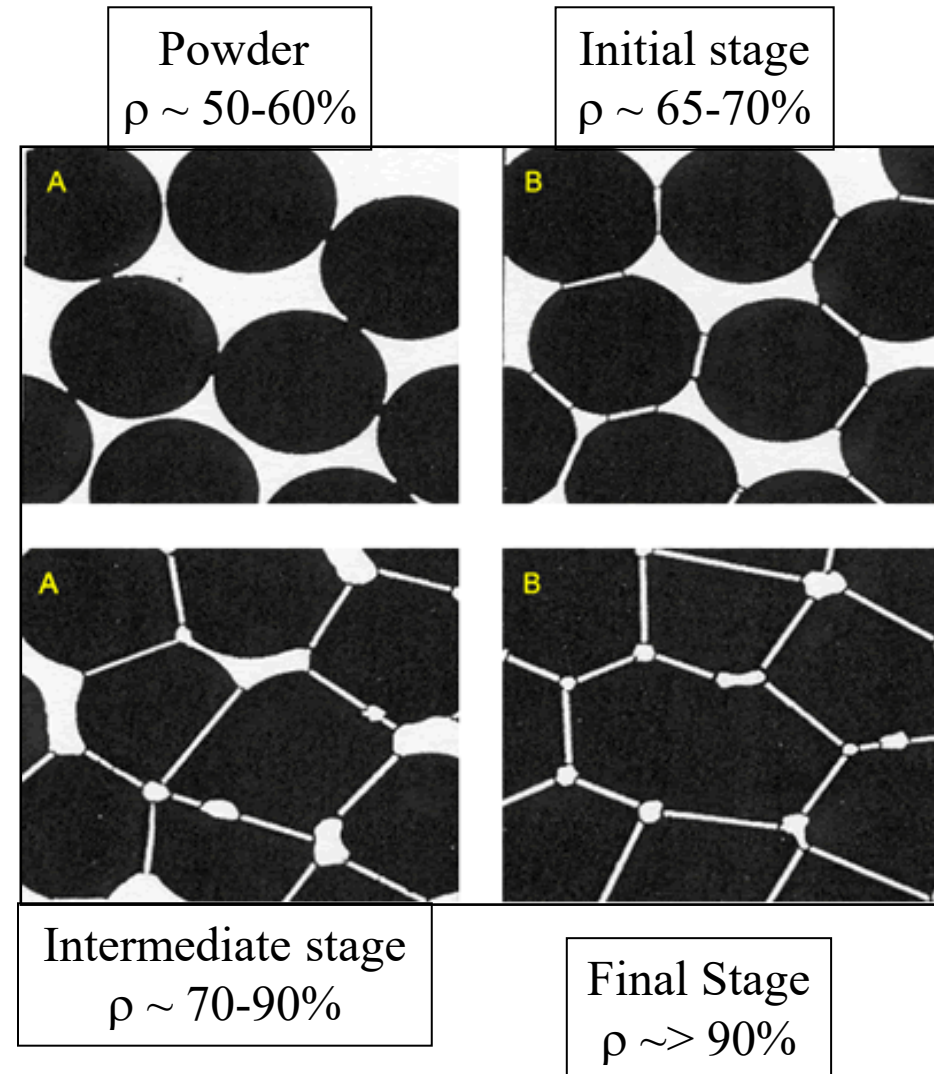
Attrition milled 1hr - slip cast - 99%



FS. Shiau, TT. Fang, TH Leu, Materials Chemistry and Physics, 57, 33-40 (1998).

Current and future technologies dependent on ceramics

- ❖ Dye sensitized solar cells – photocatalysis - *Energy*
- ❖ Water splitting ..Hydrogen for energy... *Energy*
- ❖ Water - purification for drinking...*Sustainability*
- ❖ Li batteries ... *Energy*
- ❖ Solid Oxide Fuel Cell (SOFC) - *Energy*
- ❖ Dental applications, hip replacements... - *Health*
- ❖ Optical applications... *Watch industry...Health...*

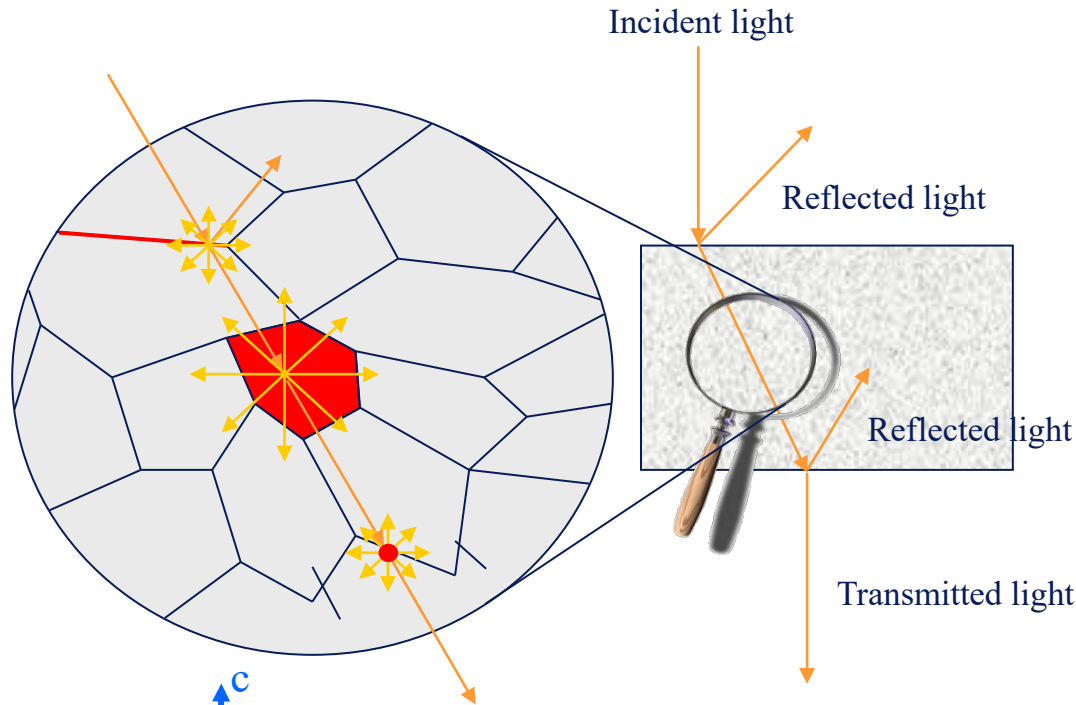


Transparent Polycrystalline Alumina (PCA)

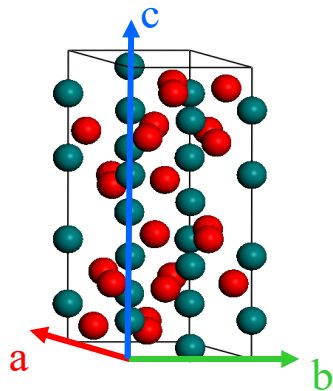
Why is microstructure important? - Example optical properties

PCA

Scattering sources



- Grain boundaries
- Grains themselves
- Sample surfaces
- Pores / precipitates



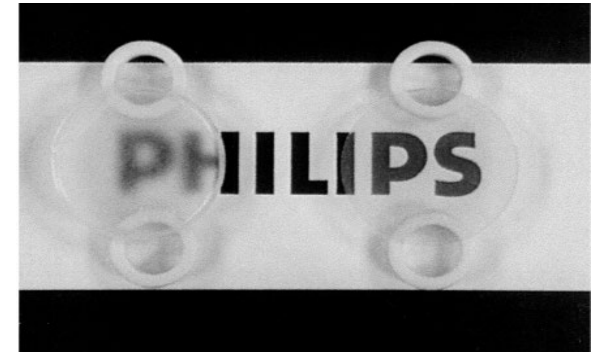
- Hexagonal lattice
 - $n_a = n_b = 1.760$
 - $n_c = 1.768$
- Birefringent



- $\Delta n = [0.0, \Delta n_{\max} = |n_a - n_c|]$
- $\Delta n_{\max} = 0.008$

Transparent Polycrystalline Alumina (PCA)

- Can produce **transparent, hard** ($H V_{10} \geq 20$ GPa): Al_2O_3 *
 - Need grain sizes **<500 nm - fully dense> 99.9%**
- Apetz & van Bruggen *
 - 50-70% **Real – In-line Transmission (RIT)**
 - cf 86% for single crystal Al_2O_3 - sapphire
- Krell[§] **“Careful” colloidal Processing**
- sinter 95% density close porosity - post HIP
- Swiss Watch industry needs > 80%
- Why polycrystalline
 - Easier to shape than sapphire - “hard” work !!
- How can we provide the required microstructures?
 - Reduce grain growth
 - Avoid second phases (dopants) and porosity
 - Can we do it using SPS - can we do it by **dry pressing?**



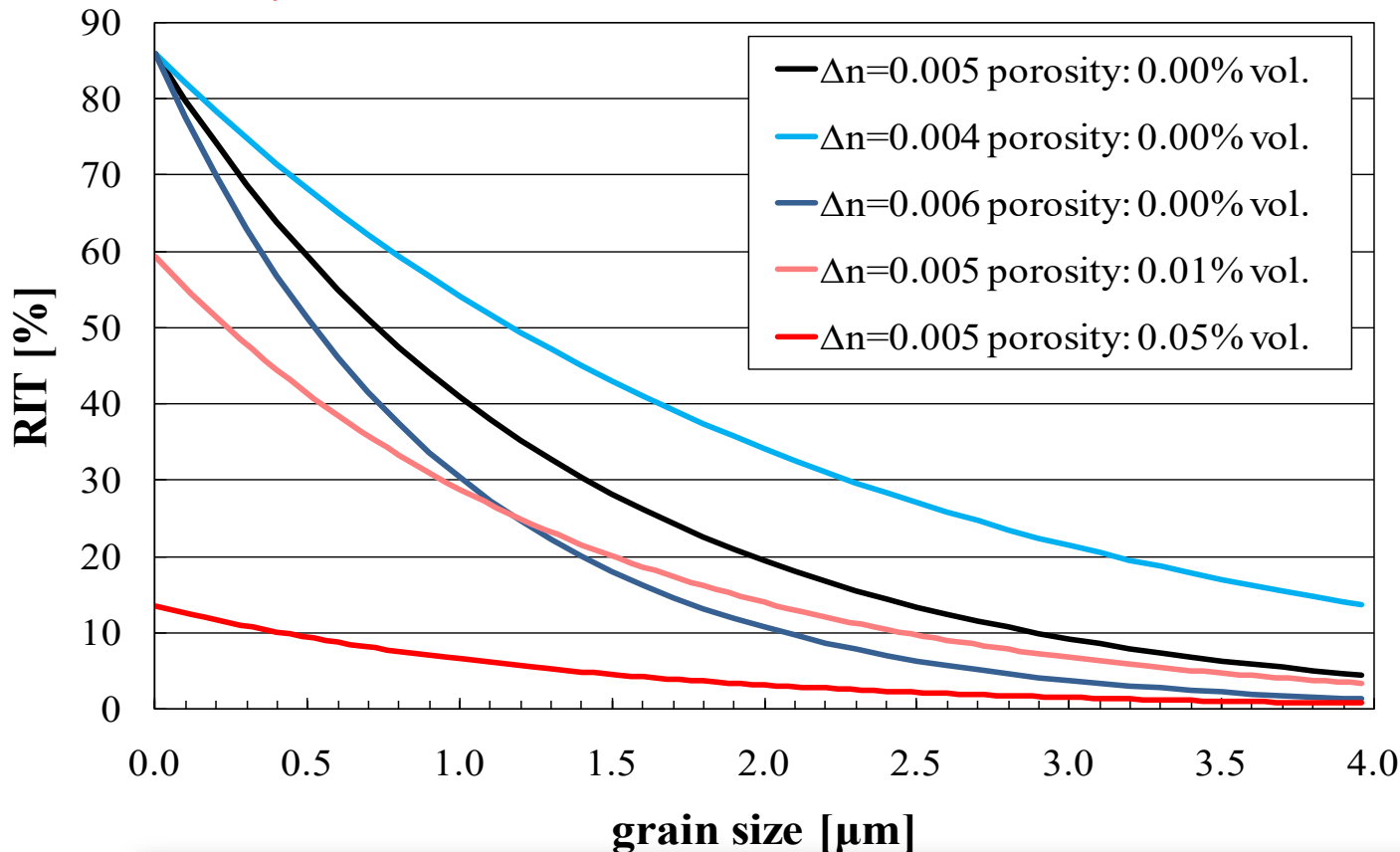
* R. Apetz & MPB van Bruggen, *J. Am Ceram. Soc.* 2003, § A. Krell & J. Klimke *J. Am. Ceram. Soc.* (2006)

Transparent PCA – grain size

Effects of microstructure on RIT

- $\langle \Delta n \rangle$ and porosity affect shape of curve
- Porosity reduces maximum RIT

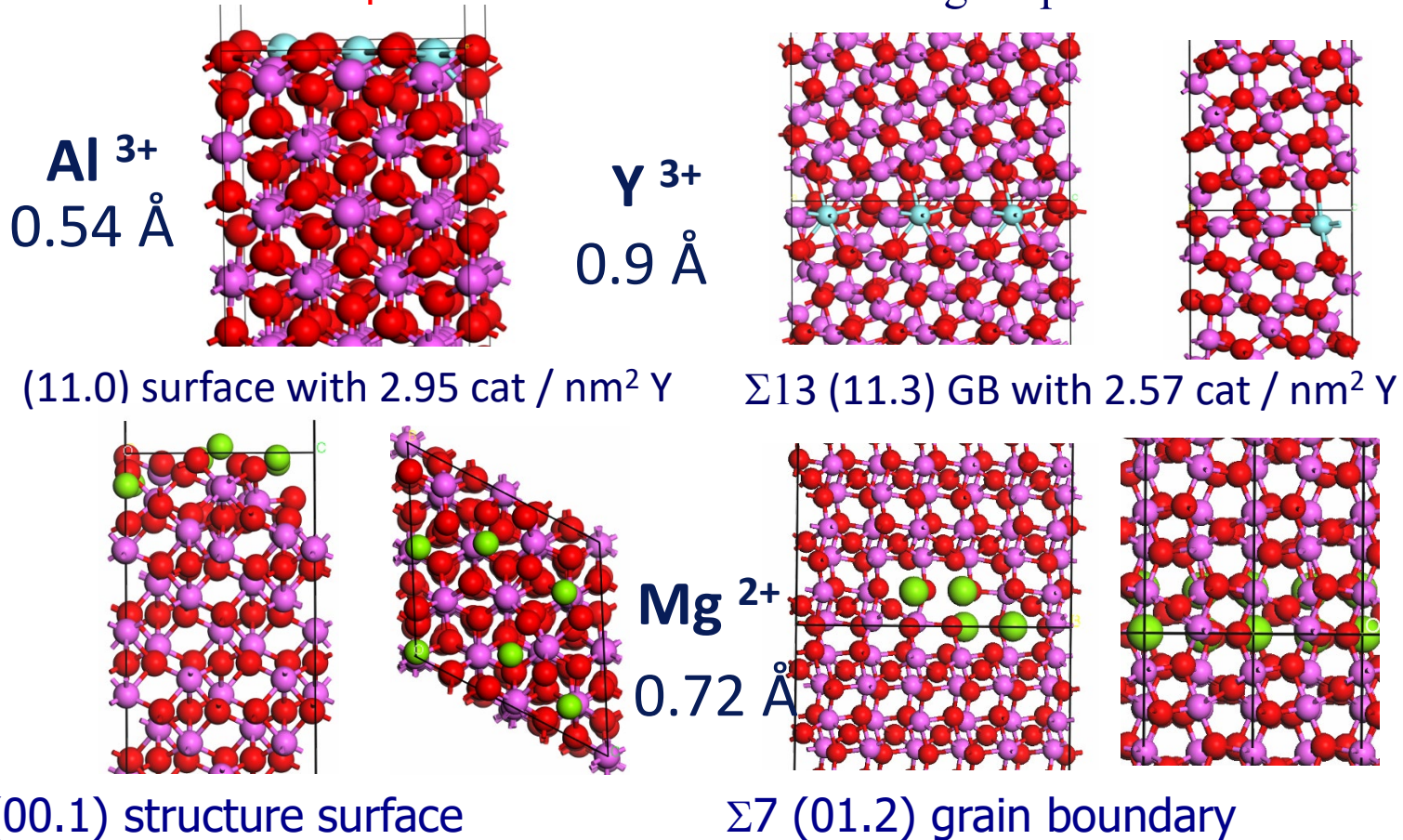
$\lambda = 640$ nm; thickness = 1 mm; pore size = 50 nm



To improve the real in-line transmittance (RIT), - FULL DENSIFICATION +
GRAIN ALIGNMENT AND / OR SMALLER GRAINS

Atomistic View of Grain Boundary

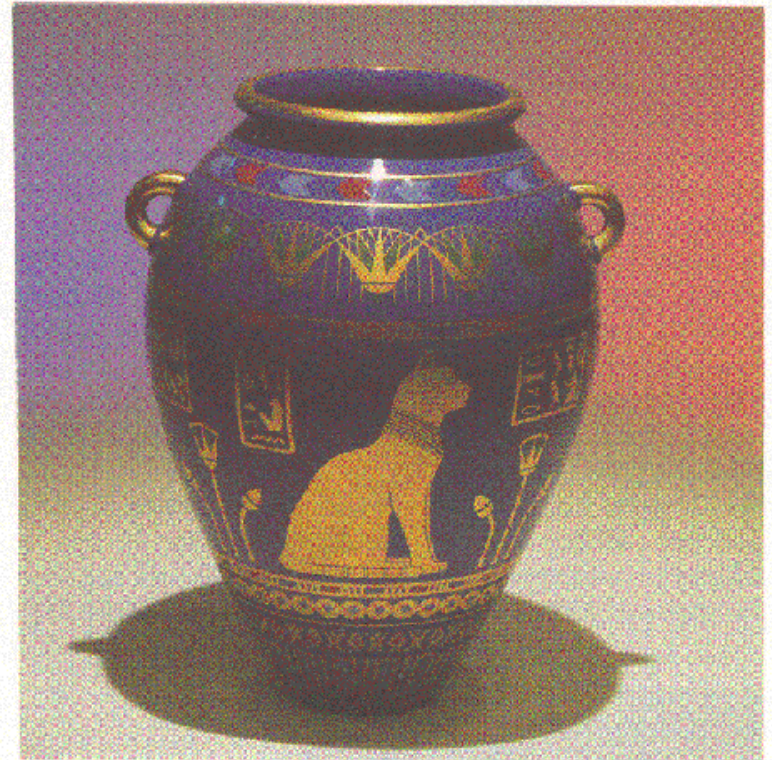
- Dopants used to control microstructure – Y and Mg often used with alumina
- Significant segregation for both ions to surfaces and grain boundaries*
 - **Y often forms patterns** at the interface but Mg no patterns seen



* Galmarini et al - J. Amer. Ceram.Soc -91 [11] 3643 (2008).

History, Examples and Applications

- ◆ The word ceramic comes from the Greek and means clay or earthenware.
- ◆ Clay was used as a raw material for making pottery, bricks and tiles
- ◆ The term **ceramic** more generally means a solid which is **neither** a **metal** nor a **polymer**



- ◆ A **ceramic** is a solid material which often requires heat treatment to develop it

Periodic table and materials

Periodic Table of the Elements

	IA																	0
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	IIIB	IVB	VB	VIB	VII B	— VII —			IB	IIB	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	+Ac	Rf	Ha	Sg	Ns	Hs	Mt	110	111	112	113					

* Lanthanide Series

+ Actinide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

History, Examples and Applications

- ◆ The main qualities of ceramics are their
 - high hardness
 - heat resistance
 - chemical resistance,
- ◆ While their biggest flaw is
 - the fragility – low toughness
- ◆ Strong chemical bonds
- ◆ Oxides mainly ionic
- ◆ Non-oxides mainly covalent
- ◆ High melting points
- ◆ Cannot simply melt and cast
- ◆ **Need forming methods using powders → Powder Technology**



Summary: Primary Bonds

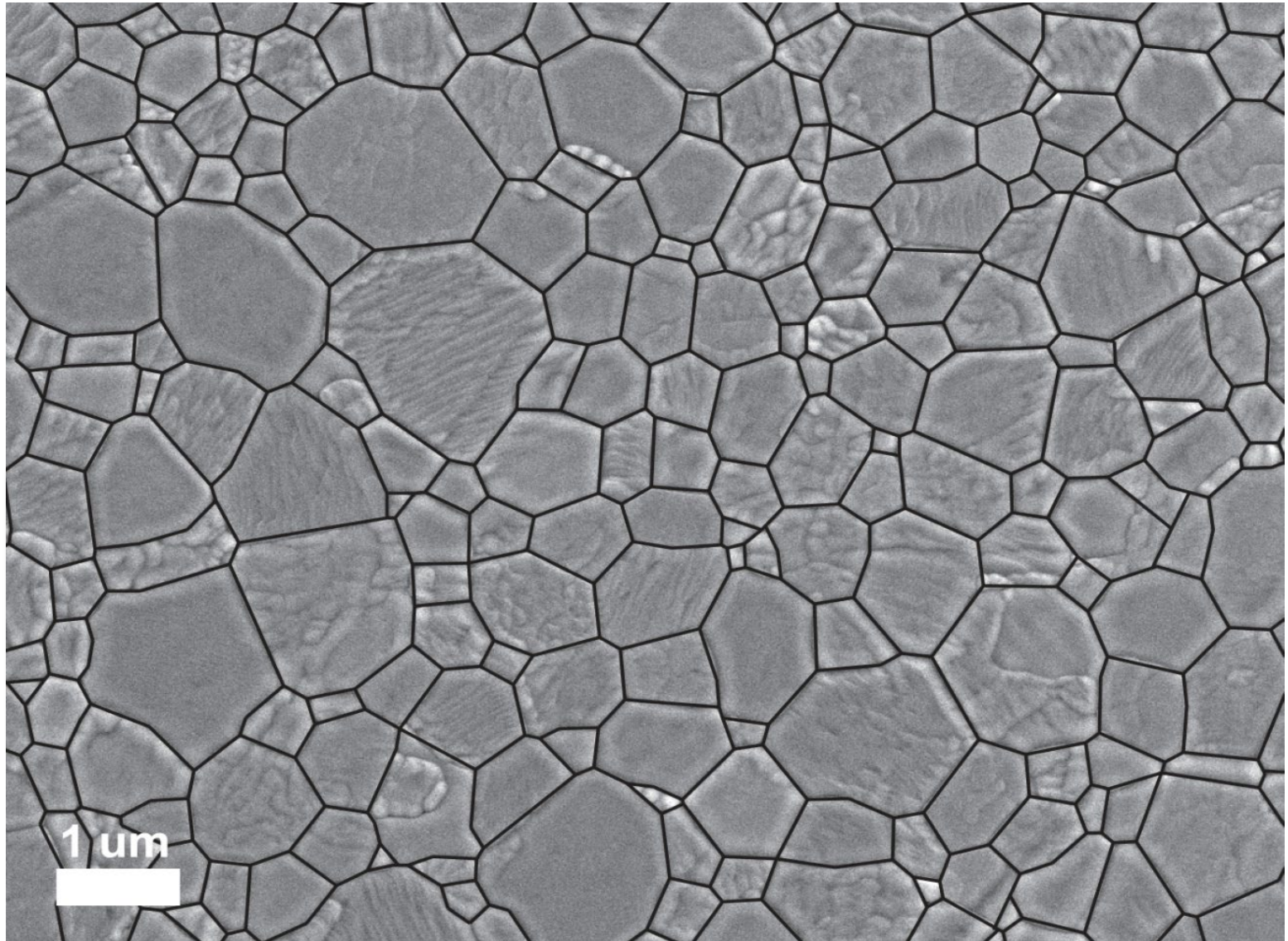
Ceramics
(Ionic & covalent bonding)

Large bond energy
large T_m
large E
small α

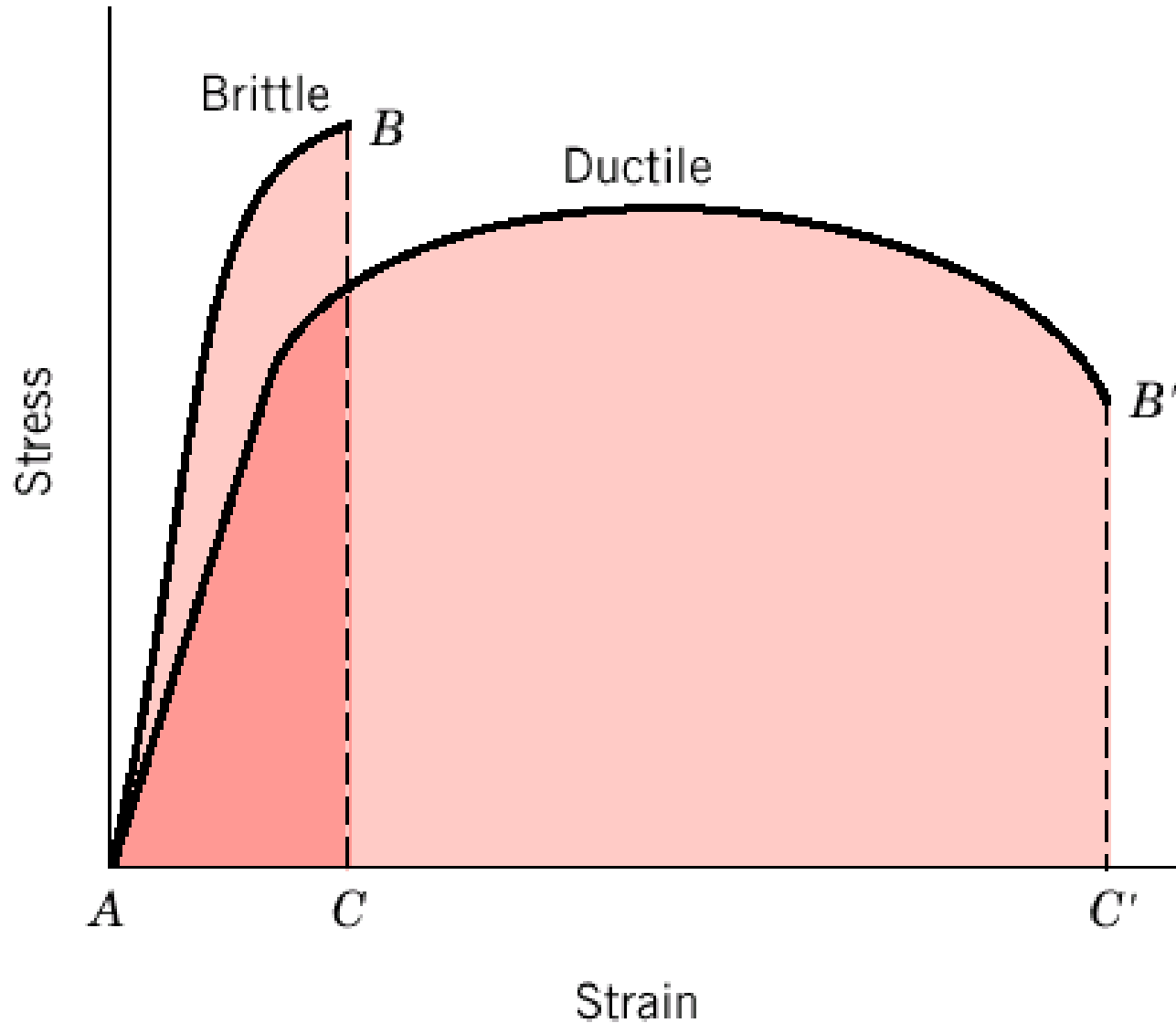
Metals
(Metallic bonding):

Variable bond energy
moderate T_m
moderate E
moderate α

Microstructure - Alumina (Al_2O_3)



Stress – Strain Curve... ceramic brittle... metal ductile



Manufacture of Ceramics - Traditional

Class	Examples	Application
Earthenware	Fired clay	Bricks, tiles, pipes
Traditional	Porcelain	Dishes, sanitary (toilets wash basins), electric isolators
Abrasives-mechanical	Alumina (carborundum), silicon carbide, diamond, zirconia, cermets (WC-Co), nitrides	Cutting tools Abrasive paper, discs Forging bits
Refractory	Magnesia	Metal casting

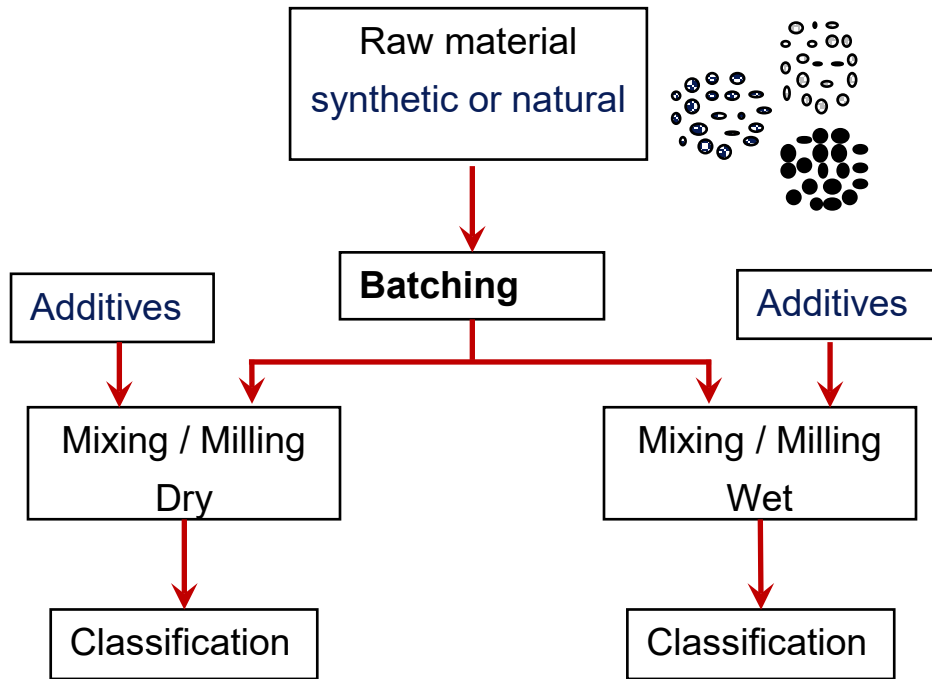


Manufacture of Ceramics - Technical

Class	Examples	Application
Magnetic	Iron oxides, mixed oxides (ferrites)	Motors, communication, energy transfer
Electronic	Barium titanate	Capacitors
	Strontium titanate	Sensors
	Mixed titanates-zirconates (PZT)	piezoelectrics
	Zirconia	Ionic conductor
	Zinc oxide	Varistor
Bioceramics	Procelaine	Insulator (electrical)
	Calcium phosphates	Cements, bone replacment
	Alumina	Structural protheses (hips joints)



Ceramic Processing – 1 - Powders



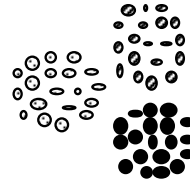
- ❖ Commercial powders, often modified for application
- ❖ milling step in order to break up the agglomerates,
- ❖ Synthesized by solid route or by precipitation
- ❖ Different types of equipment - practical aspects and some scientific principles

- **known** chemical purity,
- good reactivity
(size $\sim 1 \mu\text{m}$ and specific surface $\sim 5\text{-}15 \text{ m}^2/\text{g}$) and
- good homogeneity - physical and chemical.

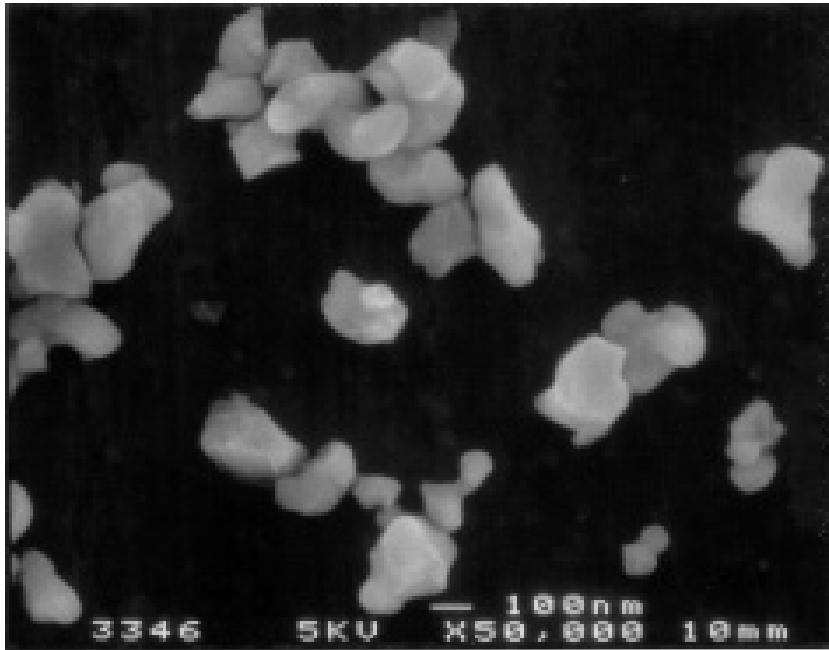
Ceramic Processing - Powders (2)

Raw materials

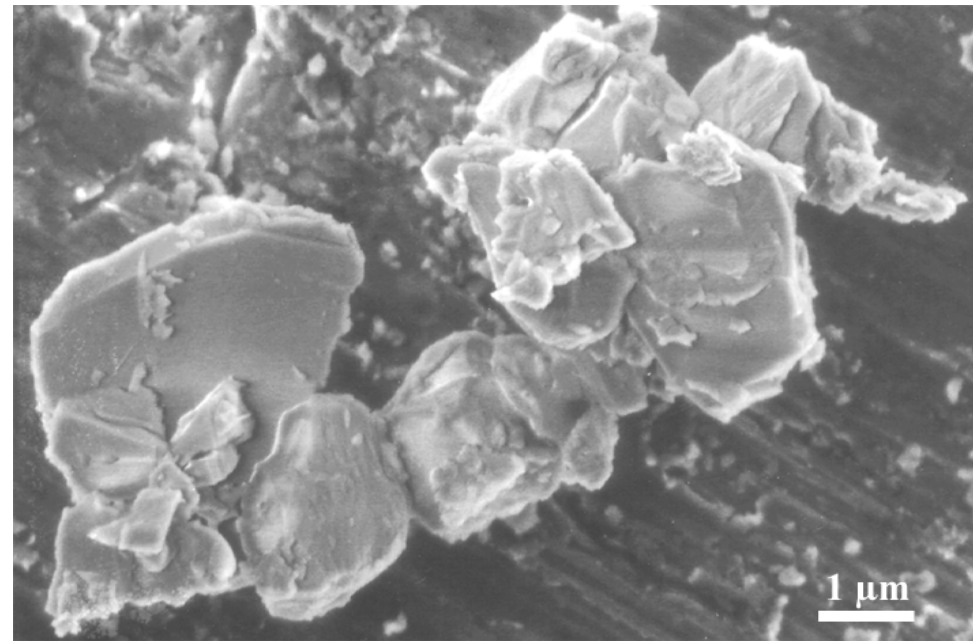
Raw material
synthetic or natural



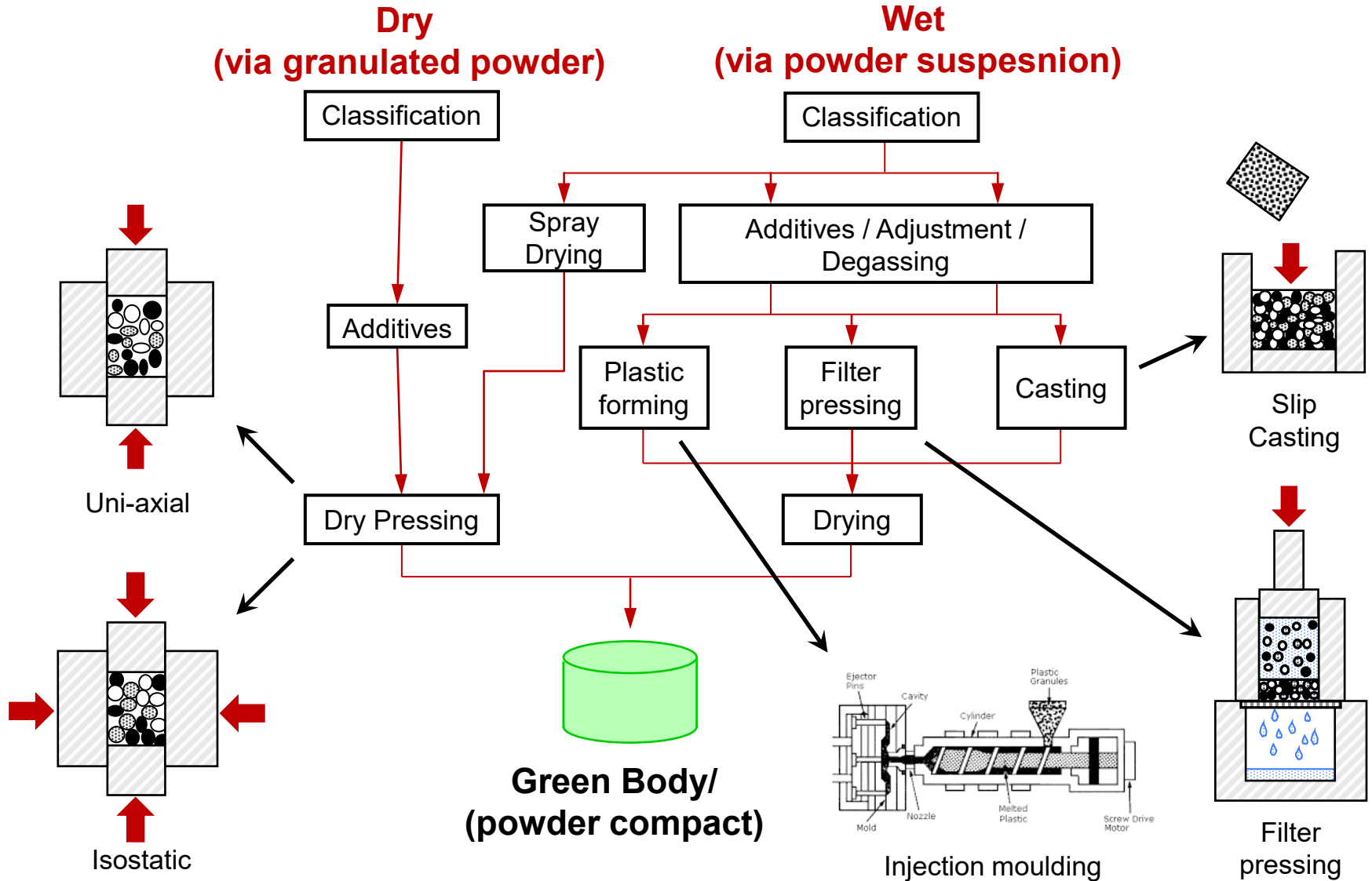
(a) *alumina powder – technical ceramic – synthetic powder*



(b) *feldspar powder – traditional ceramics – natural powder*

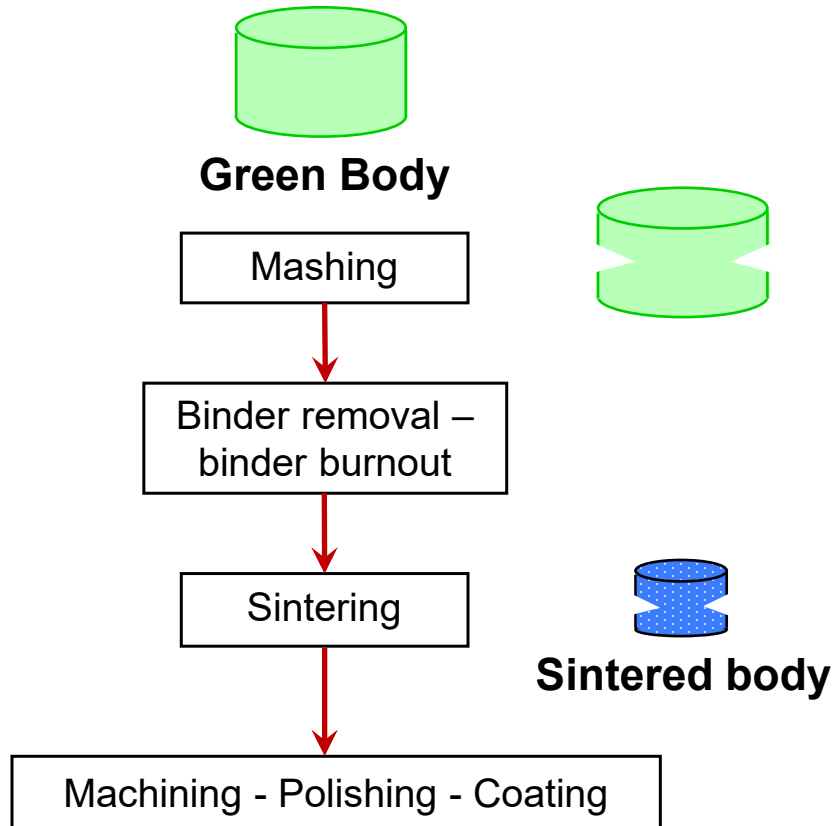


Manufacture of Ceramics - Ceramic Processing

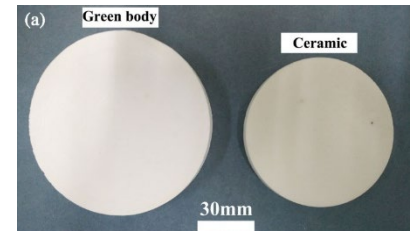


Manufacture of Ceramics - Ceramic Processing - Firing

◆ Sintering (firing) and Finishing



Source: ceramicartsdaily.org



Gan et al. DOI:10.1002/app.48889



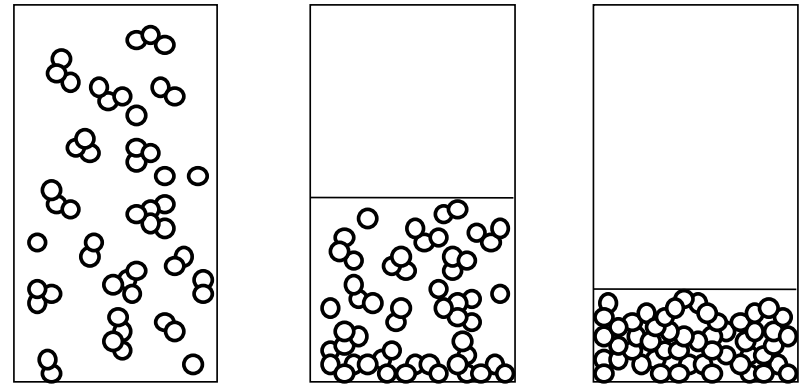
© CeramTec

Powder Suspensions – Interparticular Forces

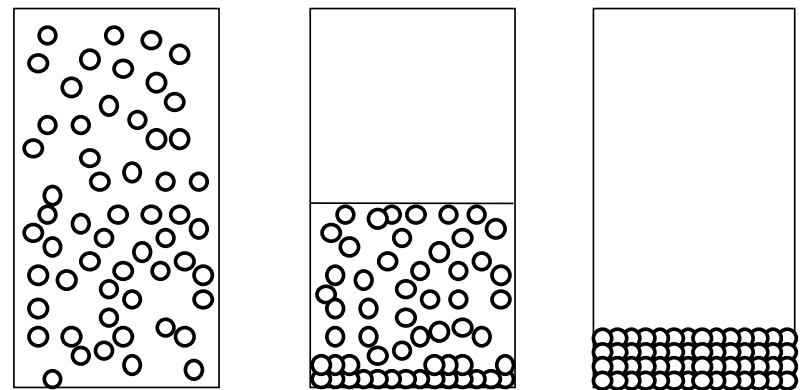
◆ Suspension

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

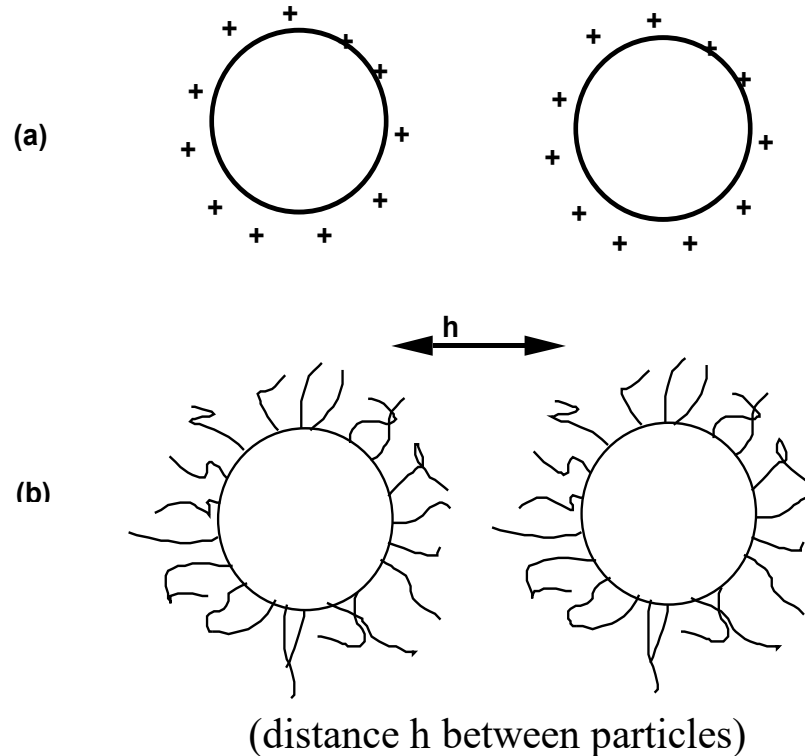
◆ Attractive

Van der Waals forces

◆ Repulsive

(a) electrostatic,

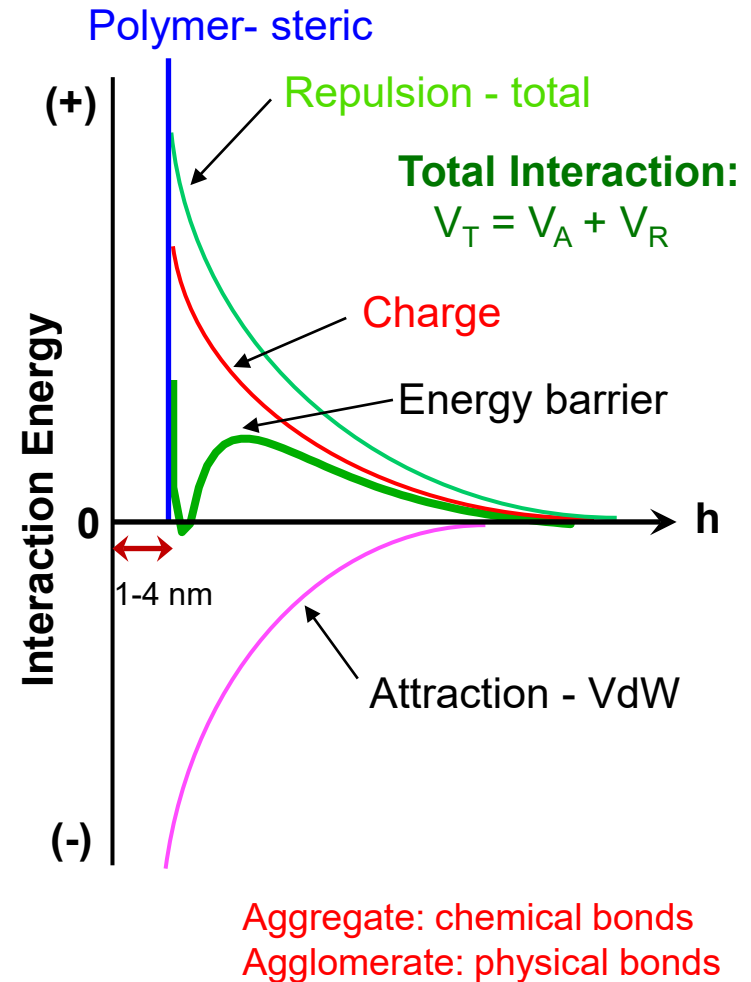
(b) soluble polymers - steric
polymer adsorption



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

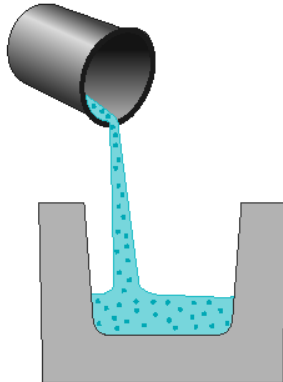
Overall Interaction Energy

- ◆ 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

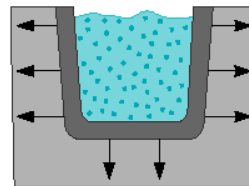


Slip casting – large complex shapes

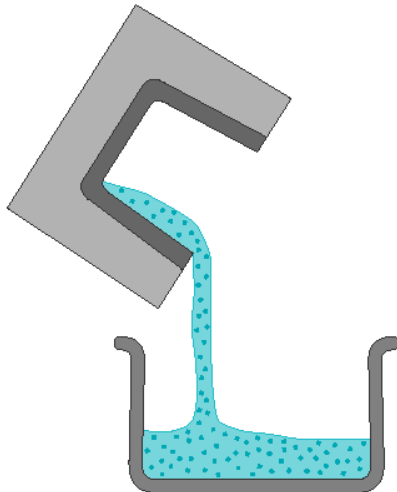
Slip = concentrated suspension



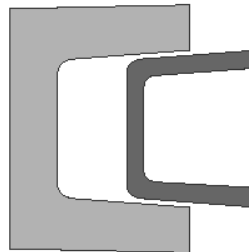
(a)
Fill mold with slip



(b)
Mold extracts liquid, forms compact along mold walls



(c)
Excess slip drained



(d)
Casting removed after partial drying



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

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

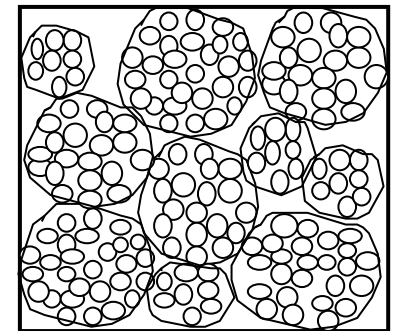
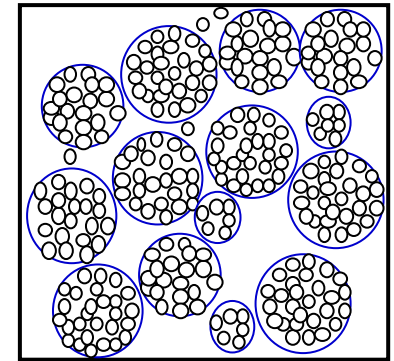
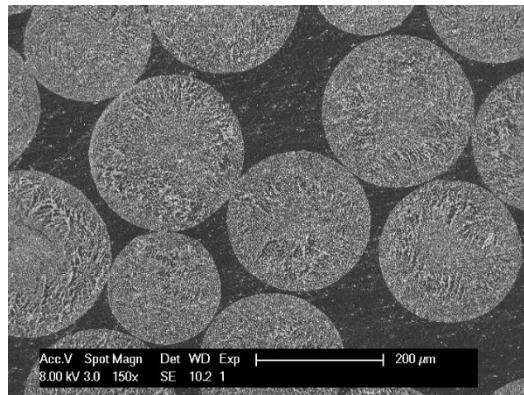
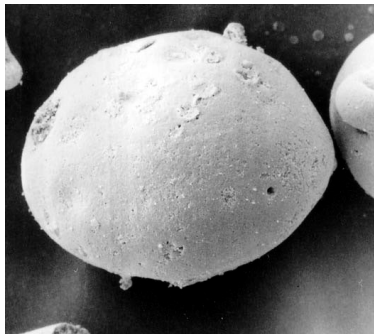
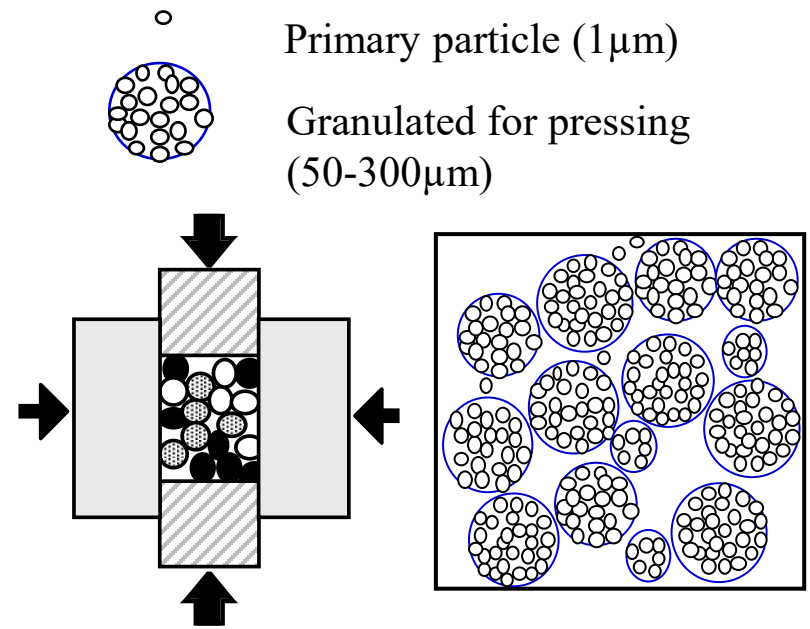
Dry pressing – small simple geometries

◆ Pressing of **spray dried granules**

effects of powder parameters on green compact density

◆ Compaction 3 stages

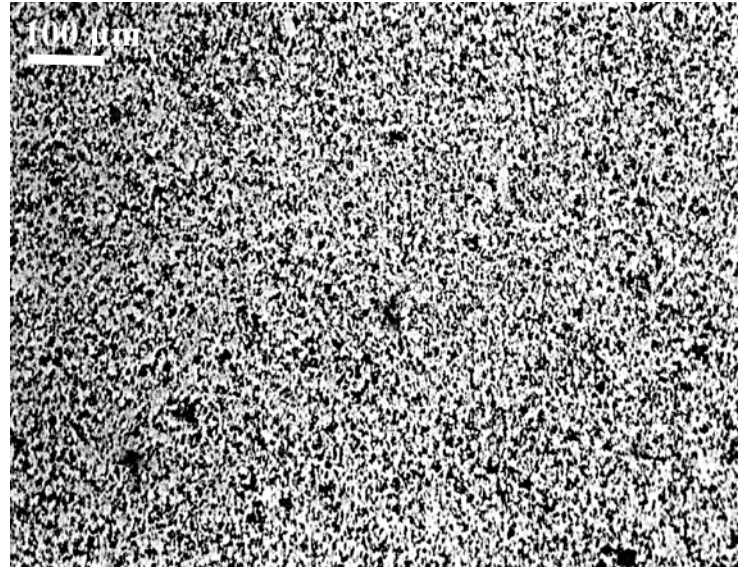
- Rearrangement
- Deformation of granules
- Fracture of granules
(rarely reached in practice)



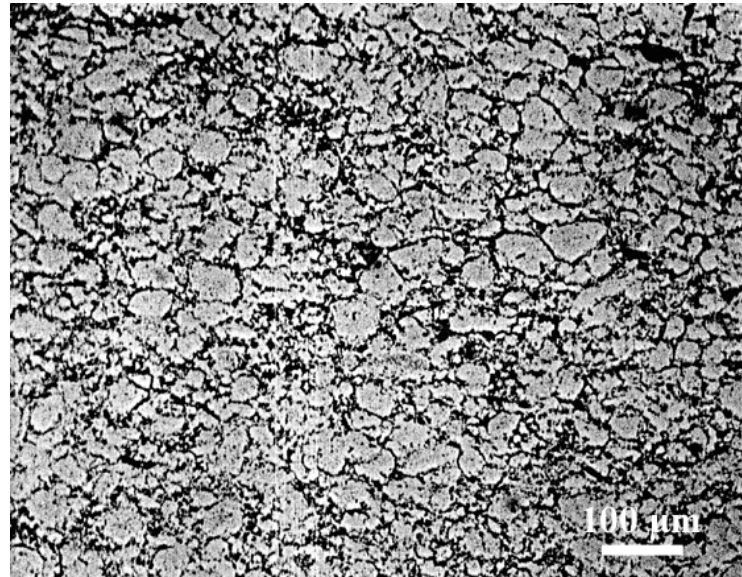
Shaping and microstructures

(c) Cermets - $\text{TiCN-Ni-Mo}_2\text{C-Al}_2\text{O}_3$

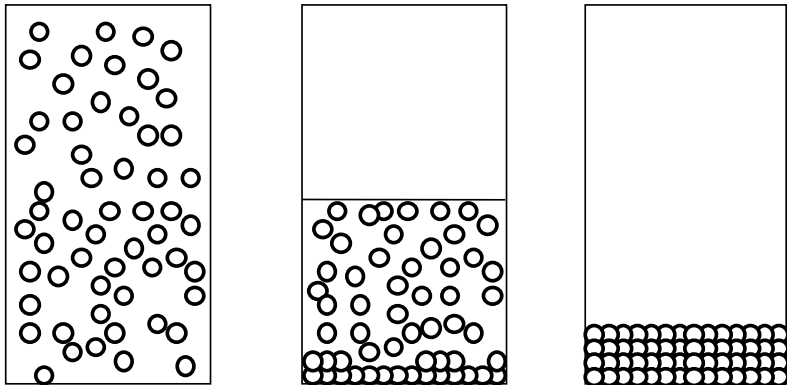
- wet forming, e.g. filter pressing
- without production of hard granules or agglomerates
- more homogeneous microstructure
- c.f. dry pressing with « poor » hard granules...need additives



Wet
Homogeneous
microstructure

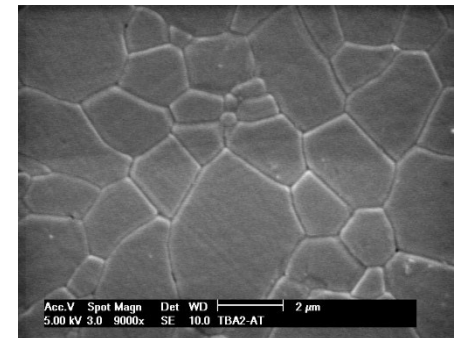
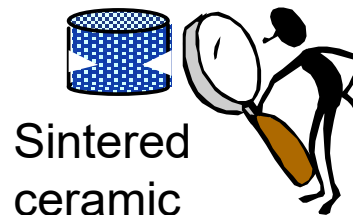
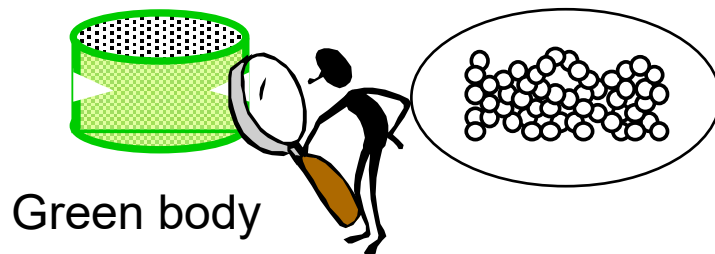


Dry pressing
Hard granules –
inhomogeneous
microstructure



Sintering and Control of Microstructures

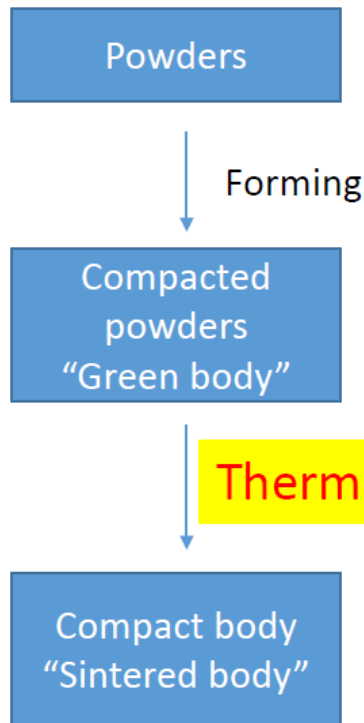
1. Sintering fundamentals
2. Solid state sintering
3. Grain growth & microstructure
4. Liquid phase sintering
5. Examples and practice



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:

1. Sintering: fundamentals

Curvature of the particle (overall surface)

External applied pressure (external applied fields)

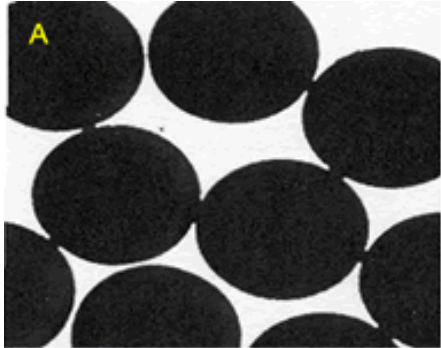
Chemical reactions (within the solid or with a gas phase)

Types of sintering

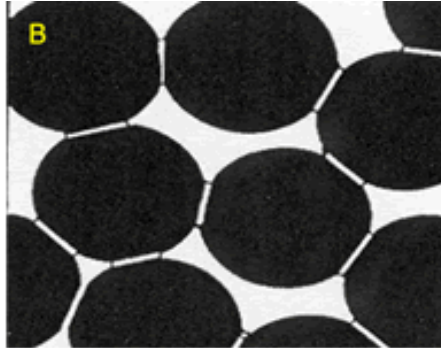
- ◆ Generally, there are three **types** sintering:
- ◆ ***in solid phase***: all constituents **remain in solid state** throughout sintering. Densification involves a **grain shape change**. The transport of matter mainly occurs **by diffusion** in solid phase and at grain boundaries.
- ◆ Temperatures between 0.5 and 0.8 of 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.

Idealised models for the different stages of sintering

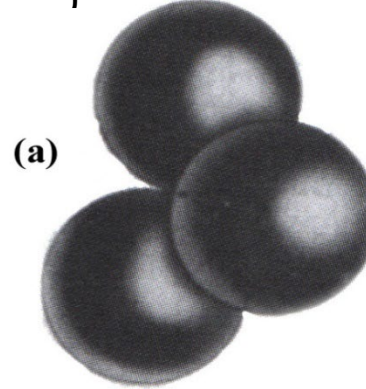
Powder
 $\rho \sim 50-60\%$



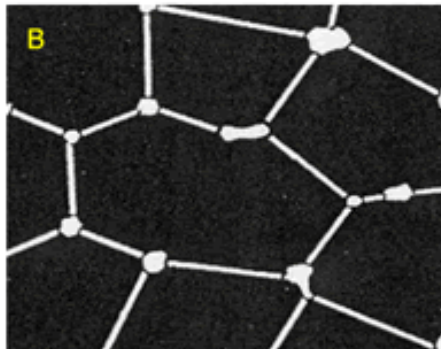
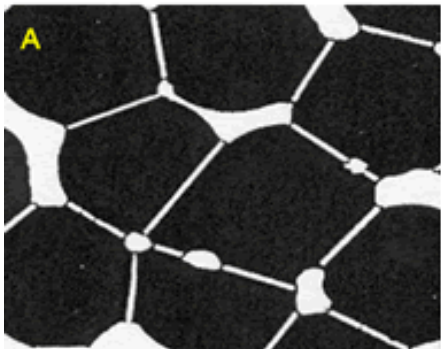
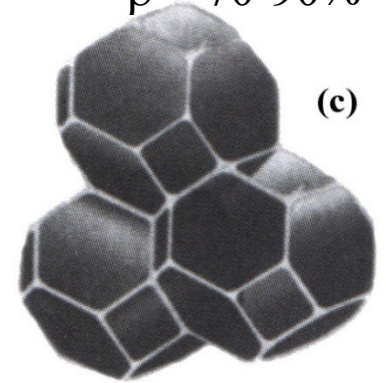
Initial stage
 $\rho \sim 65-70\%$



Powder
 $\rho \sim 50-60\%$

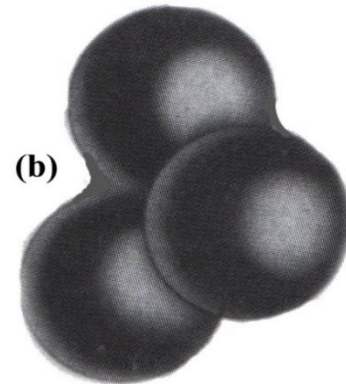


Intermediate stage
 $\rho \sim 70-90\%$

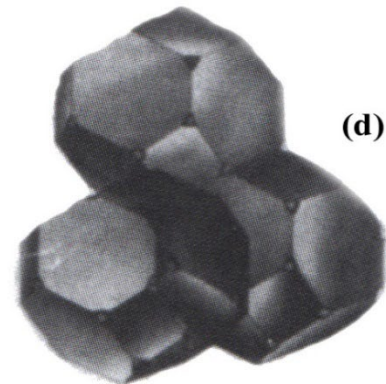


Intermediate stage
 $\rho \sim 70-90\%$

Final Stage
 $\rho \sim > 90\%$



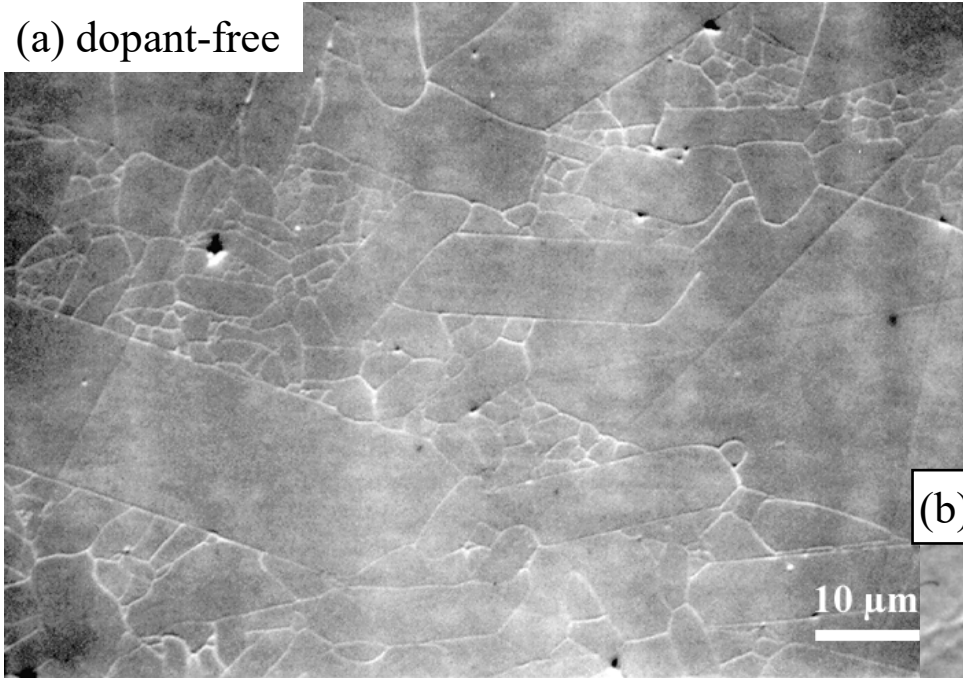
Initial stage
 $\rho \sim 65-70\%$



Final Stage
 $\rho \sim > 90\%$

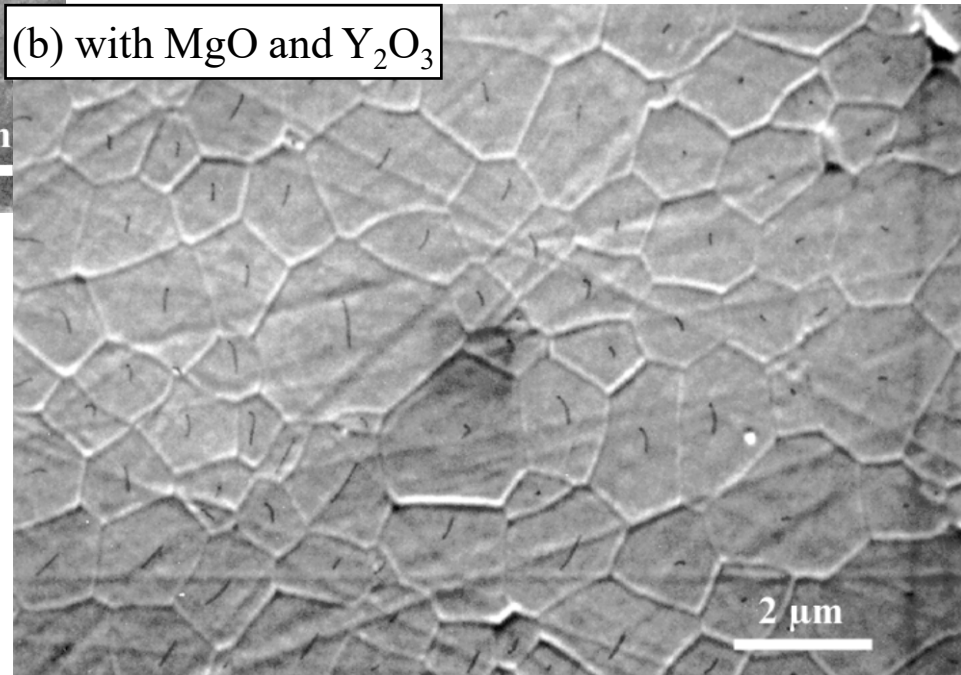
Microstructures - Alumina micrographs

(a) dopant-free

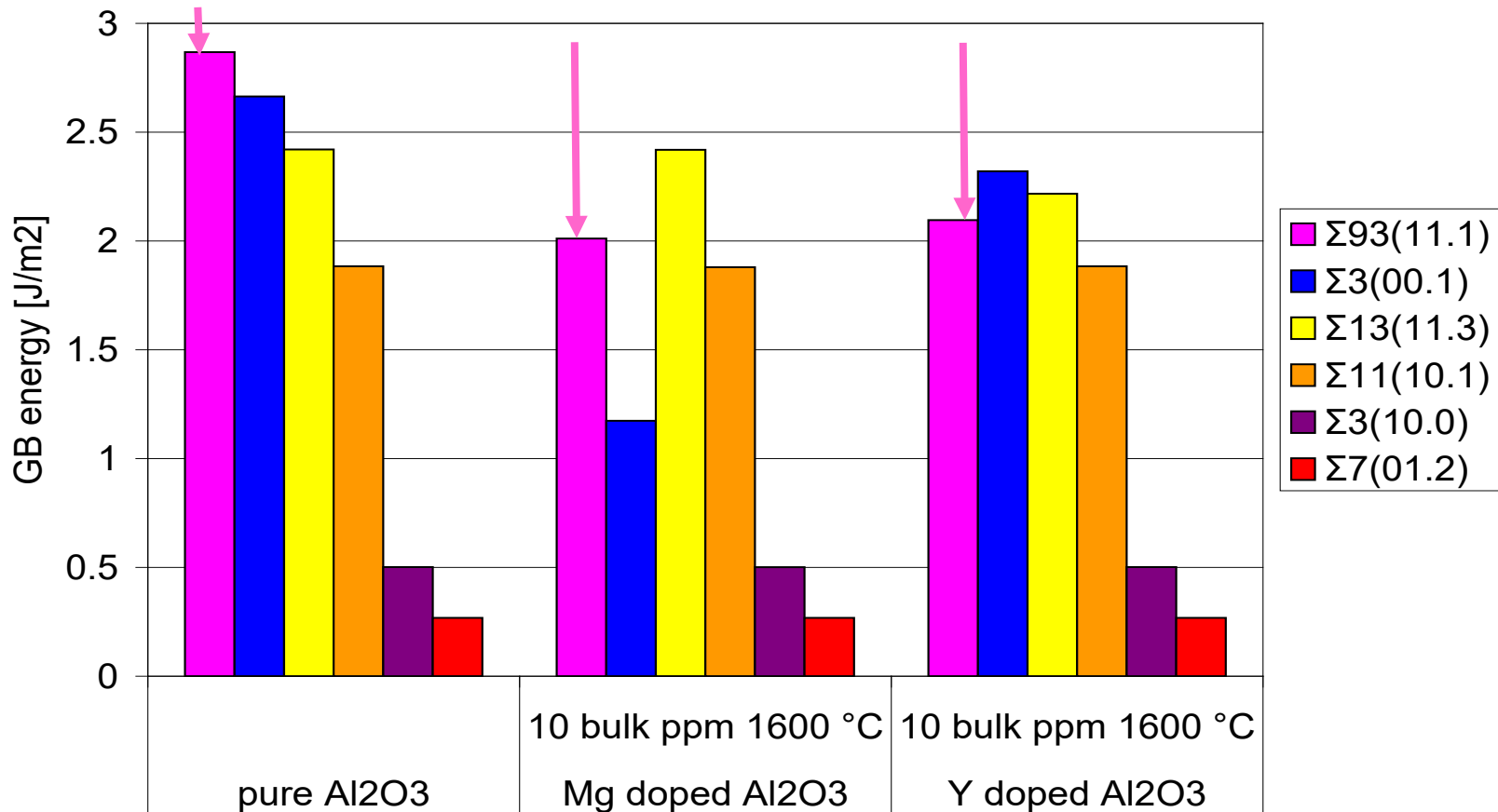


- Shows the effect of additives e.g. dopants (or impurities)
- On the microstructure and consequently on the properties of a sintered ceramic

(b) with MgO and Y₂O₃



Grain Boundary Energies



- Y and Mg have a tendency to **stabilizes high energy interfaces**
- **Stabilization** of high energy grain boundaries - driving force for grain growth - (GB energy) influenced – generally reduced

Finishing -polishing

- ◆ A final finishing step is often necessary to ensure the workpiece dimensions or e.g. the sphericity of engine bearings.
- ◆ Diamond tools are often needed as ceramics are very hard.
- ◆ E.g. ceramic knife video
- ◆ <https://www.azom.com/materials-video-details.aspx?VidID=386>
- ◆ For ceramics without a glaze or coating there is often a polishing step
- ◆ It makes the part more attractive visually and removes surface defects from which a crack can start - this can lead to an improvement of the mechanical properties ... Up to x3!
- ◆ Polishing often made with diamond suspensions or pastes



Hip joints

Learning Outcomes and questions

◆ **Acquired knowledge**

- Main properties of ceramics
- Overview of steps in ceramic processing : from powders through powder compacts (green bodies) to a sintered ceramic
- General areas of ceramic applications

◆ **Questions** (more in-depth questions in exercises)

- Why is the powder technology route the main processing route for ceramics?
- What are the strengths and weaknesses of typical ceramics?

Exam

- ◆ Oral in January exam session
- ◆ 15 min
- ◆ No preparation
- ◆ No notes etc.
- ◆ More information – Week 7
- ◆ Final grade, including plusses
- ◆ Exam: course, exercises, guest lectures

Production examples - ceramic tiles

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



Gayofores ceramic tiles

◆ <https://www.youtube.com/watch?v=8hw4SrG0Zuc>