MSE 160 – Ceramic synthesis and characterization

MSE 160 class page: bowmanlab.eng.uci.edu/class

Lab reports

Experimental methods section should be specific to your experiment, not a copy/paste from the manual

Lecture outline

Outline

- Ceramic synthesis
  - Sol-gel synthesis
  - Powder processing

Sol-gel (Solution-Gelation) Synthesis of Materials

Outline

Introduction

Liquid phase synthesis of nanoparticles

Sol-gel chemistry for ceramics

Application of sol-gel process

Liquid phase synthesis of nanoparticles

Major categories

1. Colloidal methods
2. Sol-gel processing
3. water-oil microemulsions
4. hydrothermal syntheses
5. polyol method

Precipitating nanoparticles from a solution of chemical compounds

Solution precipitation relies on the precipitation of nanometer-sized particles within a continuous fluid solvent.

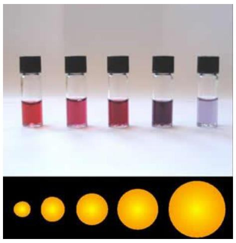
An inorganic metal salt, such as chloride, nitride and so on, is dissolved in water. Metal cations exist in the form of metal hydrate species, for example, $Al(H_2O)^{3+}$ or $Fe[(H_2O)_6]^{3+}$. These hydrates are added with basic solutions, such as NaOH or Na_4OH. The hydrolyzed species condense and are then washed, filtered, dried and calcined in order to obtain the final product.

Colloidal methods

Wet chemistry processes where different ions are mixed to form insoluble precipitates

Used to produce **metals, metal oxides, organics, and pharmaceuticals**.

Au suspensions



Basic principles of colloidal preparation were known since antiquity. E.g. gold colloids used for high quality red and purple stained glass from medieval times to date. However, proper scientific investigations of colloidal preparation methods started only in 1857 when Faraday has published results of his experiments with gold.

Sol-gel (Solution-Gelation) technique

“Sol”
colloidal solution made of solid particles few hundred nm in diameter, suspended in a liquid phase.

“Gel”
a solid macromolecule immersed in a solvent, formed by cross linking.

Sol-gel (Solution-Gelation) technique

Simple process and at relatively low process cost.

T**ransformation of a liquid into a gel state,** with post-treatment and transition into solid oxide material

High purity and uniform nanostructure achievable at low temperatures.

“Sol”
colloidal solution made of solid particles few hundred nm in diameter, suspended in a liquid phase.

“Gel”
a solid macromolecule immersed in a solvent, formed by cross linking.

Sol-gel for ceramics

Synthesis of ceramic materials of **high purity and homogeneity** without fusion of oxides (solid state synthesis).

Process occurs in liquid solution. **Hydrolysis and condensation** reactions create a new phase (the sol).

Metal alkoxide $M\text{-}O\text{-}R + H_2O \rightarrow M\text{-}OH + R\text{-}OH$ (hydrolysis)

What is “R”?

(M = Si, Zr, Ti)

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What is “R”?

R = alkyl group (e.g. $(CH_3)^-$, $(C_2H_5)^-$, $(CF_3)^-$, etc.)

(M = Si, Zr, Ti)

Sol-gel for ceramics

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M-O-R + H_2O → M-OH + R-OH (hydrolysis)

M-OH + HO-M → M-O-M + H_2O (water condensation)

(M = Si, Zr, Ti)

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M-OH + HO-M → M-O-M + H_2O (water condensation)

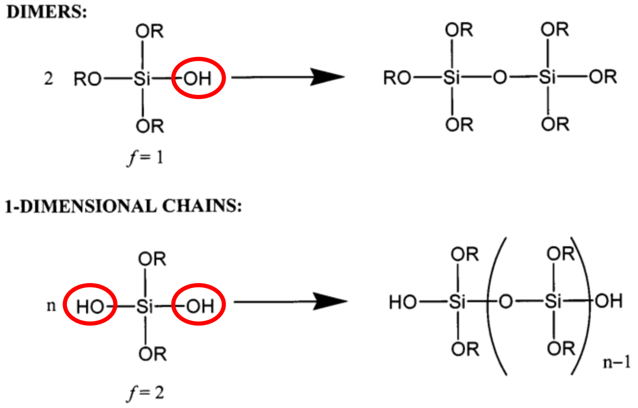
M-O-R + HO-M → M-O-M + R-OH (alcohol condensation)

(M = Si, Zr, Ti)

Sol-gel for ceramics – controlling the product

Hydrolysis of the alkoxide precursor strongly influences the structure of the M-O-M network (e.g. Si - O - Si).

Because **OH^- is a marginally better leaving group than -OR**, the condensation process can be tailored to favor the formation of dimers, chains, or 3-D agglomerates



Sol-gel for ceramics – controlling the product

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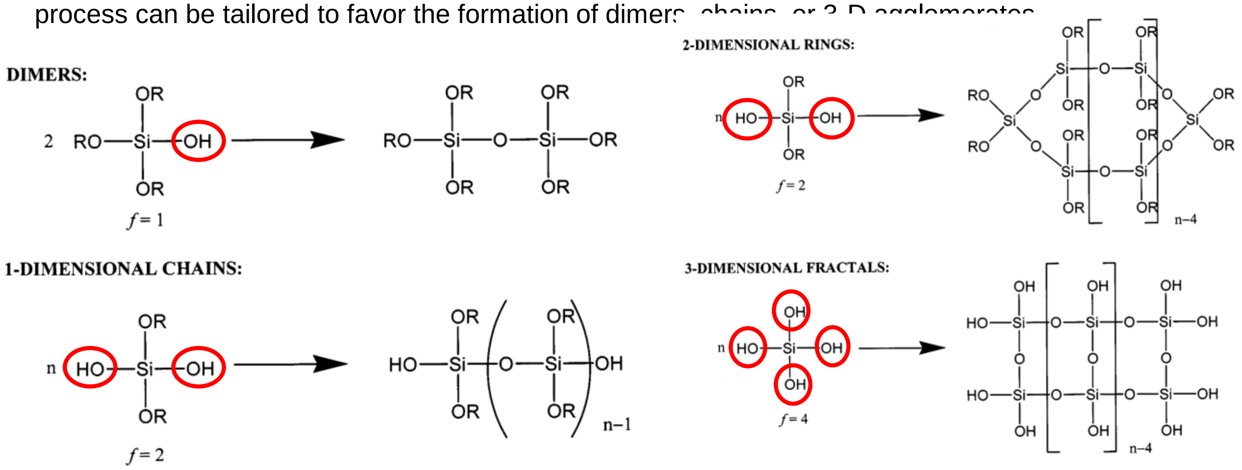
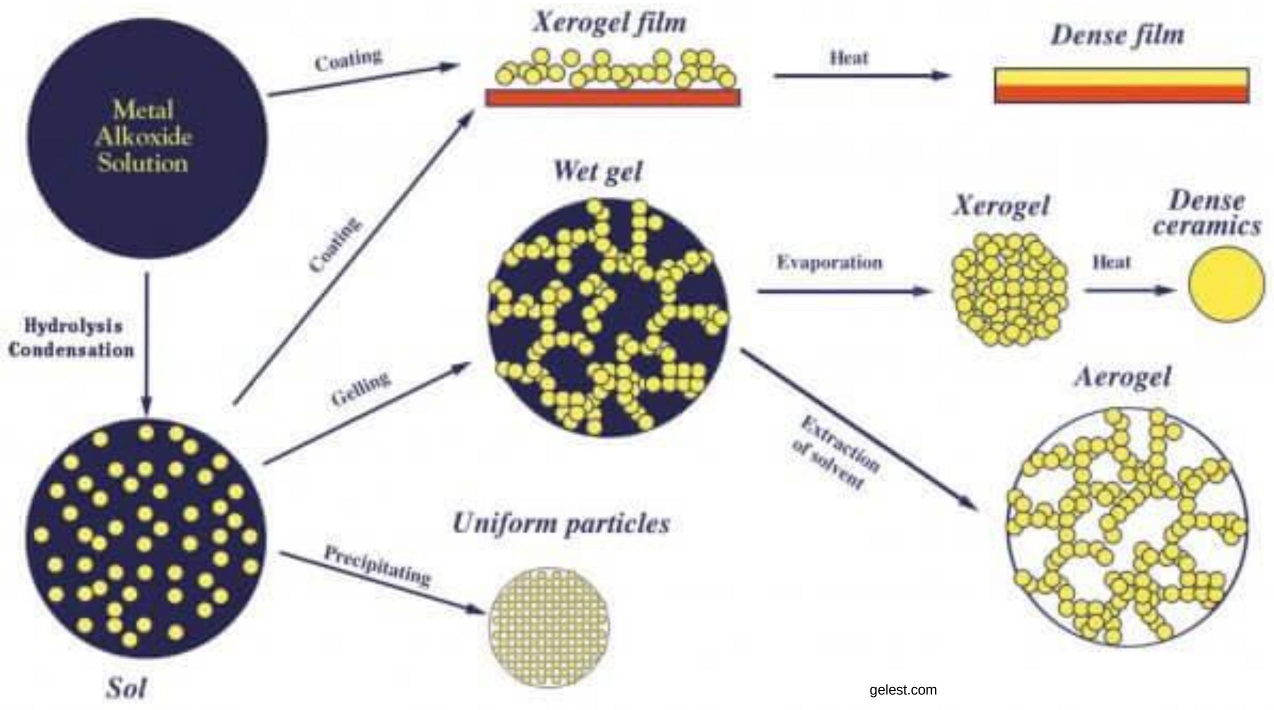
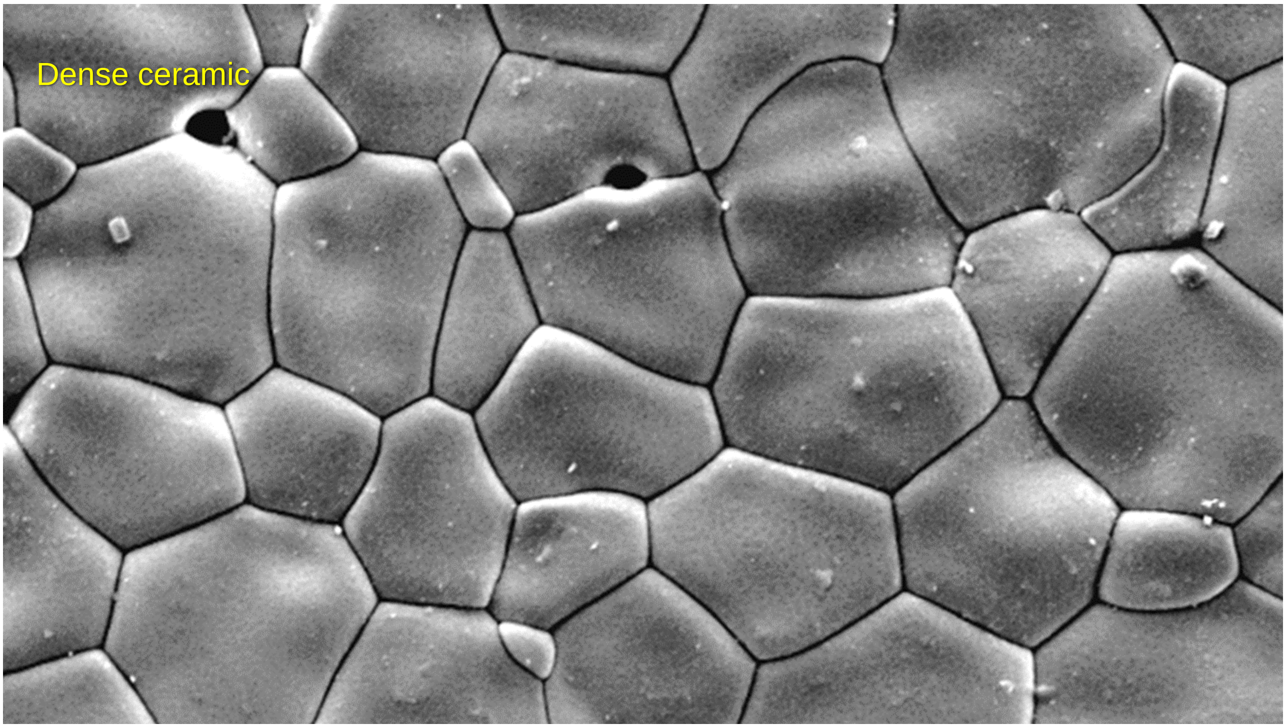
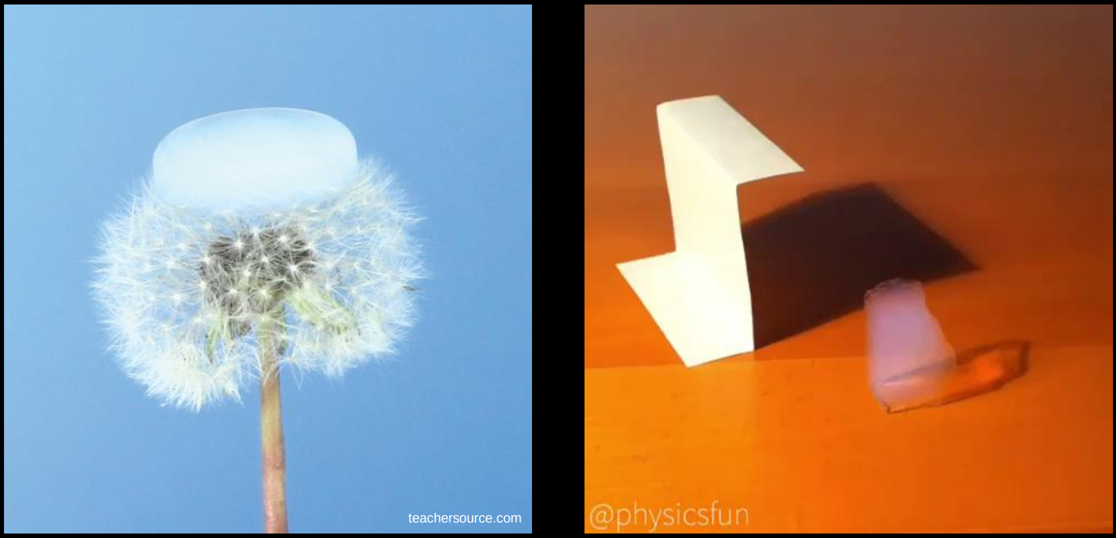



Metal Alkoxide Solution
Coating
Xerogel film
Heat
Dense film
Coating
Wet gel
Xerogel
Dense ceramics
Evaporation
Heat
Hydrolysis Condensation
Gelling
Aerogel
Extraction of solvent
Uniform particles
Precipitating
Sol

gelest.com


Dense ceramic

Aerogel – solvent replaced by gas



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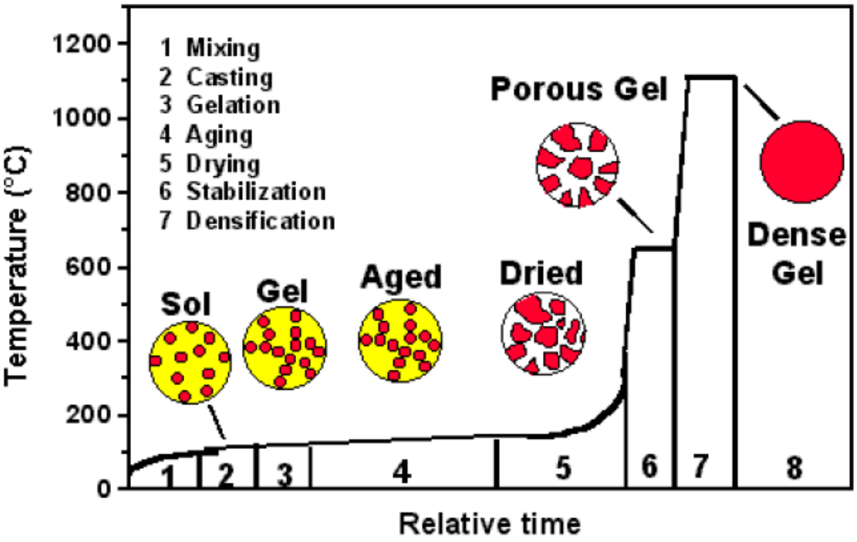
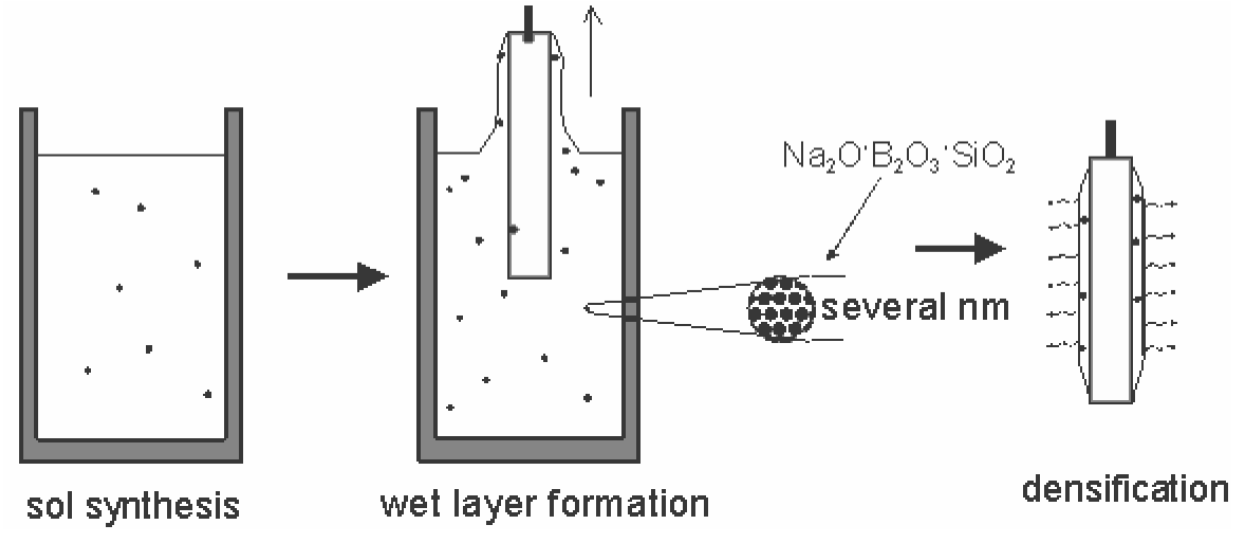
Possible to generate ceramic precursors at low temperature

Gel glass processing sequence



Common application - fabrication of coatings and films

Dip coating process



Common application - fabrication of coatings and films

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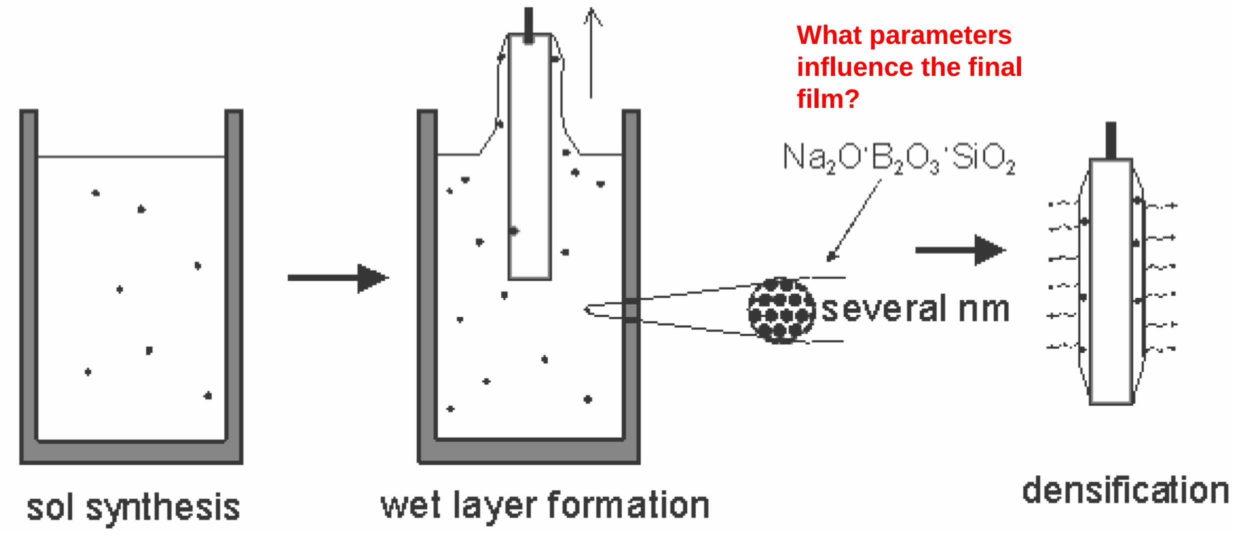
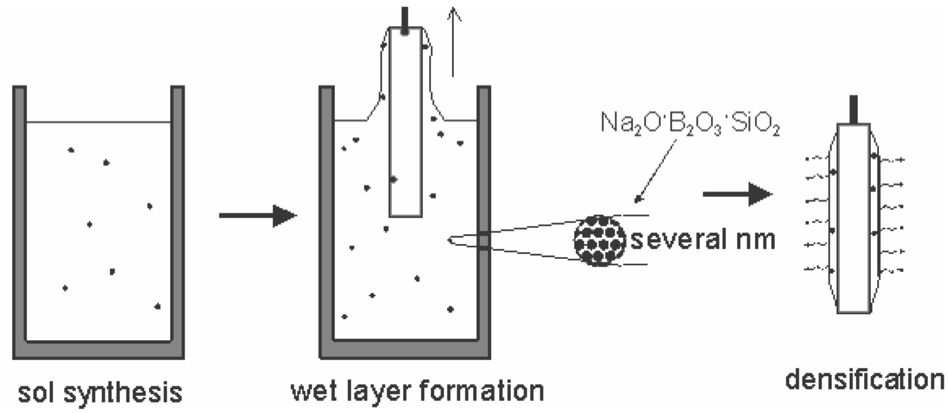


What parameters influence the final film?

Common application - fabrication of coatings and films

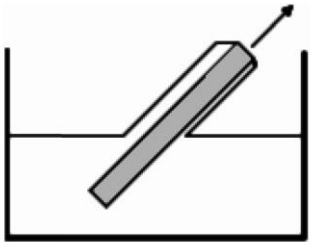


Dip coating process
Substrate is immersed in a sol and withdrawn with well-defined speed under controlled temperature and atmospheric conditions. The sol forms a film with thickness mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid. Gelation (densification) of the layer occurs by solvent evaporation, and finally annealing (heating) yields the oxide coating.

Common application - fabrication of coatings and films

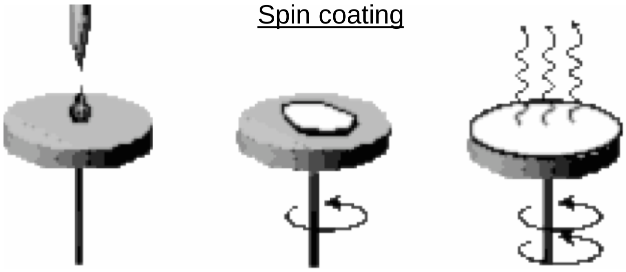
Angle-dependent dip coating
Coating thickness depends on the angle between the substrate and the liquid surface

Angle-dependent dip coating

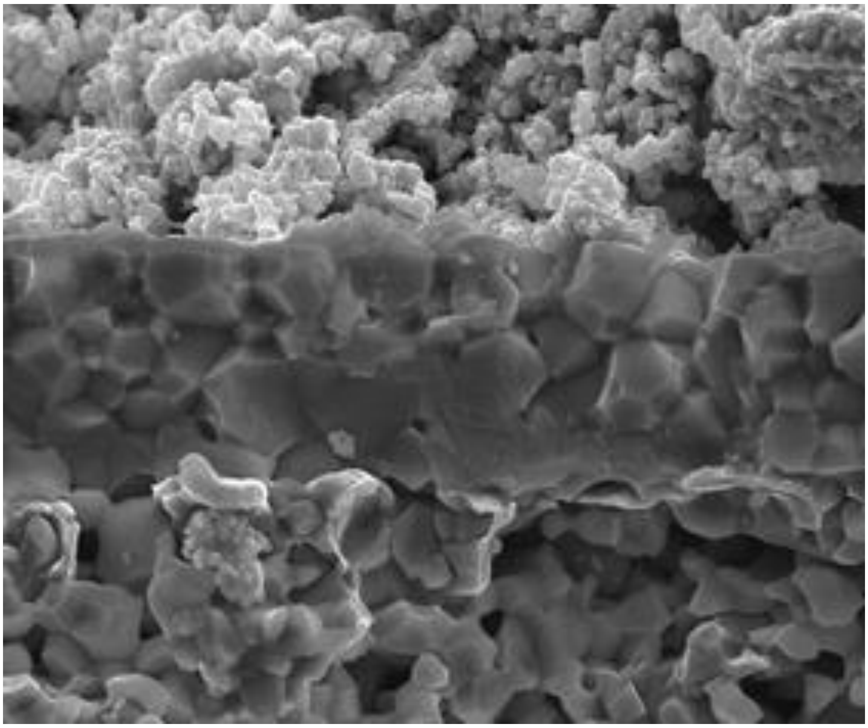


Spin coating
Used to make a thin coating on relatively flat substrates

Spin coating



Dae-Hyeong Kim,
Seoul National University



Cathode
Porous perovskite oxide

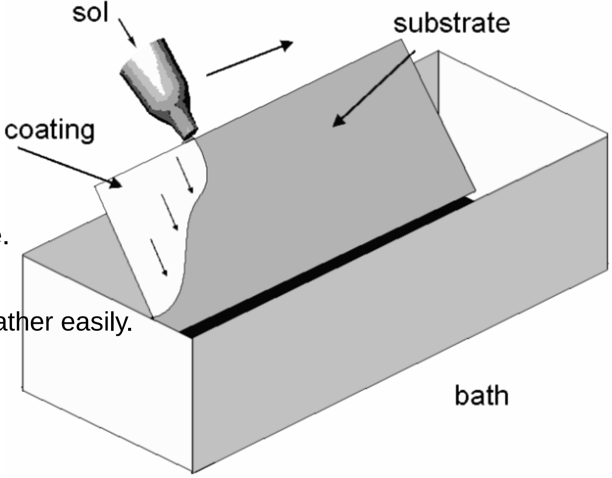
Electrolyte
Dense fluorite oxide

Anode
Porous ceramic-metal composite

C. Ding *et al.*,
Energy Environ. Sci., (2010)

Flow coating

Flow coating process



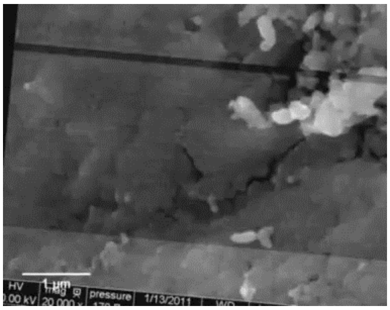
Coating thickness depends on
the angle of inclination of the substrate,
the liquid viscosity and the solvent evaporation rate.

The advantage of the flow-coating process
is that non-planar large substrates can be coated rather easily.

Powder processing

Outline

- **Applications**
- **Synthesis**
- **Processing**
- **Sintering**

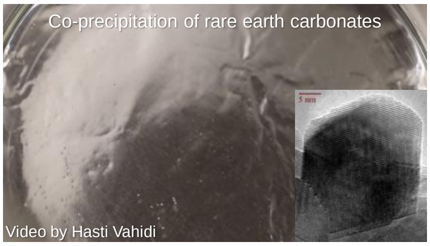


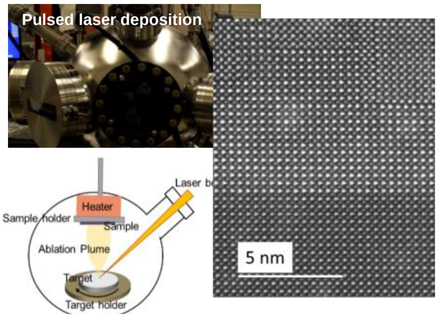
References

Ceramic Materials Science and Engineering by C.B. Carter & M.G. Norton *Springer*

Research activities

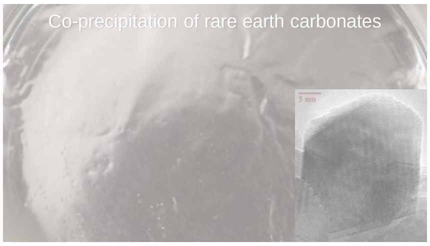
Synthesis of nanoscale oxide materials

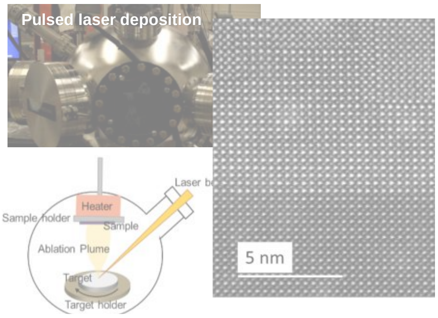




Research activities

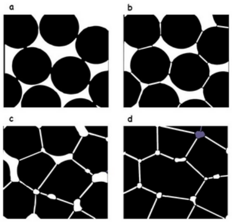
Synthesis of nanoscale oxide materials

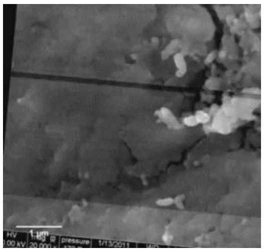


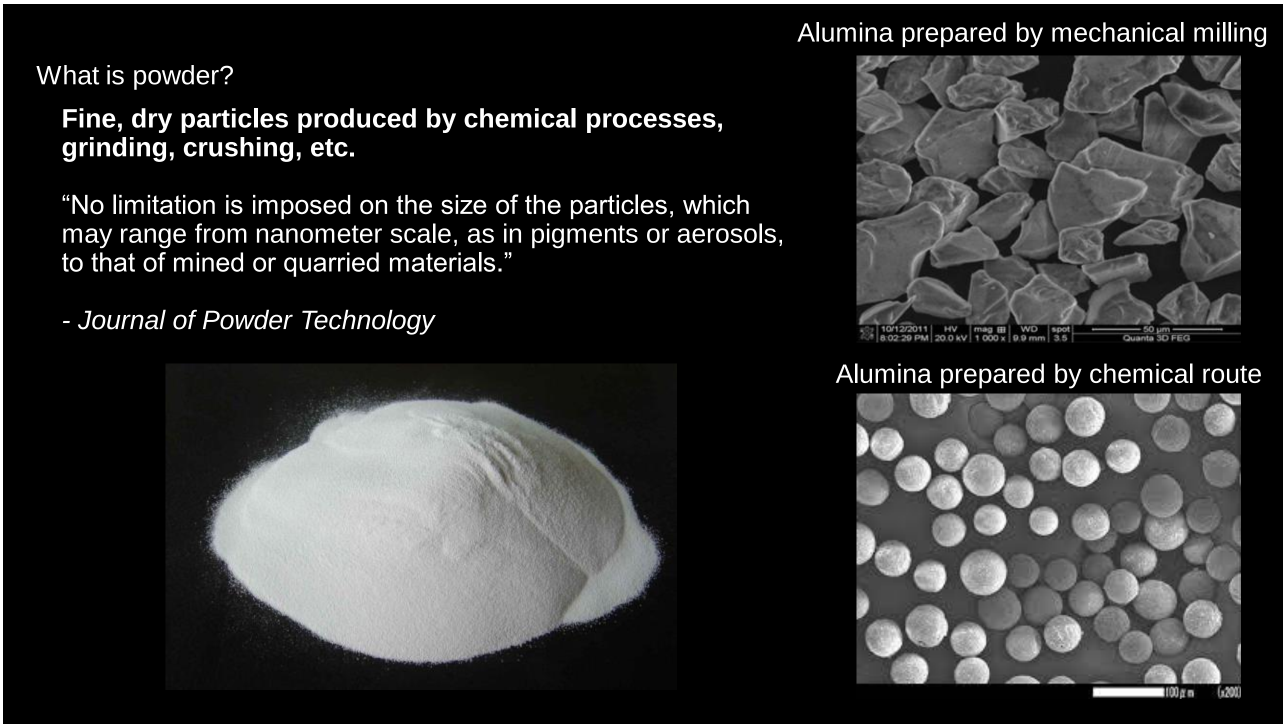


Processing bulk oxide ceramics

Powder sintering







Alumina prepared by mechanical milling

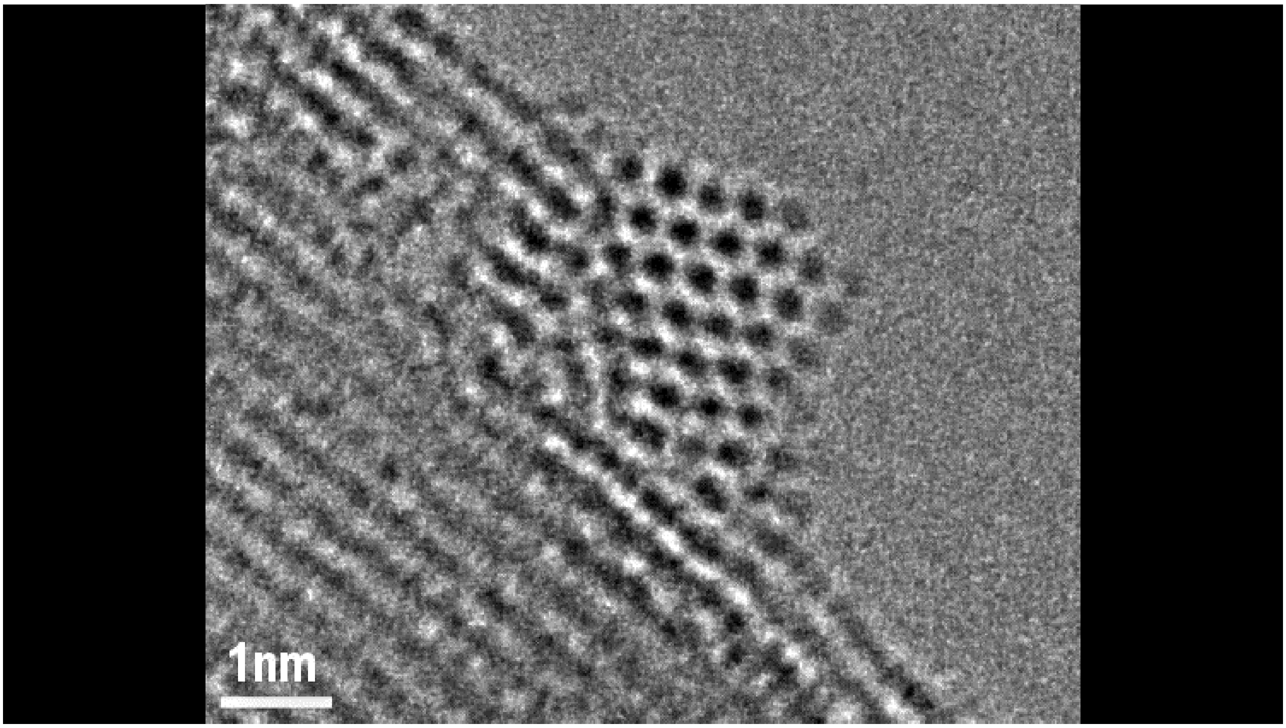
What is powder?

Fine, dry particles produced by chemical processes, grinding, crushing, etc.

“No limitation is imposed on the size of the particles, which may range from nanometer scale, as in pigments or aerosols, to that of mined or quarried materials.”

- *Journal of Powder Technology*

Alumina prepared by chemical route



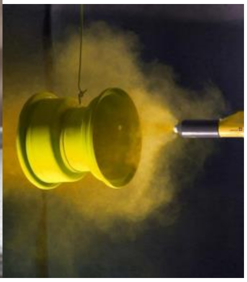
Powder applications

What are some applications for powders?

Powder applications

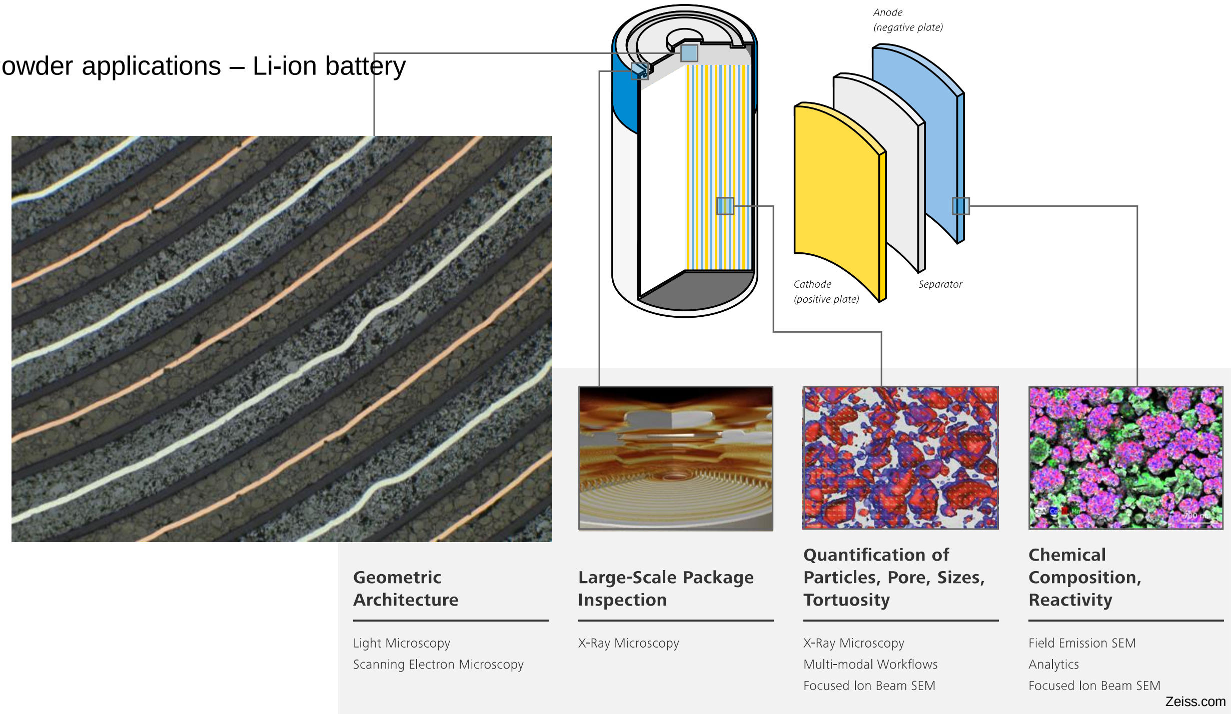
What are some applications for powders?

Pharmaceuticals, chemicals, foods, pigments, structural and functional materials, environmental and energy related materials

Powder applications – Powder metallurgy

Powder applications – Li-ion battery

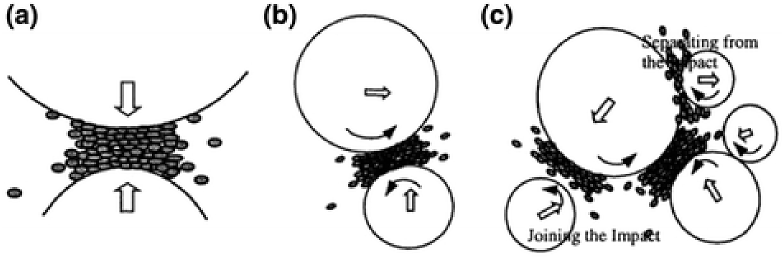


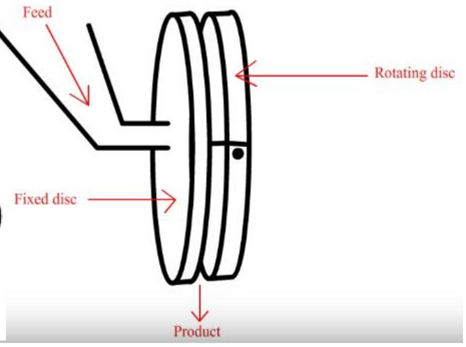
Zeiss.com

Powder synthesis – Mechanical attrition milling

Nanoparticles are formed in a mill where energy is used to transform course-grained materials into nanostructured powders.

size distribution of 1-100 nm with high crystallinity





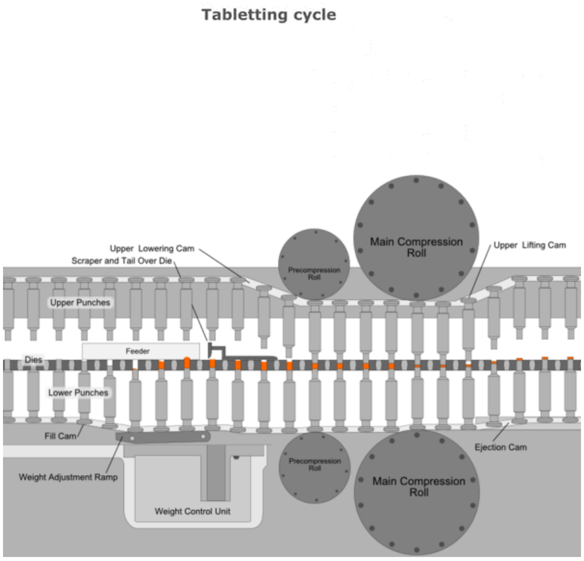
"High-Energy Milling" A.K. Alves *et al.*
Novel Synthesis and Characterization of Nanostructured Materials
pp 77-85 Springer

Powder processing – Tableting

Method for pressing powder into solids (e.g. drugs, candy, biomaterial)

Dye mold is filled, and then the mixture is compressed and ejected

What are important variables?



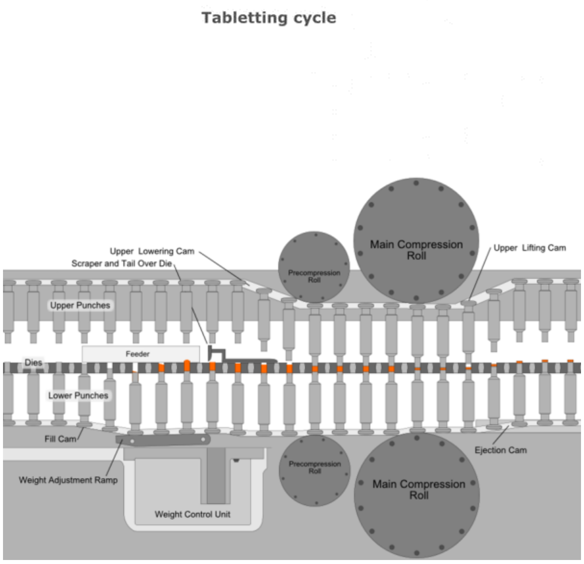
Powder processing – Tableting

Method for pressing powder into solids (e.g. drugs, candy, biomaterial)

Dye mold is filled, and then the mixture is compressed and ejected

What are important variables?

particle size, flow properties of powder, pressure (powder polymorph)

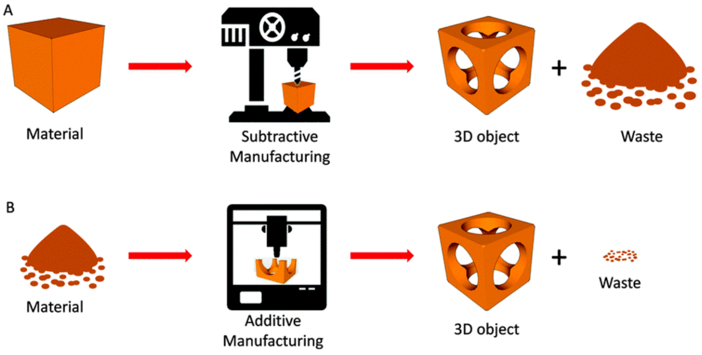


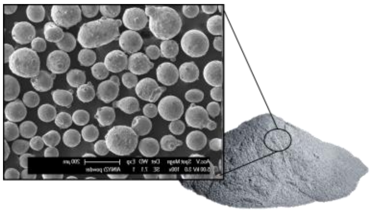
Powder processing – Additive manufacturing

Three-dimensional objects iterative addition of thin layers of material

produce metals, ceramics, polymers and composites using photopolymerization, jetting, extrusion, directed energy deposition, and lamination

What pros and cons of additive manufacturing can you think of?

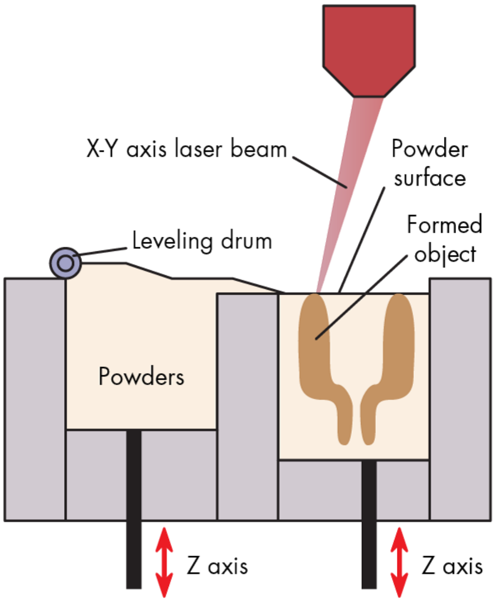




Julie Schoenung Research Group,

Powder processing – Additive manufacturing

Selective laser melting



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Powder processing – Additive manufacturing

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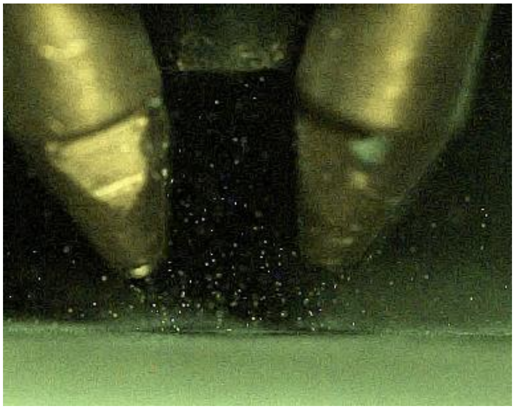
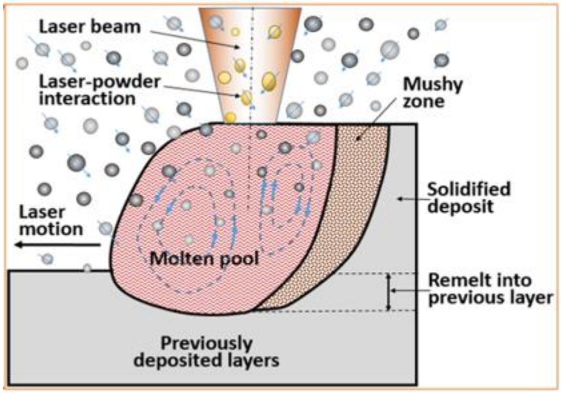
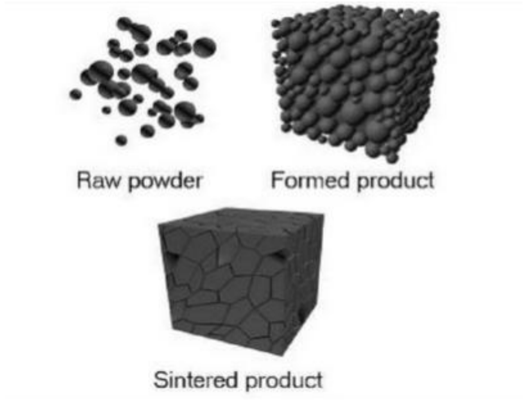
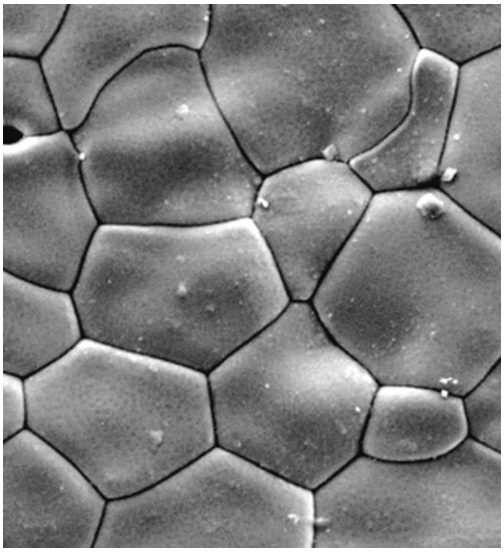




Julie Schoenung Research Group, UC Irvine

Powder processing – Sintering

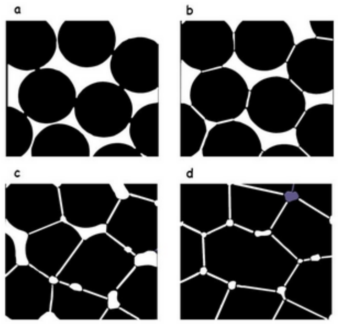




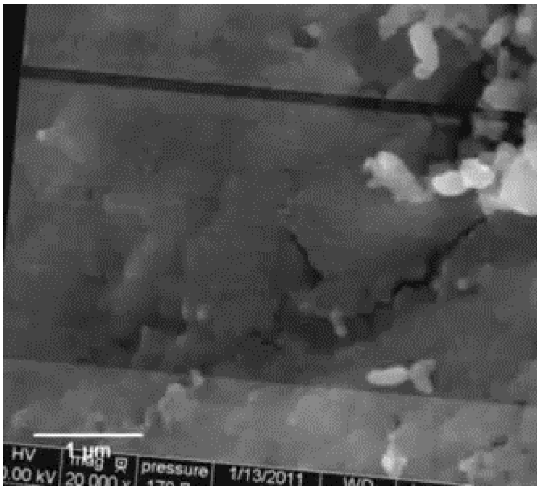
Sintering – Overview

Sintering is the process of transforming a powder into a solid body using heat.

The most important process in **making bulk dense and porous ceramics**, but also needed for **powder metallurgy**.



a) Green body, loose powder
b) Initial stage: increase of the interparticle contact area from 0 to 0.2 grain diameter, increase of the density from 60 to 65%
c) Intermediate stage: further increase of the contact area, stage characterized by continous pore channels along three grain edges, increase of the density from 65 to 90%.
d) Elimination of the pore channel along three grain edges, increase of the density to 95 - 99%

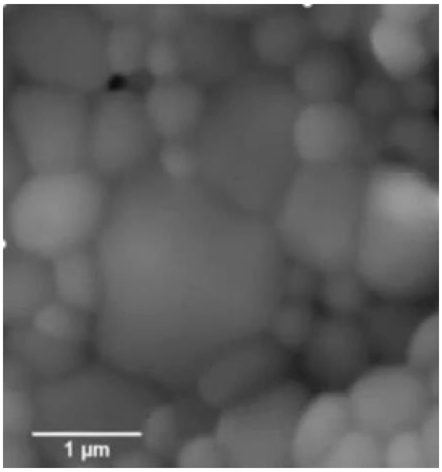


What are the features of the sintered microstructure?

Sintering – Overview

how best to **pack particles** (that are usually modeled as spheres), **movement of grain boundaries** (GBs), and knowing how the packing geometry and GB migration is affected by the need to balance **surface tensions (interface energies)**.

Sintering is driven by the tendency to **reduce the total energy of the system**.
This is especially true for nanoparticles. Why?



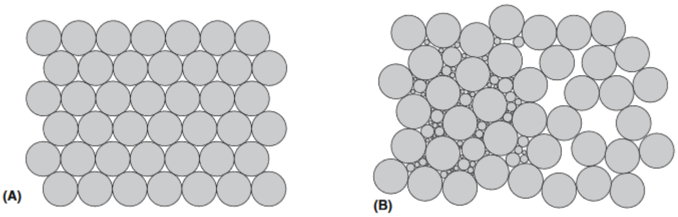
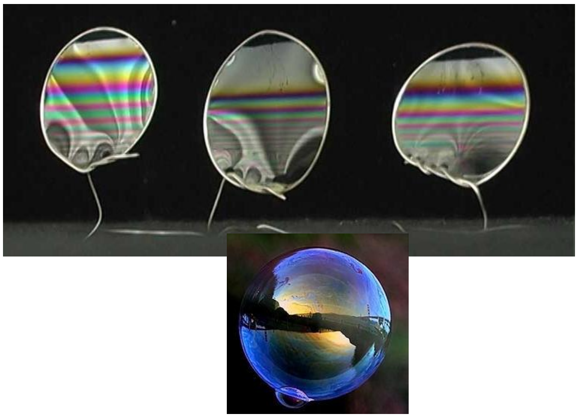


FIGURE 24.1 Model grain/shape distributions in 2D; packing identical spheres can never achieve less than 26% porosity: (a) ideal planar packing, (b) less-dense packing of larger spheres, part with inserted smaller spheres giving a higher local density.

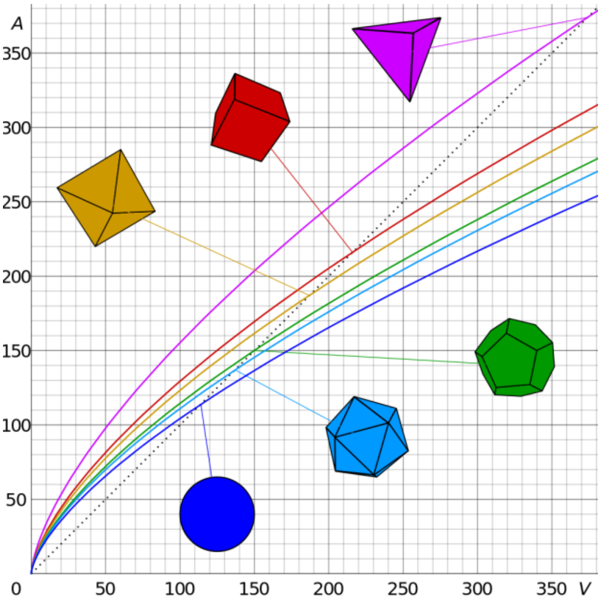
Sintering – Surface area and energy

Driven by tendency to reduce the total energy of the system by **increasing radius of curvature** of surface and by **minimizing surface area**.

A curved surface wants to be flat



Surface area to volume ratio



Sintering – Surface area and energy

Sintering is driven by the tendency to reduce the total energy of the system by **increasing radius of curvature** of surface and by **minimizing surface area**.

The extra energy of a surface with a radius of curvature, *R*, may be calculated as a stress (σ) in a **Laplace equation**

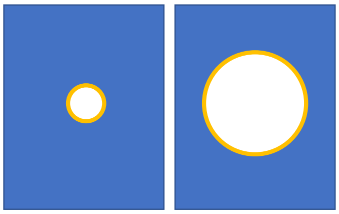
$$\boxed{\sigma = \gamma / R}$$

where γ is the surface energy.

In nanomaterials, this sintering stress may reach very high values.

Example:

the sintering stress may be as large as 300 MPa in 10 nm particles compared to only 3 MPa for 1 µm particles, if γ has a typical value of 1.5 J/m2.



Which has more surface (energy), left or right?

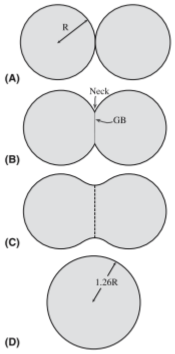


FIGURE 24.6 Coalescence of two spheres (a–d).

Which has less circumference, A or D?

Sintering – Surface area and energy

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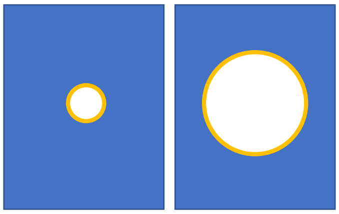


Which has more surface (energy), left or right? **Right**

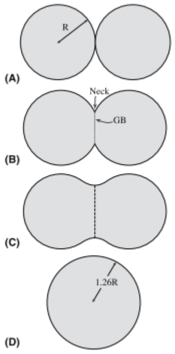


FIGURE 24.6 Coalescence of two spheres (a–d).

Which has less circumference, A or D? **D**

At some critical radius, the particle will continue to grow to minimize surface area.

Sintering – Mass transfer

Material must transfer from one part of the structure to another. **Solid phase sintering. Liquid phase sintering** achieved by phase transition.

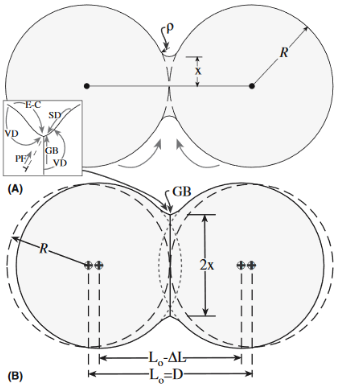


FIGURE 24.5 (a, b) Sintering and curvature. The two-sphere model showing the transport paths, the two curvatures (ρ and *x*), and the process leading to densification.

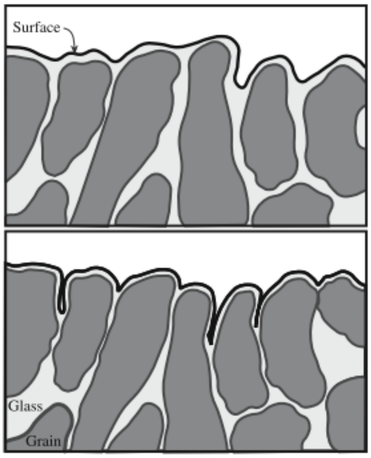


FIGURE 24.13 Liquid at surfaces.

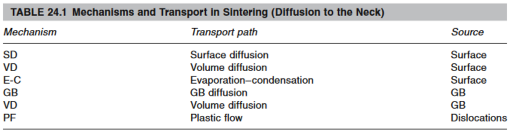
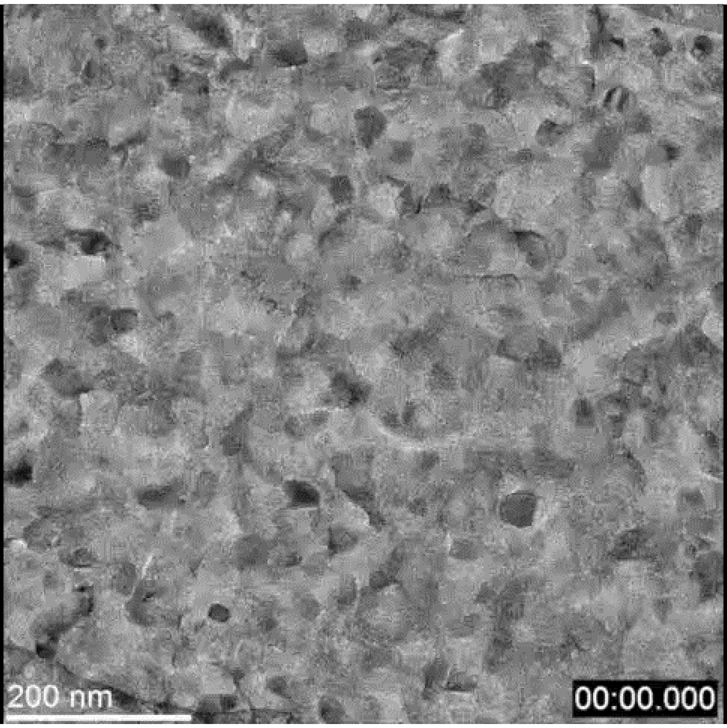


TABLE 24.1 Mechanisms and Transport in Sintering (Diffusion to the Neck)

Mechanism	*Transport path*	*Source*
SD	Surface diffusion	Surface
VD	Volume diffusion	Surface
E-C	Evaporation–condensation	Surface
GB	GB diffusion	GB
VD	Volume diffusion	GB
PF	Plastic flow	Dislocations

Oxide annealing:
900 °C, *in situ* TEM

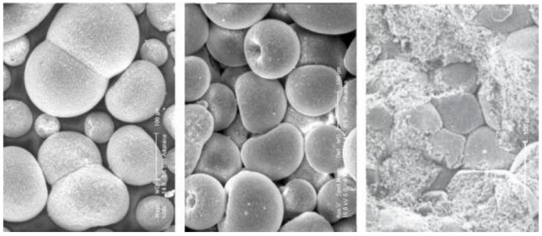


Sintering – Compaction

A compact (a.k.a. green body) is formed by pressing the powder

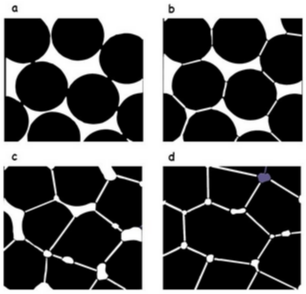
Sintering defects may be related to the microstructure of green body. Inhomogeneities in **density**, **packing**, and **particle size** in green compact will limit the final **sintered density**.

Alumina particles during compaction



Sintering – Densification

Sintering starts when compact is heated to temperatures about **2/3 * T_{melt},** when **diffusion becomes significant**. Elimination of large pores originating from the green compact requires high sintering temperatures which promotes grain growth.



a) Green body, loose powder
b) Initial stage: increase of the interparticle contact area from 0 to 0.2 grain diameter, increase of the density from 60 to 65%
c) Intermediate stage: further increase of the contact area, stage characterized by continous pore channels along three grain edges, increase of the density from 65 to 90%.
d) Elimination of the pore channel along three grain edges, increase of the density to 95 - 99%

Material	Particle size, nm	Temperature, K	Percentage of densification
TiC	140–170	1900	91
TiC	5000	3070	91
ZrO_2	nano sized	1745	100
ZrO_2	conventional	> 1975	100
TiO_2	12–14	1300	100
TiO_2	1300	>1630	100
TiN		1823	100
TiN		1823	63

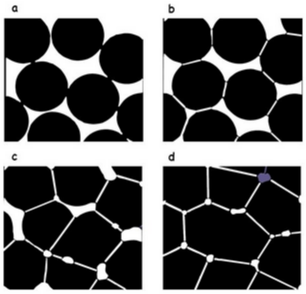
Higher temperature may be needed for larger particles

What is the relative particle size?

Sintering – Densification

Sintering starts when compact is heated to temperatures about **2/3 * T_{melt}**, when **diffusion becomes significant**.

Elimination of large pores originating from the green compact requires high sintering temperatures which promotes grain growth.



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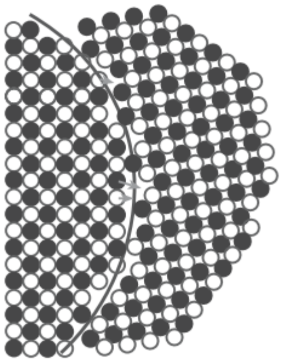
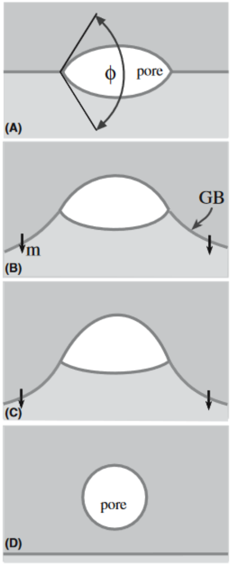


FIGURE 24.11 Atomistic model for GB migration.

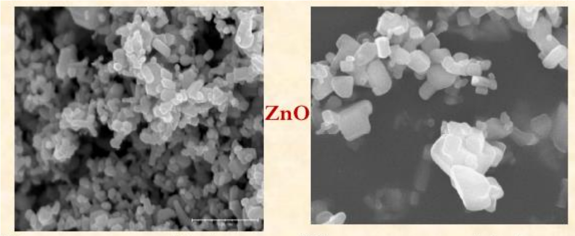
Pores may persist as grains grow



Sintering – Parameters

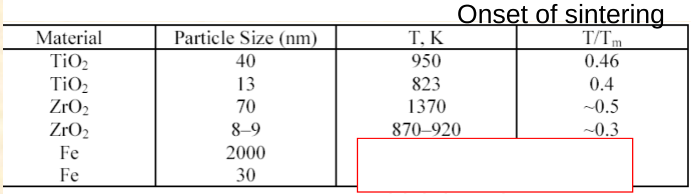
$$\frac{d\rho}{dt} \sim \frac{1}{d^n} exp\left(-\frac{Q}{RT}\right)$$

The general relationship between sintering parameters
n is a constant, p is the **density**, Q is the **activation energy for sintering** and d is the **mean powder particle diameter**. The n is usually about 3 and Q is considered to be equal to the activation energy for grain boundary diffusion.



48 nm average particle size
30 m2/g specific surface area

790 nm average particle size
3.2 m2/g specific surface area



		Onset of sintering	
Material	Particle Size (nm)	T, K	T/T_m
TiO_2	40	950	0.46
TiO_2	13	823	0.4
ZrO_2	70	1370	~0.5
ZrO_2	8–9	870–920	~0.3
Fe	2000		
Fe	30		

Which has the lowest sintering temperature?

Sintering – Parameters

$$\frac{d\rho}{dt} \sim \frac{1}{d^n} exp\left(-\frac{Q}{RT}\right)$$

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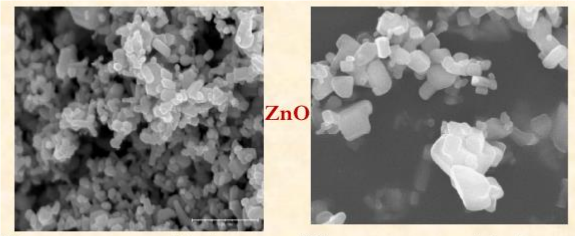

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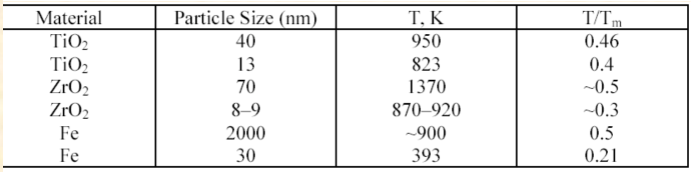

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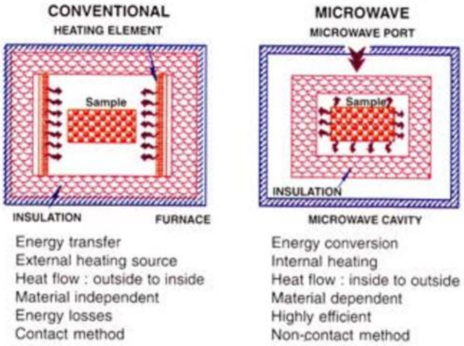
ZrO_2	8–9	870–920	~0.3
Fe	2000	~900	0.5
Fe	30	393	0.21

Which has the lowest sintering temperature?

Sintering methods – Conventional & microwave furnace

Microwave sintering has **rapid processing time**, two to 50 times faster than conventional heating.

There is also an acceleration of sintering and diffusion in the material because of high electrical fields; thus densification can occur at lower temperatures.



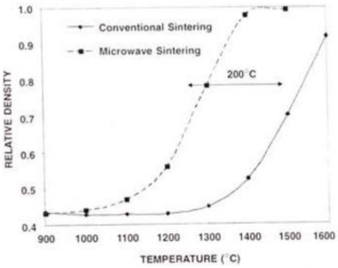
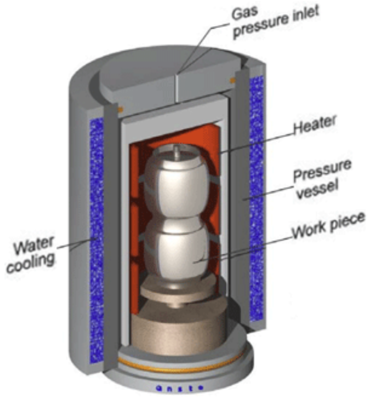


Fig. 2 – Sintered density vs temperature plots for microwave and conventionally sintered alumina.

Dinesh Agrawal *Transactions of the Indian Ceramic Soc.* (2006)

Sintering methods – Hot isostatic press (HIP)

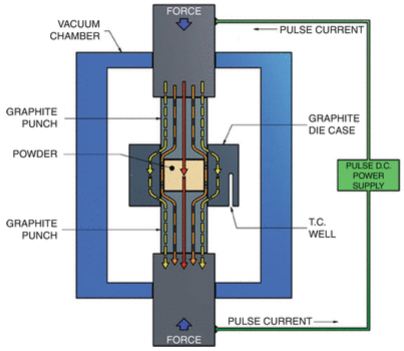


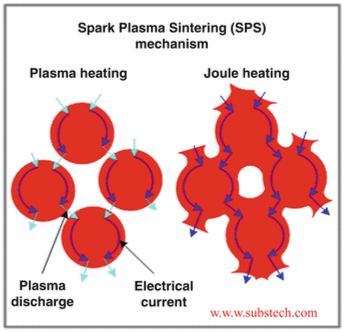
Process to densify powders or cast and sintered parts in a furnace at high pressure (100-200 MPa) and at temperatures from 900 to 1250°C for example for steels and superalloys.

Gas pressure acts uniformly in all directions to provide isostropic properties and 100% densification.

High performance alternative to conventional processes such as forging, casting and machining

Sintering methods – Field assisted “spark plasma” sintering



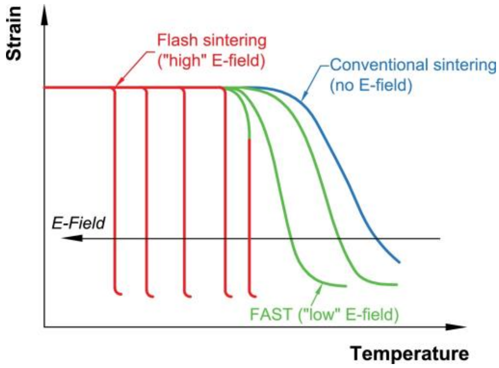


Plasma state is achieved by pulsed current
Surface temperature of particles rises rapidly by self heating, so particle growth is controlled.

(I) The electrons are withdrawn from one power (the cathode) and accelerate toward the anode.
(II) The electrons collides the gas atoms in the powder gap, then the gas is ionized.
(III) The accelerated electrons hit to the anode, the ions of the sintered materials are evaporated like a sputtering process.

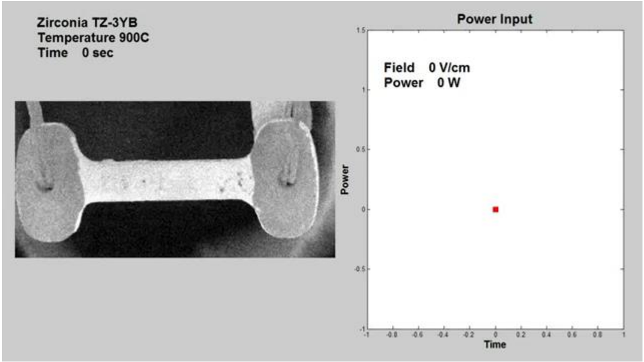
Initial activation through the application of a pulsed voltage; subsequent heating and densification by DC current. Typically **less than 10 minutes** for the full densification of both conductive and non-conductive materials.

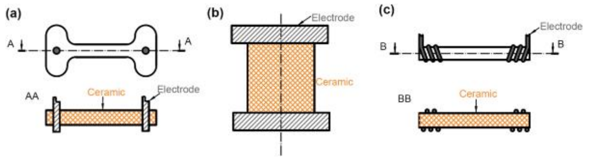
Sintering methods – Field-assisted “flash sintering”



A newer densification technology for ceramics allowing a dramatic reduction of processing time and temperature.

Reduce energetic costs associated with firing.
Develop out-of-equilibrium microstructures.





“Flash sintering of ceramics” M. Biesuz V.M.Sglavo

References (see Class page)

Given throughout