2nd*Joint European Summer School on Fuel Cell and Hydrogen Technology*

Manufacturing Methods

Department of Chemical Engineering
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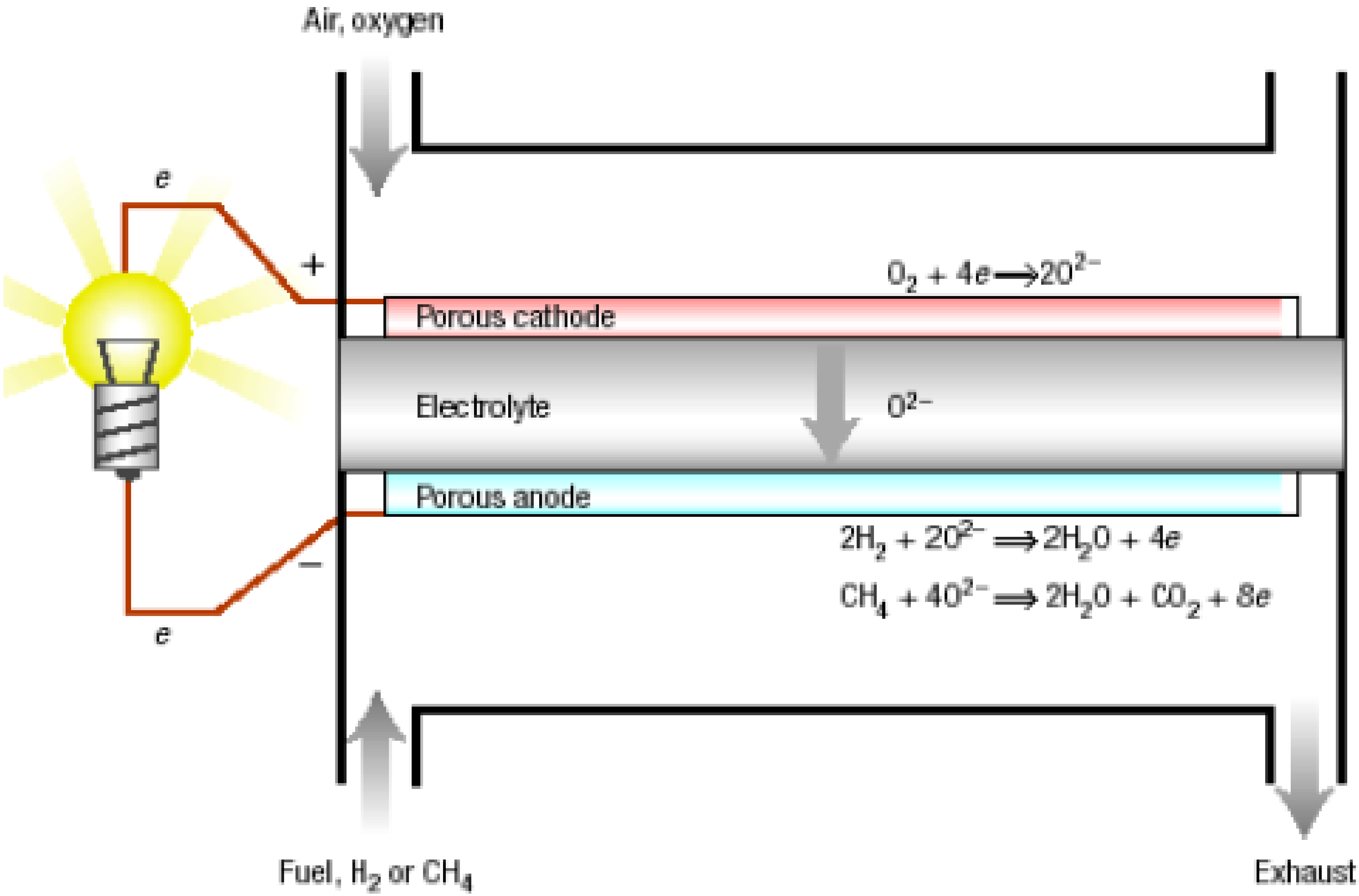
SOFC Principles



Materials – Example (Common)

Component composition	Component	Fabrication Requirements
Ni/YSZ cermet	Anode	■Porous ■Ni content – Conductivity ■No Reactions ■(Mechanical Integrity)
$Sr_xLa_{1-x}MnO_{3-\delta}$	Cathode	■Porous ■Conductivity ■No Reactions ■(Mechanical Integrity)
Y_2O_3-ZrO_2	Electrolyte	■Dense ■Ionic Conductivity ■No Reactions ■(Mechanical Integrity)

SOFC Company Examples

Company	Type	Electrolyte	Anode	Cathode
Acumentrics	Anode support tubular	Dip Coating	Extrusion	Dip Coating
Advanced Ceramic Reactor Team	Anode Support Micro-Tube	Dip Coating	Extrusion	Dip Coating
Ceres Power	Stainless Steel Supported	Electrochemically Deposited	Electrochemically Deposited	Electrochemically Deposited
Delphi/Batelle	Anode Supported Planar	Tape Casting	Tape casting	Screen printing
FCE	Anode Supported Planar	Screen printing	Tape casting	Screen printing
GE (Stopped)	Anode Supported Planar	Tape Calendaring	Tape Calendaring	Screen printing
Rolls Royce (SOFCo)	Electrolyte Supported planar	Tape casting	Screen printing	Screen printing
SWPC	Cathode Supported Tubular	Plasma Spray	Screen Printing	Extrusion

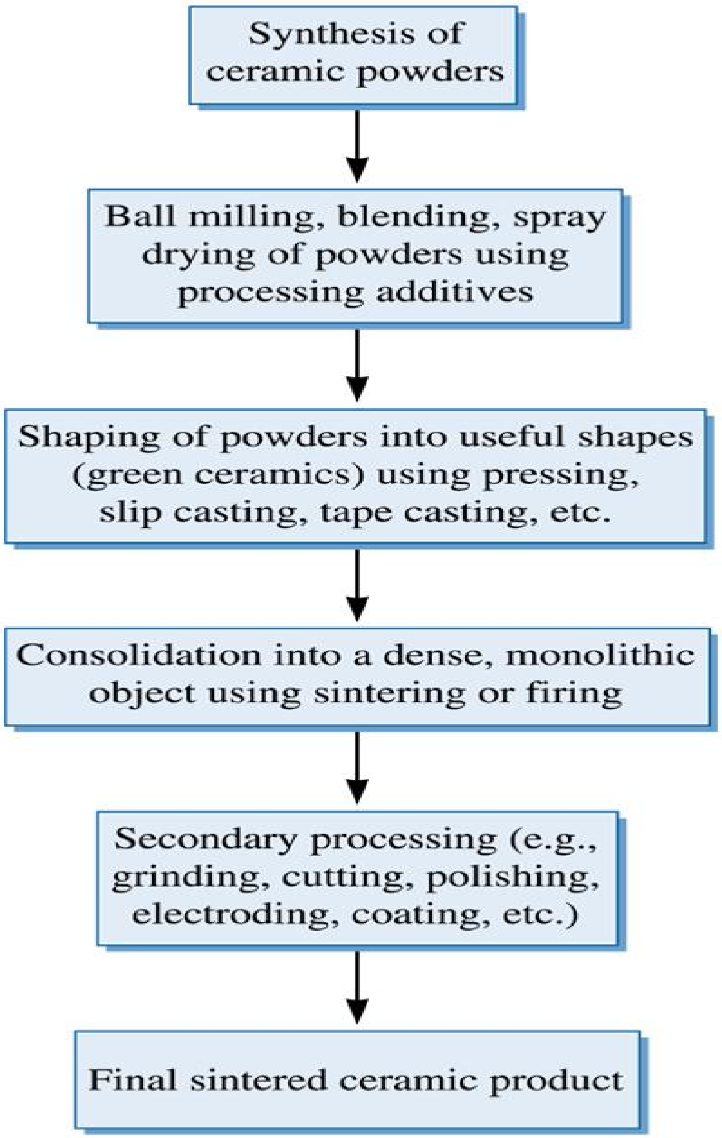
Common SOFC Processing Steps

Raw materials preparation	Forming	Conditioning
Powder Production Powder Preparation Size Reduction/Milling	Extrusion Tape casting Dip coating Flame/Plasma Spray EVD CVD Sputtering Calendaring	Drying Bisque Firing Sintering

Powder Processing

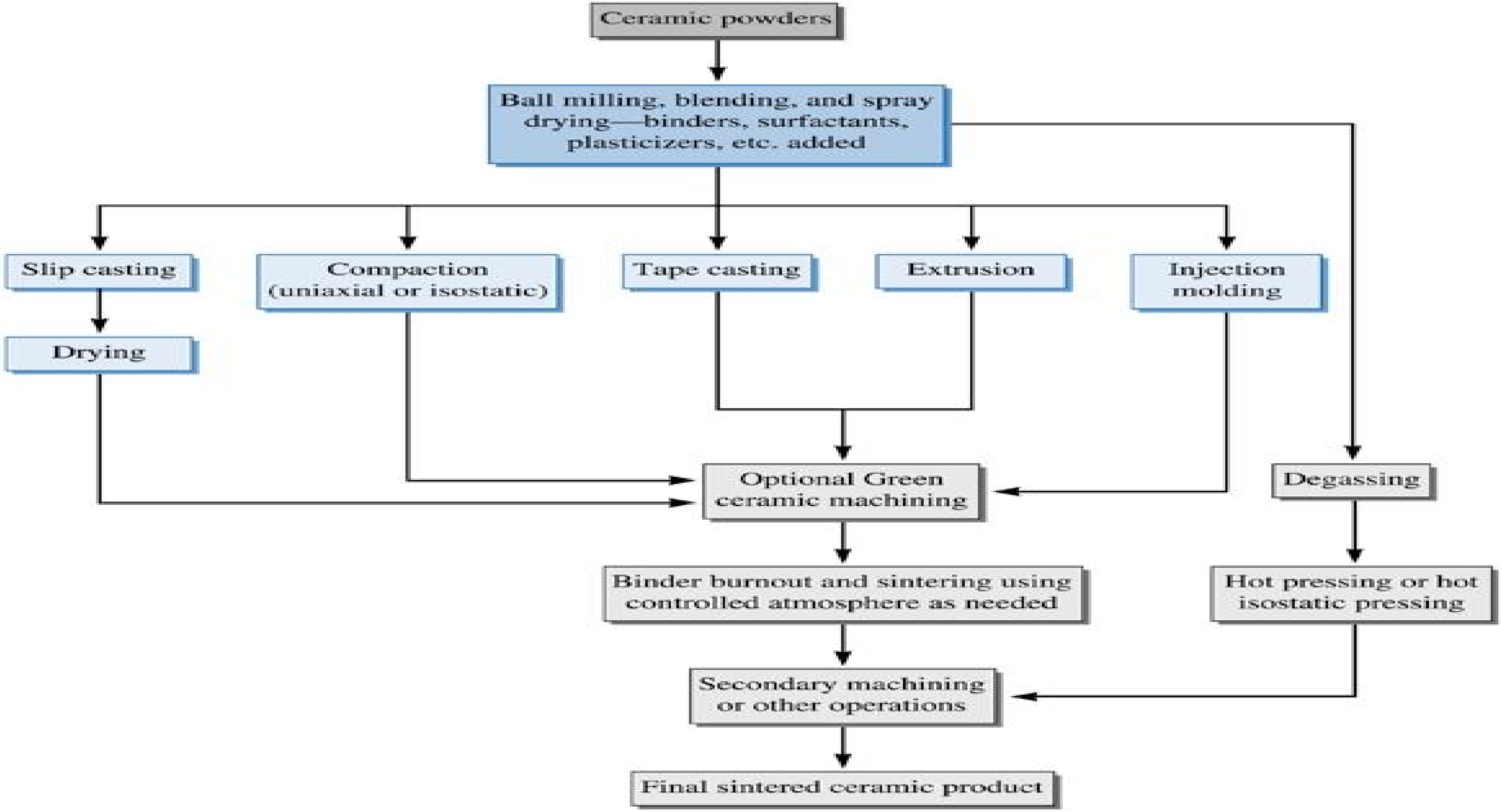
Terminology

- Green ceramic - A ceramic that has been shaped into a desired form but has not yet been sintered.
- Fired Ceramic – A ceramic that has already been fired/sintered into its final shape
- Calcination - Heating of chemicals to decompose and or react with different chemicals; used in traditional synthesis of ceramics.

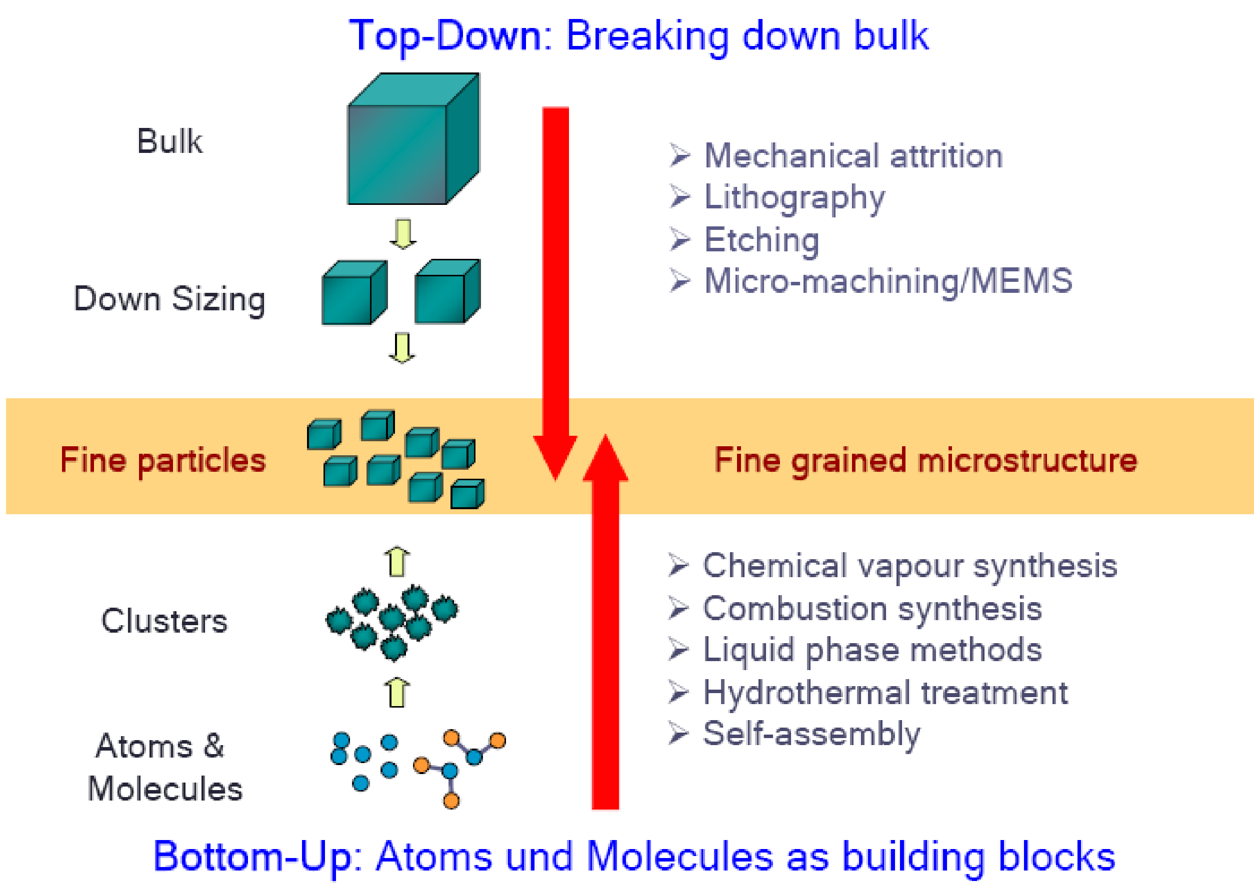


- Typical Steps in Fabrication

Techniques for Processing



Concepts – Powder Synthesis



Requirements for Powders

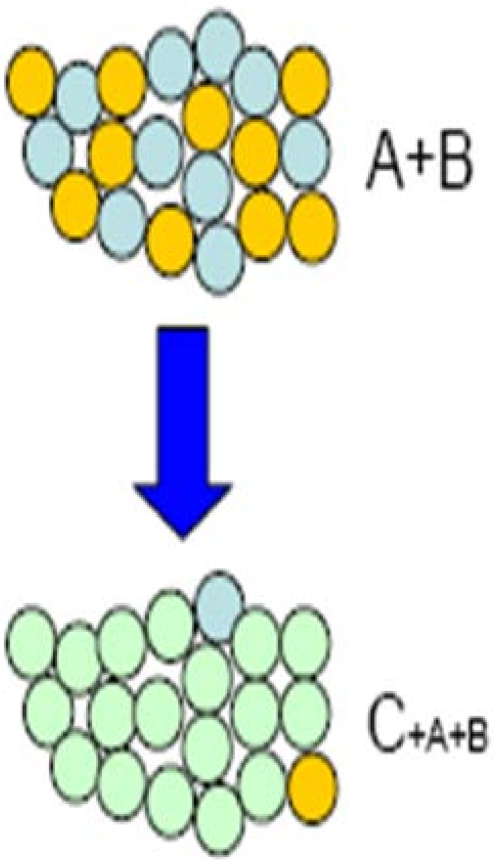
- Fine
- High Purity
- Narrow Particle Size Distribution
- Homogenous Composition
- Good flow characteristics
- Good Agglomeration
- Stability
- Defined Morphology

List of Common Powder Synthesis Techniques

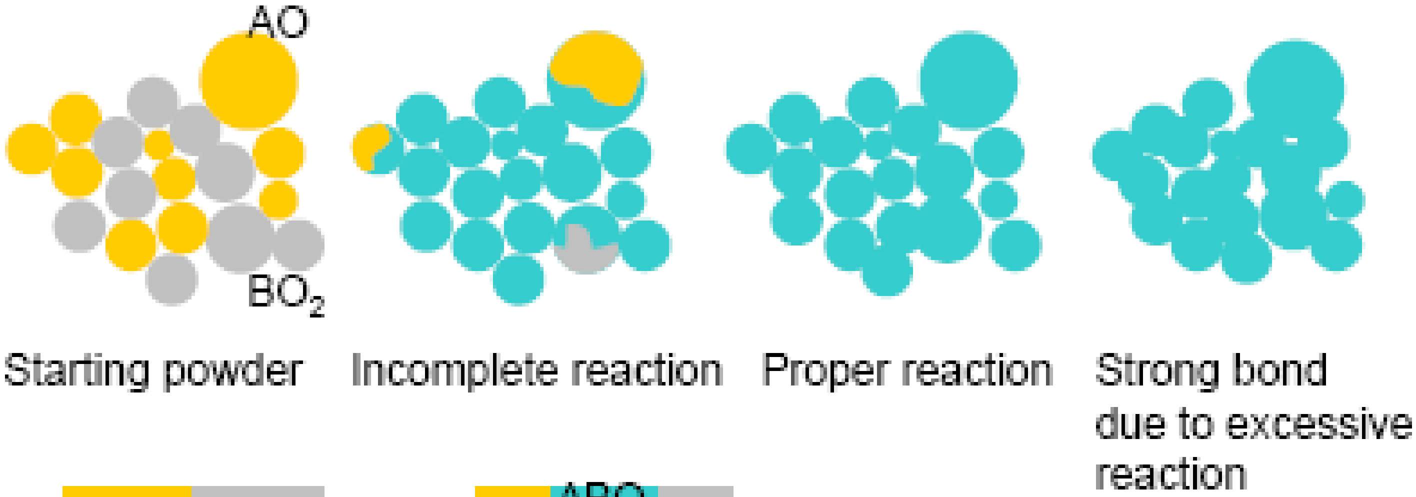
- Solid State
- Co-Precipitation
- Sol Gel Processing

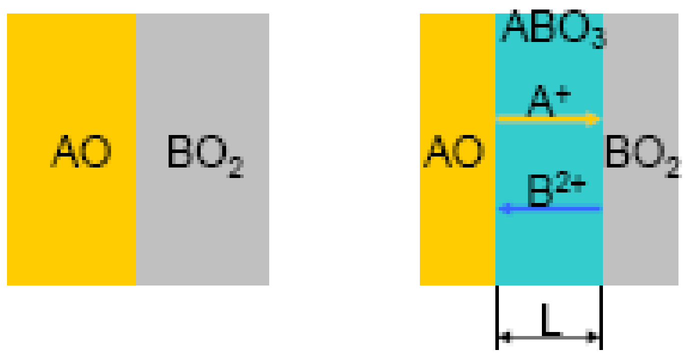
Solid State Synthesis

- Reaction between solids:
- **ADVANTAGES:**
  - Simple
  - Inexpensive
- **DISADVANTAGES:**
  - Wide particle size distribution
  - Coarse particle sizes
  - Contamination issues during grinding
  - High temperatures required
  - Compositional variation due to incomplete reaction
  - Difficult to control particle shape



Solid State





$$L \propto t^{1/2}$$

Chemical Synthesis

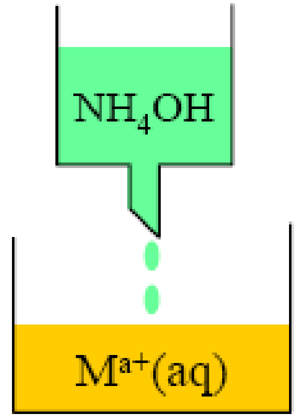
Atomic scale mixing

(Nano)Crystalline material
at low temperature

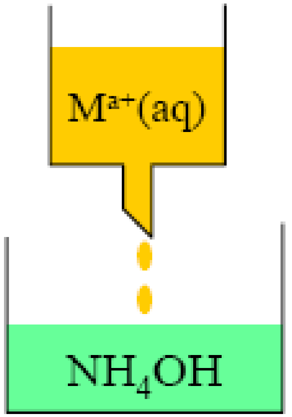
Phase purity and selectivity

Pre-defined reaction chemistry
and single-step synthesis

Precipitation: Normal strike and Reverse strike



Normal strike



Reverse strike

	Normal strike	Reverse strike
adding	precipant solution	salt solution
to	salt solution	precipant solution
pH	Low ⇒ High	High ⇒ Low
solubility of cation	High ⇒ Low	Low ⇒ High
nucleation rate	Low ⇒ High	High ⇒ Low

Pros and Cons

- **Advantages:**
  - Easy and cost effective
  - Relatively inexpensive starting materials
  - Easy to get nano-sized particles
  - Intimate mixing of cations can be achieved (when the solubility of the two precipitates is the same)
  - Can remove impurity (if it remains in solution)
- **Disadvantages:**
  - Often results in aggregation
  - Can be difficult to get intimate mixing

Issues to Address

- Often results in aggregation of particles during the precipitation, washing or firing; due to:
  - Growth of the precipitate (thus make sure the precipitate is in easily washable form)
  - Employ washing solution with constant pH (thus the electrostatic repulsion between particles is kept)
  - Ball mill dried aggregate with less polar solvent (eg ethanol, butanol etc)

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Other Methods – Precipitation

- Oxalate route (formation of $C_2O_4^-$ ion)
- Carbonate route (formation of CO_3^{2-} ion)

Sol-Gel Method

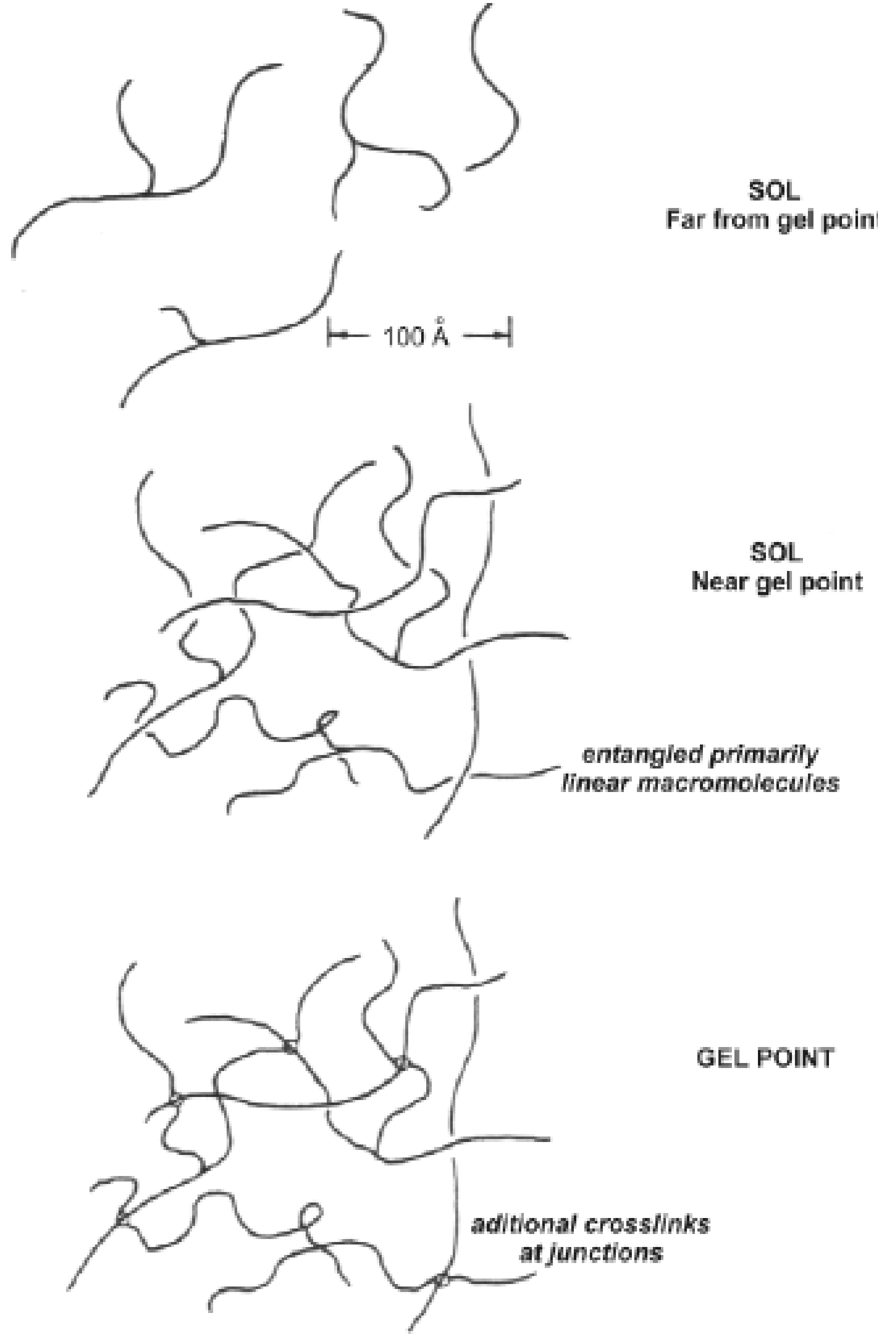
- The Sol-Gel is a process occurring in liquid solution of *organometallic precursors* (Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.), which, by means of *hydrolysis and condensation reactions*, leads to the formation of a new phase (SOL).

- M-O-R + H2O ➔M-OH + R-OH (hydrolysis)

- M-OH + HO-M➔M-O-M + H2O (water condensation)
  OR
- M-O-R + HO-M ➔ M-O-M + R-OH (alcohol condensation)
  - (M = Si, Zr, Ti, etc)

Sol-Gel Method

- The **SOL** is made of solid particles of a diameter of few hundred of nm suspended in a liquid phase.
- The particles condense in a new phase (**GEL**) in which a solid macromolecule is immersed in a liquid phase (solvent).
- Drying the GEL by means of low temperature treatments (25-100 C), is possible to obtain porous solid matrices (**XEROGELs**).
- Thus it is possible to generate ceramic materials at close to room temperature.



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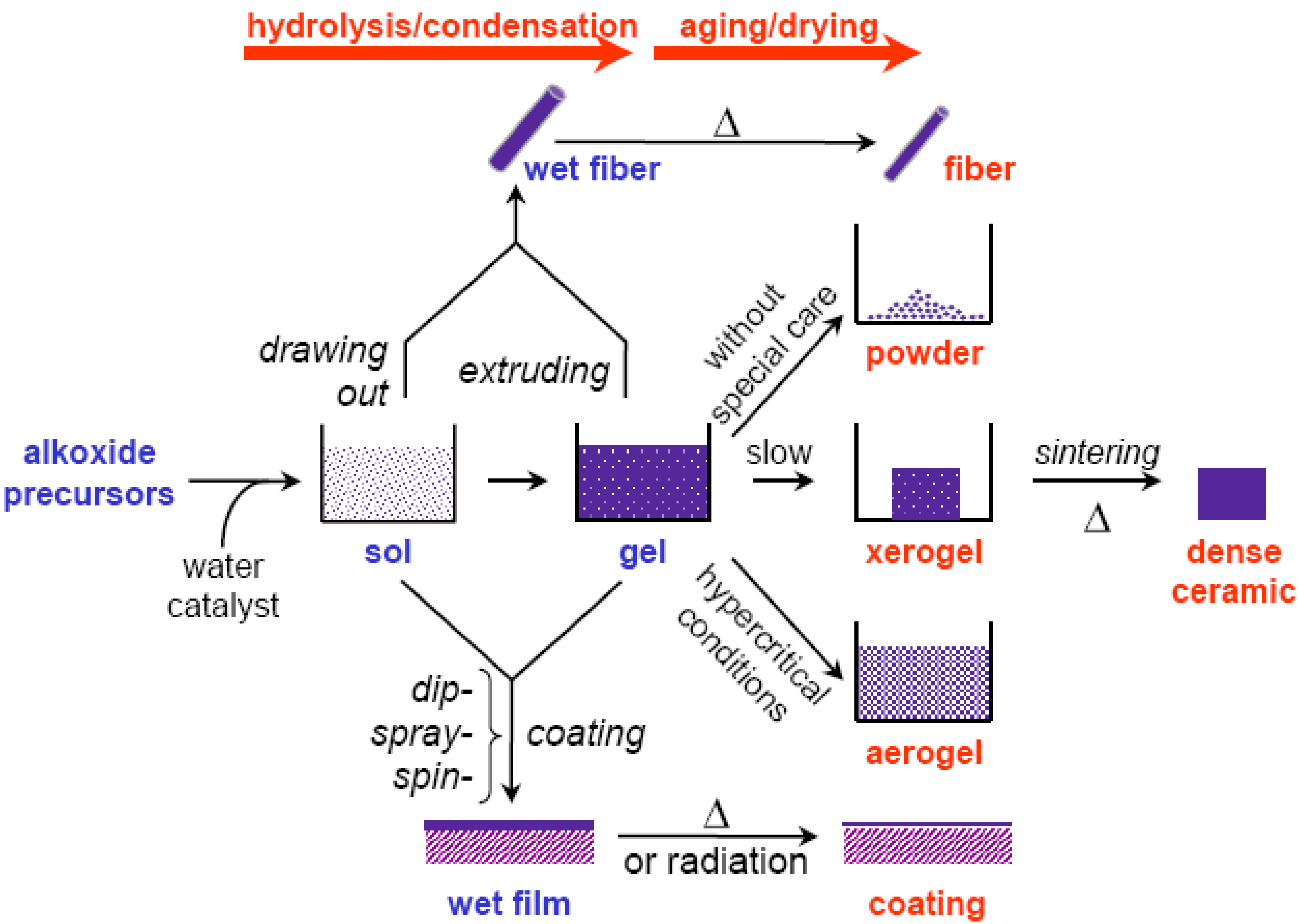
summary of sol-gel process, techniques and products



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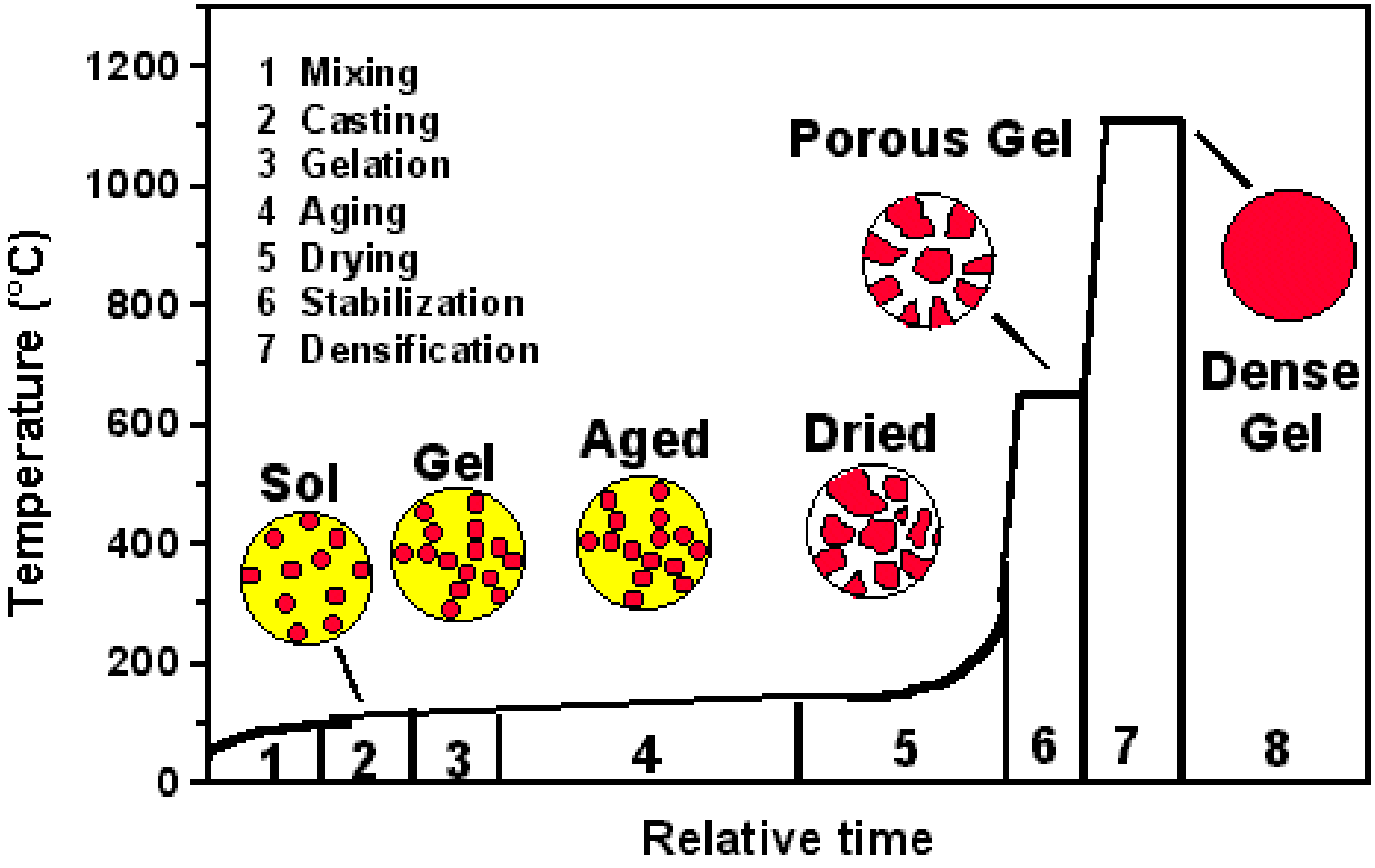


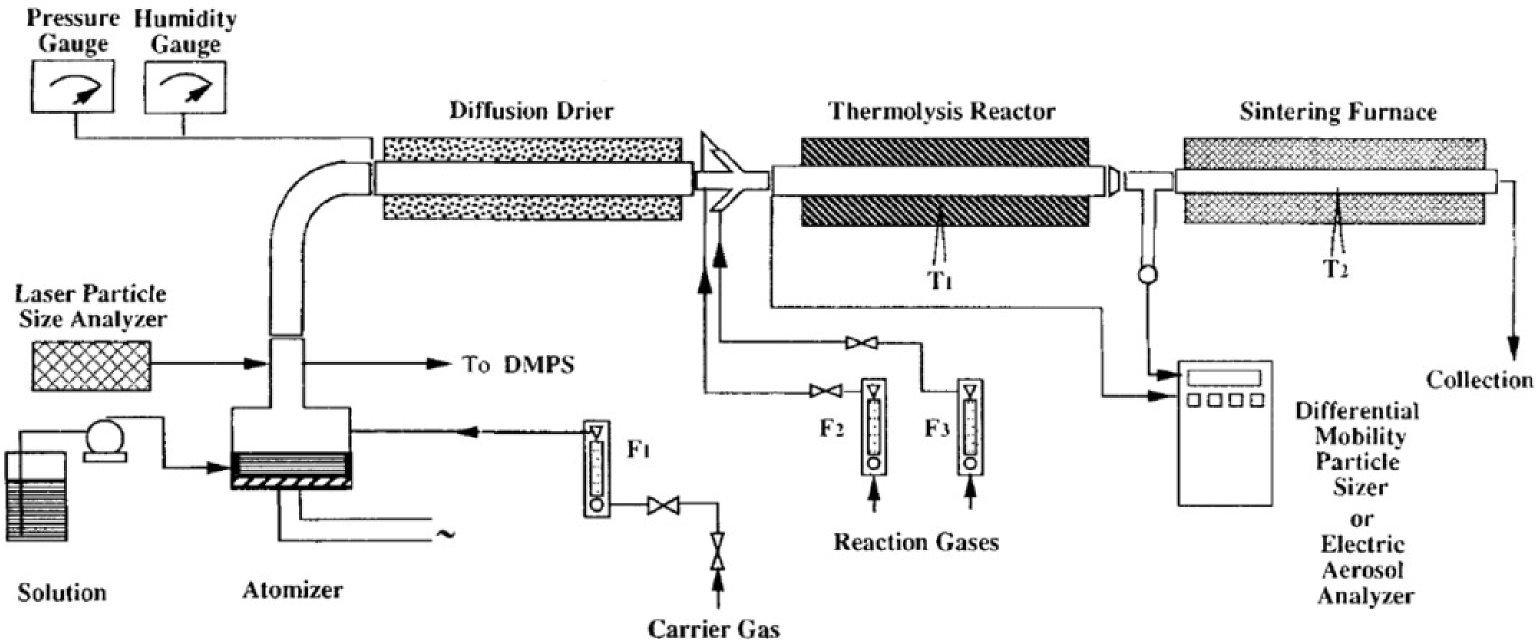
Gel glass process sequence

Spray Pyrolysis

atomization – is the production of droplets and their dispersion into the gas.
[Okuyama et al, Chem. Eng. Sci., 2003]

aerosol – defined as a suspension of solid or liquid particles in a gas.
[Okuyama et al, Chem. Eng. Sci., 2003]

"Spray pyrolysis is the aerosol process that atomizes a solution and heats the droplets to produce solid particles." [Che et al, J. Aero. Sci., 1998]



Messing et al, J. Am. Ceram. Soc., 1993

Spray Pyrolysis – the process

- there are a number of different atomizers

Table II. Characteristics of Atomizers Commonly Used for SP

Atomizer	Droplet size (µm)	Atomization rate (cm^3/min)	Droplet velocity (m/s)
Pressure	10–100	3–no limit	5–20
Nebulizer	0.1–2	0.5–5	0.2–0.4
Ultrasonic	1–100	<2	0.2–0.4
Electrostatic	0.1–10		

Messing et al, J. Am. Ceram. Soc., 1993

- atomization variables:

  droplet size – relates to the size of the end particle

  size dispersion – homogeneity of end products

  atomization rate – scalability of process is affected (i.e. industrial processes)

  droplet velocity – affects residence time within the furnaces

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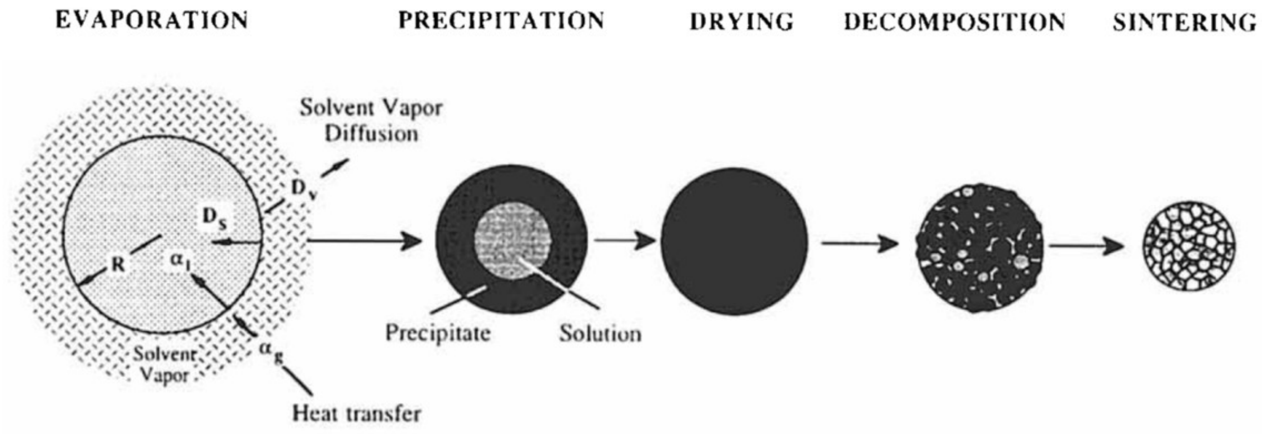
Spray Pyrolysis – droplet evolution



Messing et al, J. Am. Ceram. Soc., 1993

- evaporation – evaporation of solvent from the surface, diffusion of solvent vapour away from droplet, change in droplet temperature, diffusion of solute toward the center of the droplet, change in droplet size

- precipitation/drying – involves volume precipitation or surface precipitation of the solute, followed by the evaporation of the solvent through the nanoporous crust

- thermal decomposition or pyrolysis – forms a nanoporous structure

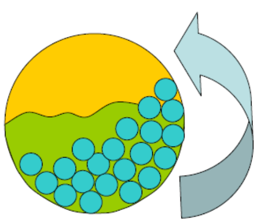
- sintering – involves the adhesion/solidification of the crystallites

Ball Milling Equipment

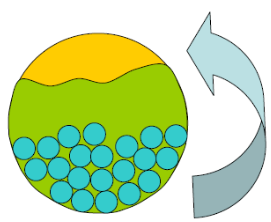
http://www.pauloabbe.com/

Milling Media: Ball

1. The highest density for the highest kinetic energy at the impact ($1/2mv^2$)
2. Cost
3. Wear resistance
4. Contamination from the ball



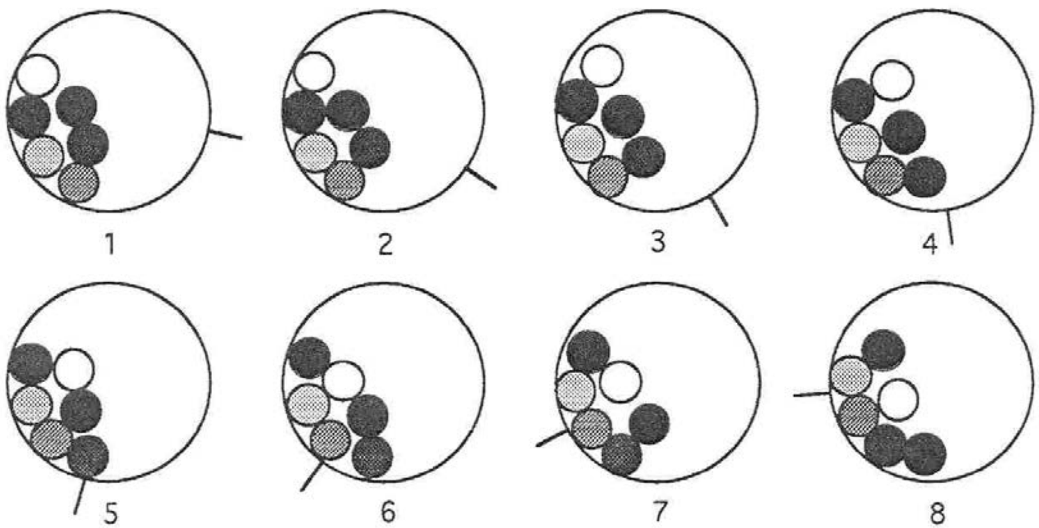
Good

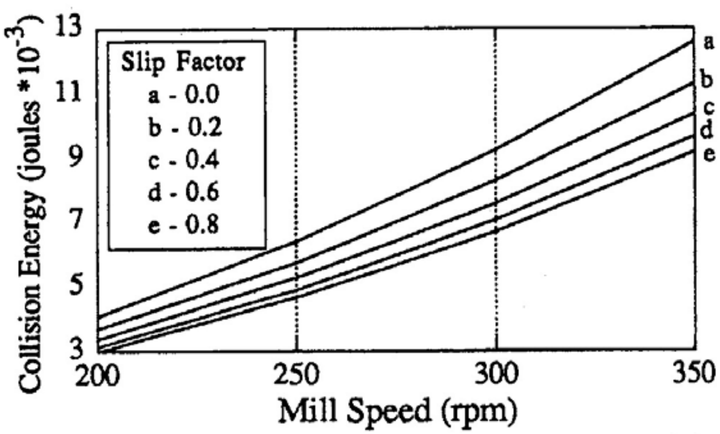


Bad

Trajectory of milling balls in a mill

- Aim is generally to have milling balls cascading and colliding with maximum energy with the opposite wall.
- In reality, there is a high slip-factor between pot and balls (80%), so observed trajectories in a mill are:

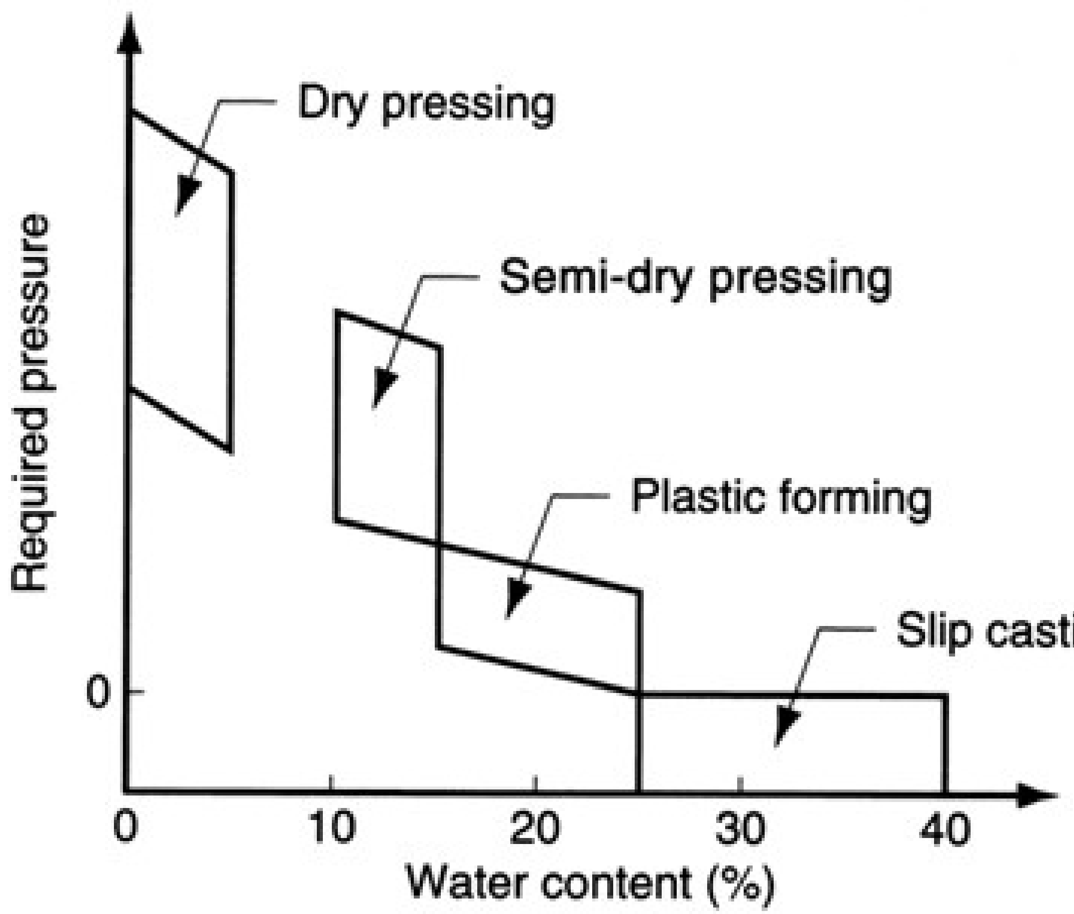




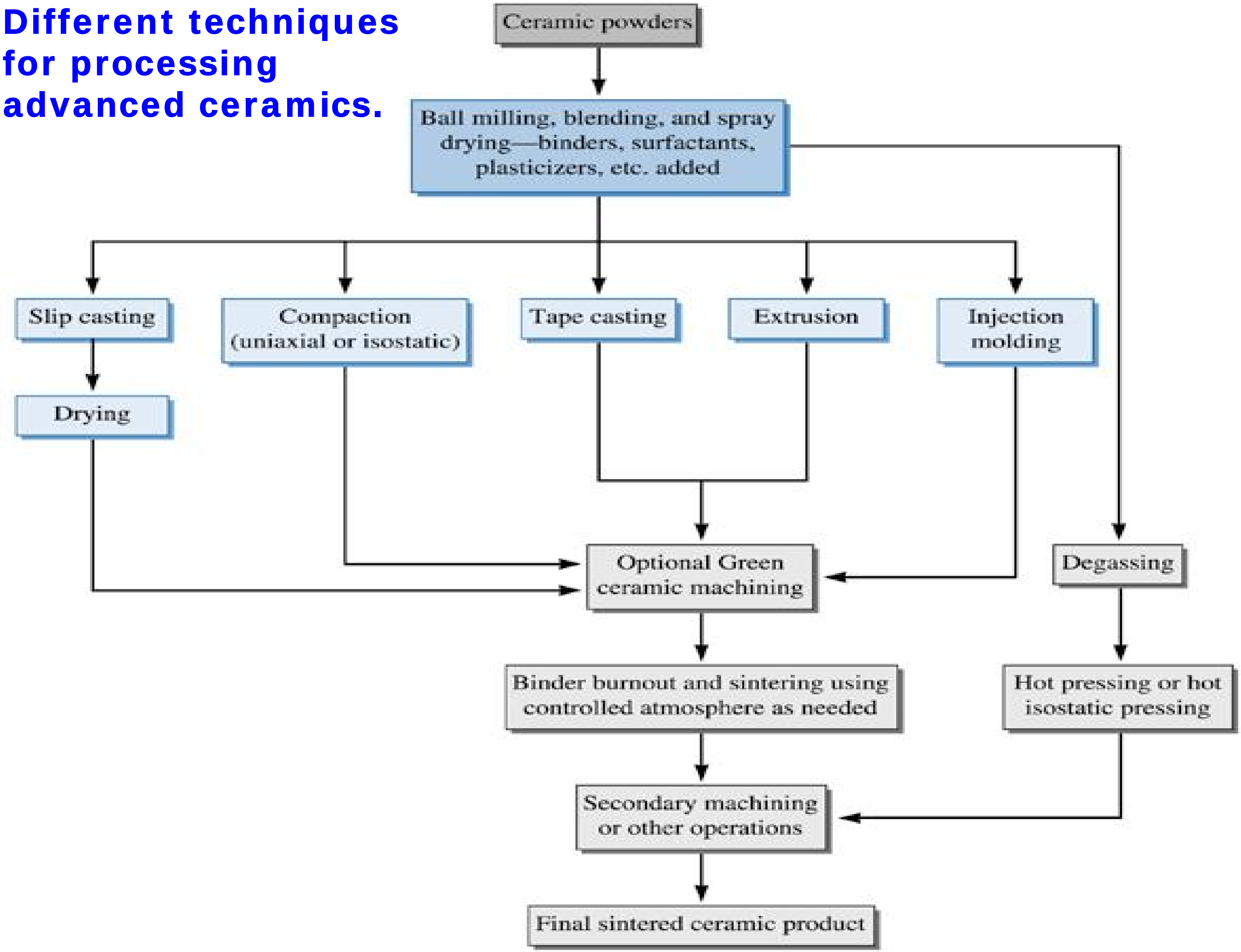
Forming Processes

- Pressure Fabrication:
  - Conventional Pressing
  - Isostatic Pressing
- Plastic Forming:
  - Extrusion
  - Jiggering
  - Plastic Forming
- Slip Casting:
  - Slip Casting
  - Pressure Casting
  - Tape Casting

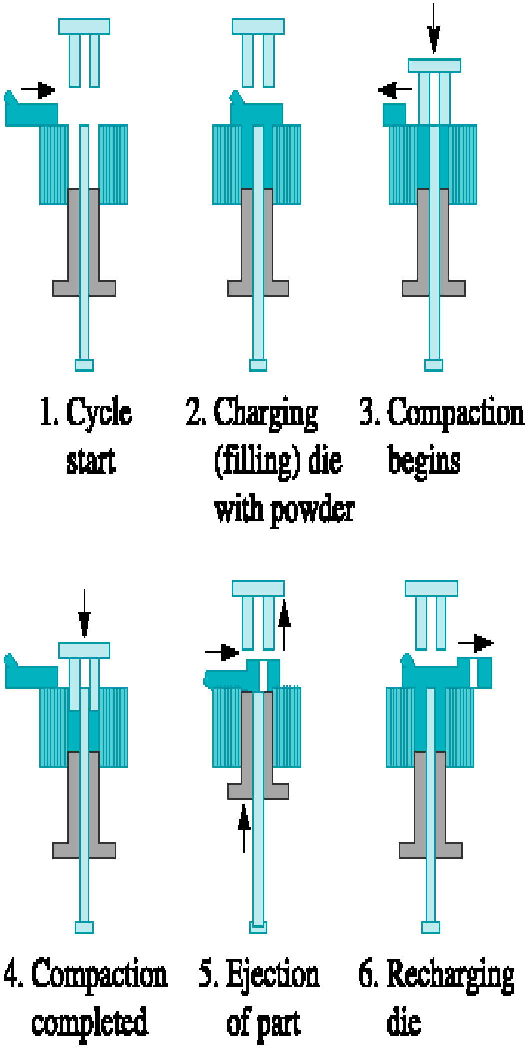
Different Forming Processes



Different techniques for processing advanced ceramics.



Uniaxial Pressing

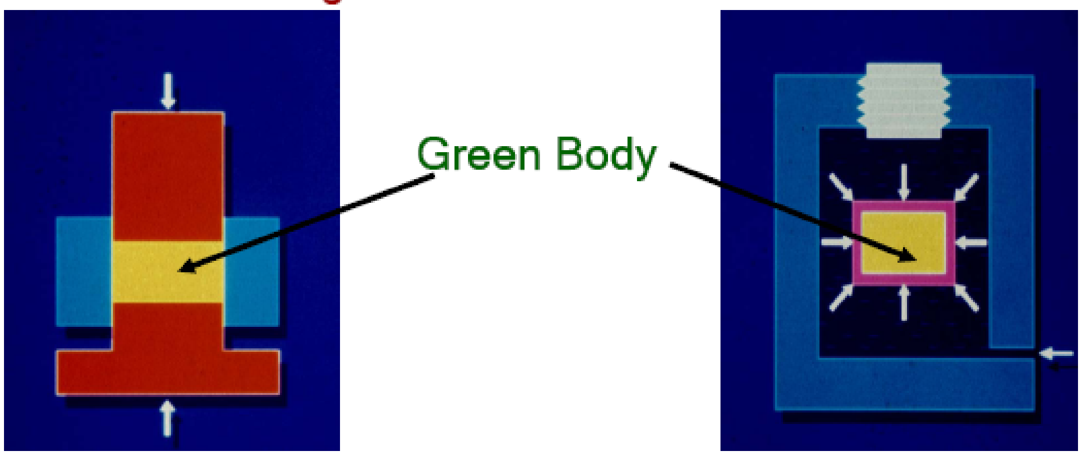


(a)

Compaction – Pressing versus Isopressing

Uni-axial Pressing

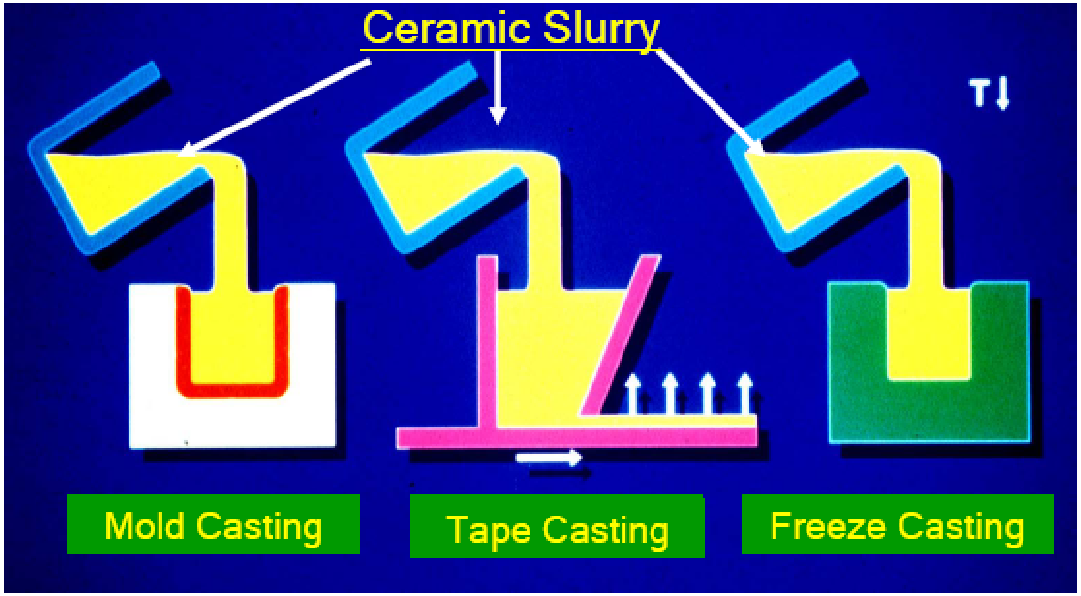
Isostatic Pressing



<u>Limitations</u>
Density variation
Die wear/Contamination
Cracking

<u>Advantages</u>
Homogeneous pressure distribution
Compaction uniformity
Enhanced shape capability

"Liquid" Shape Forming



Critical Factors

Slip (slurry) consistency, viscosity, entrapped air, chemical reactions, drain properties, shrinkage, release properties, strength of the cast-shape, etc.

Processing Additives in general

➔Deflocculant
➔Coagulant (to control agglomeration)
➔Binder/flocculant
➔Plasticizer (for binder)
➔Lubricant
➔Wetting agent (aid dispersion)
➔Antifoam
➔Foam stabilizer
➔Antistatic agent
➔Chelating agent/precipitating agent (to inactivate undesirable ions)
➔Antioxidant

Processing Aids

TABLE 21.3 Binder Viscosity Grade and Molecular Weight Guidelines

Process	Viscosity Grade[a] (mPa · s)	MW (kg/mol)
Spray drying/pressing	Low-medium	8–50
Casting		
Slip	Medium-high	20–300
Gel	Very low-medium	3–20
Tape casting	Medium-very high	100–1000
Extrusion	Medium-high	100–500
Injection molding	Medium (average value)	20–50

[a]Based on a 2-wt % solution.

Processing Pressure

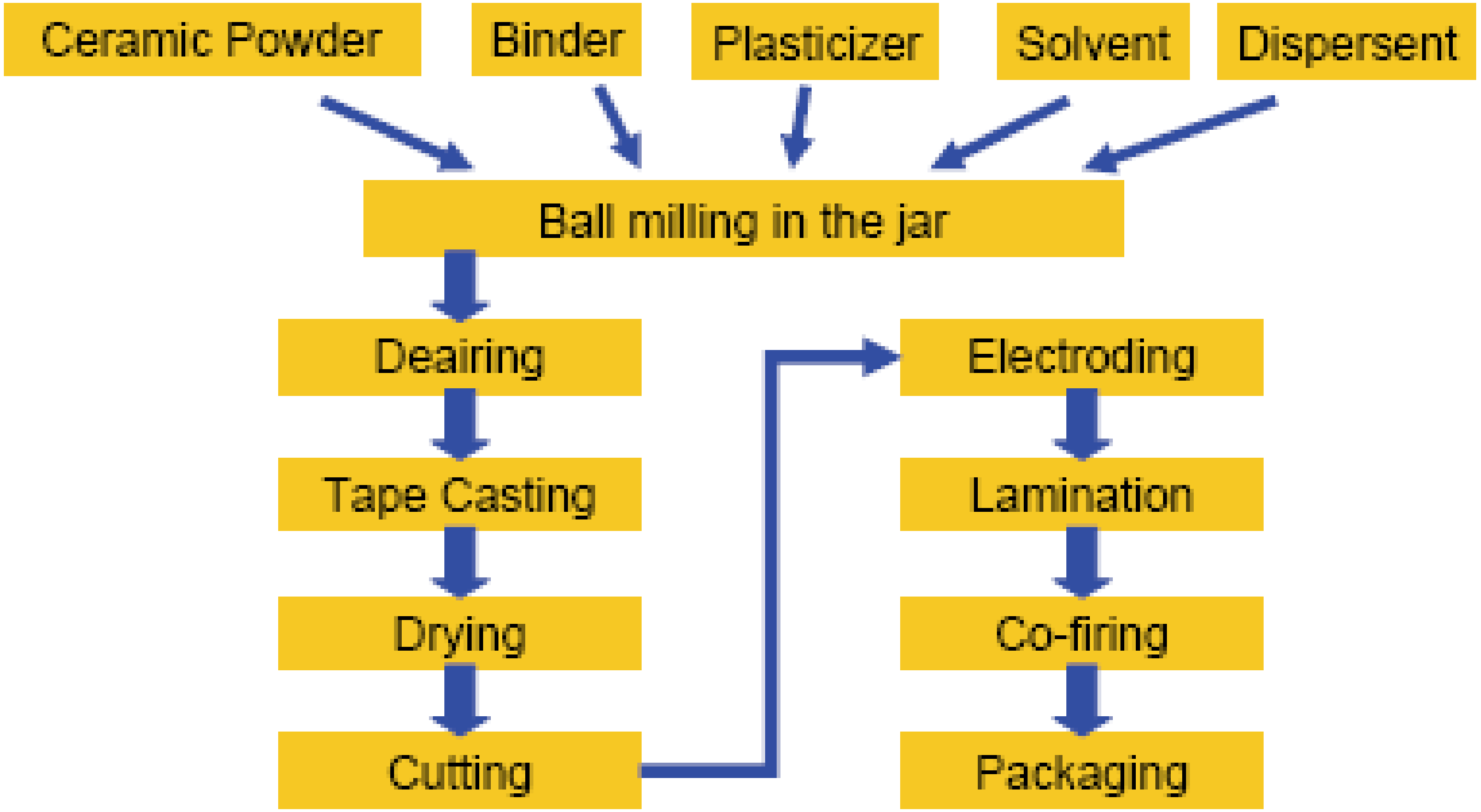
TABLE 21.5 Nominal Pressures and Shear Rates in Forming

Forming Process	Pressure (MPa)	Shear rate (1/s)
Pressing		
Roll/isostatic	>150	
Metal die	<100	
Plastic forming		
Injection molding	Varies	10–10,000
Extrusion	<40	10–1000 (die) 100–10,000 (die-land
Casting		
Slip (mold suction)	<0.2	<10 Pouring/draining
Slip (slurry pressurized)	<10	<100 Pumping
Slip (vacuum on mold)	<0.7	<10 Filling
Gel	<0.1	<10 Filling
Tape	<0.1	10–2000

In General

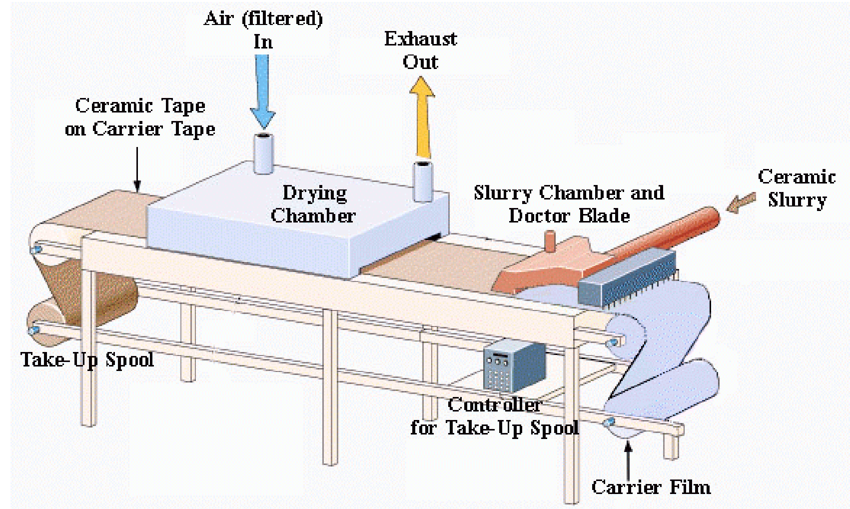
- Both technical and economic factors should be considered.
- Microstructure control is a critical issue.
- Process window reflects the ease of control; (reliability, reproducibility issue)
- Cost ~ 1/ yield
- There are often more than one process to choose for a specific ceramic product. → meaning comparison of various factors

Tape Casting

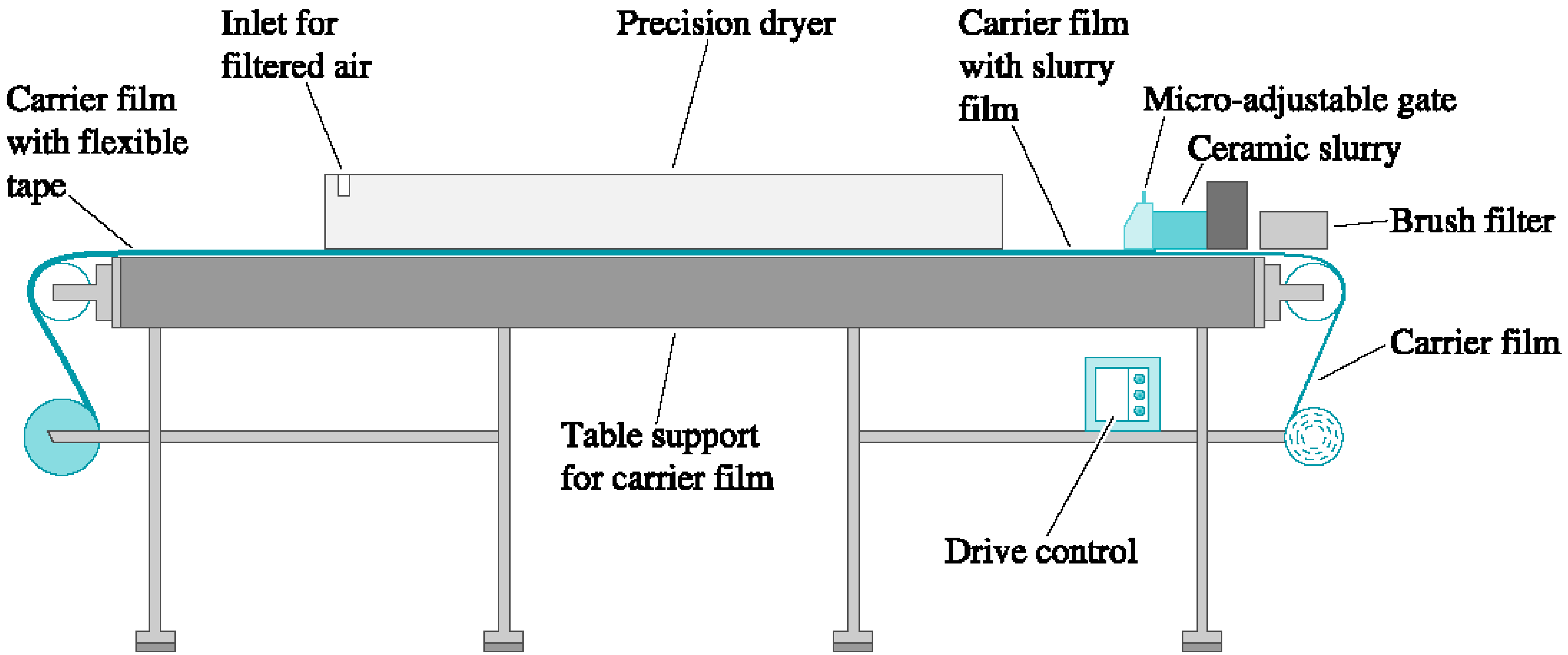


Introduction- Tape Casting

- Mass production
  - Continuous processing
- Easy fabrication
  - Stacking films
- Co-sintering
  - Lamination



Tape Casting



Tape Casting Machines

http://www.glass-ceramics.uni-erlangen.de/Staff/Research/Functceramics/

http://www.nrel.gov/ncpv/pdfs/26122.pdf

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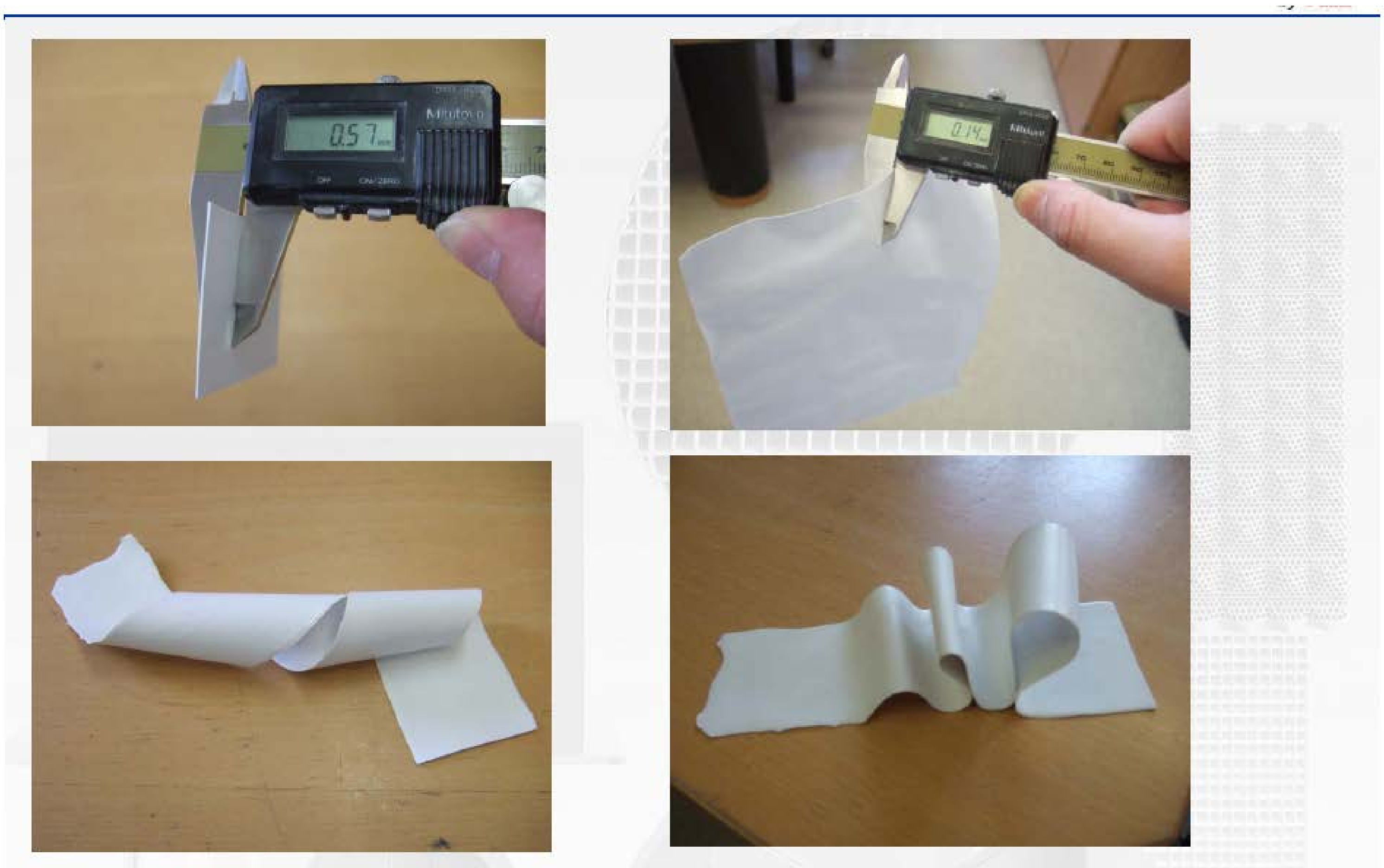
What comes out the other end



Plastic Forming: Extrusion and Injection Molding

- Similar to plastic forming technique, suitable for large scale, continuous production

- Need polymer additives, to make their behavior similar to plastic materials

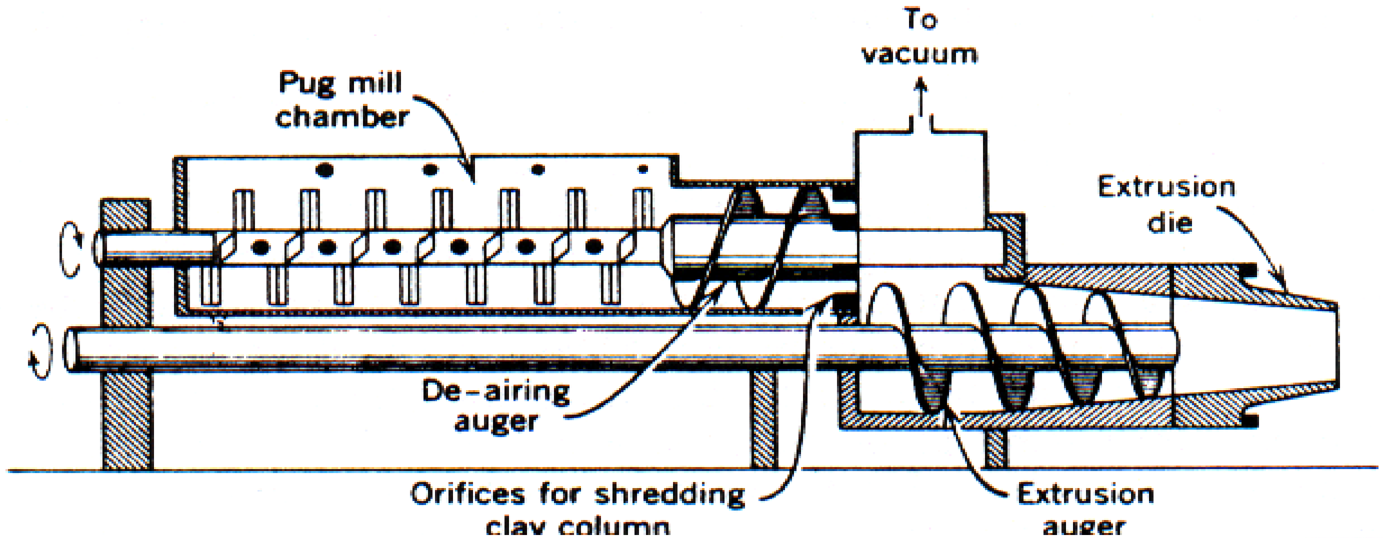
- Extruded products: tube, paltes (tile), brick, insulator (ring shape), catalyst extrudate (pellet) etc.

- Injected products: mostly small objects, and small, complex shape with thin walls

Extrusion of Ceramics

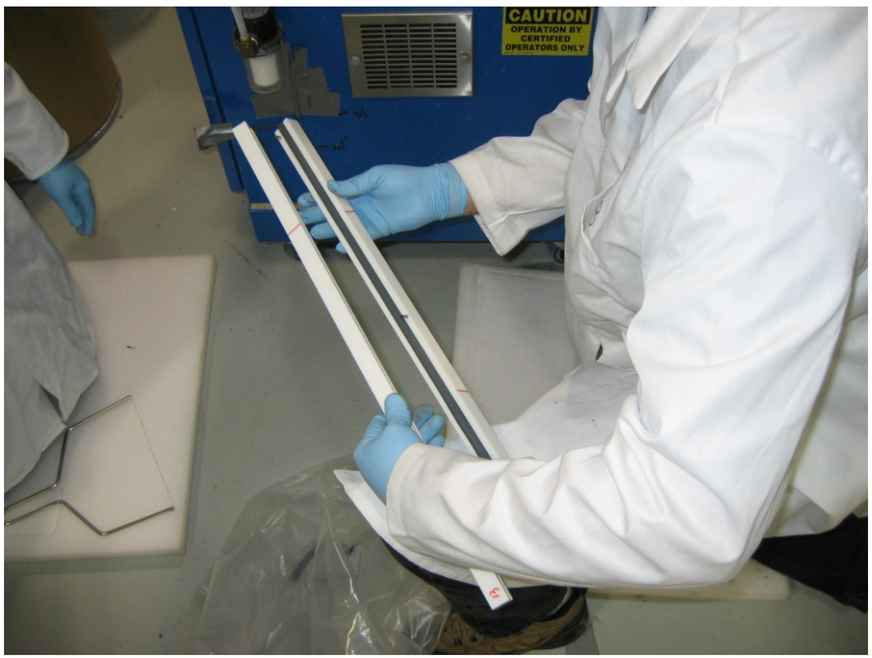
- Usually mix ceramic powder with polymer binder first, then add solvent to make paste for extrusion

- High shear mixer is often needed; screw feeder also has good mixing effect; can use piston extruder too



Extrusion

- Hydraulic Extruder
- Tube Holders



Method

- The dough is created by mixing the ceramic powders, polymer binders and wetting agent.
- A vacuum is usually applied to the mixing chamber
- Extrusion is performed using a ram or screw extruder with an die of the correct dimensions.
- The extrudates are typically dried quickly and uniformly, usually into tube holders,

Extruded Shapes

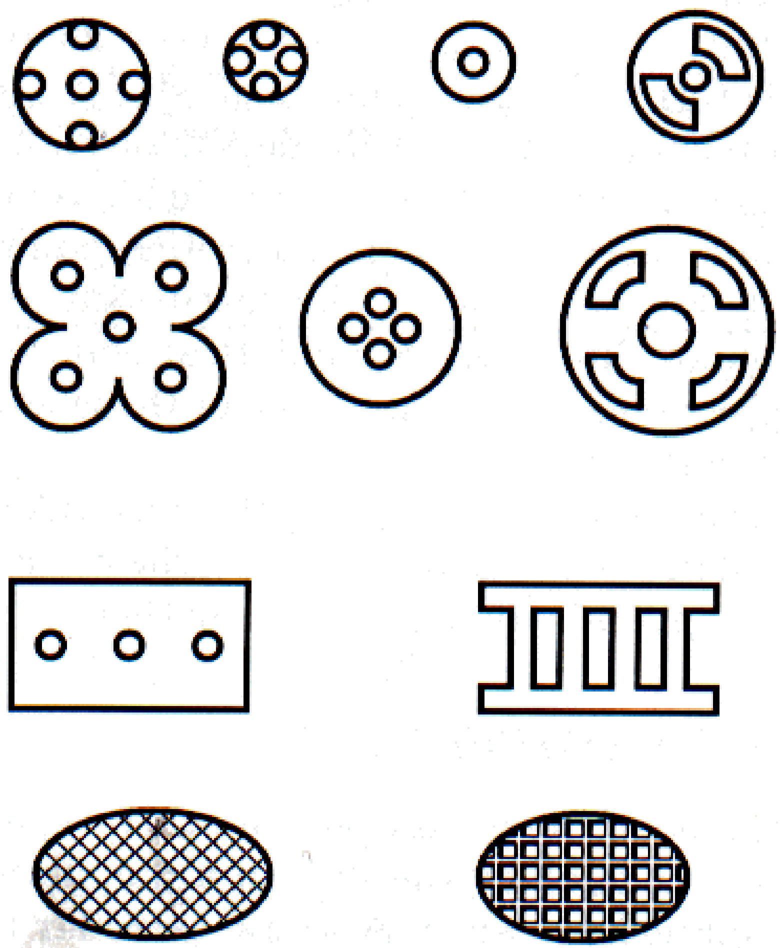
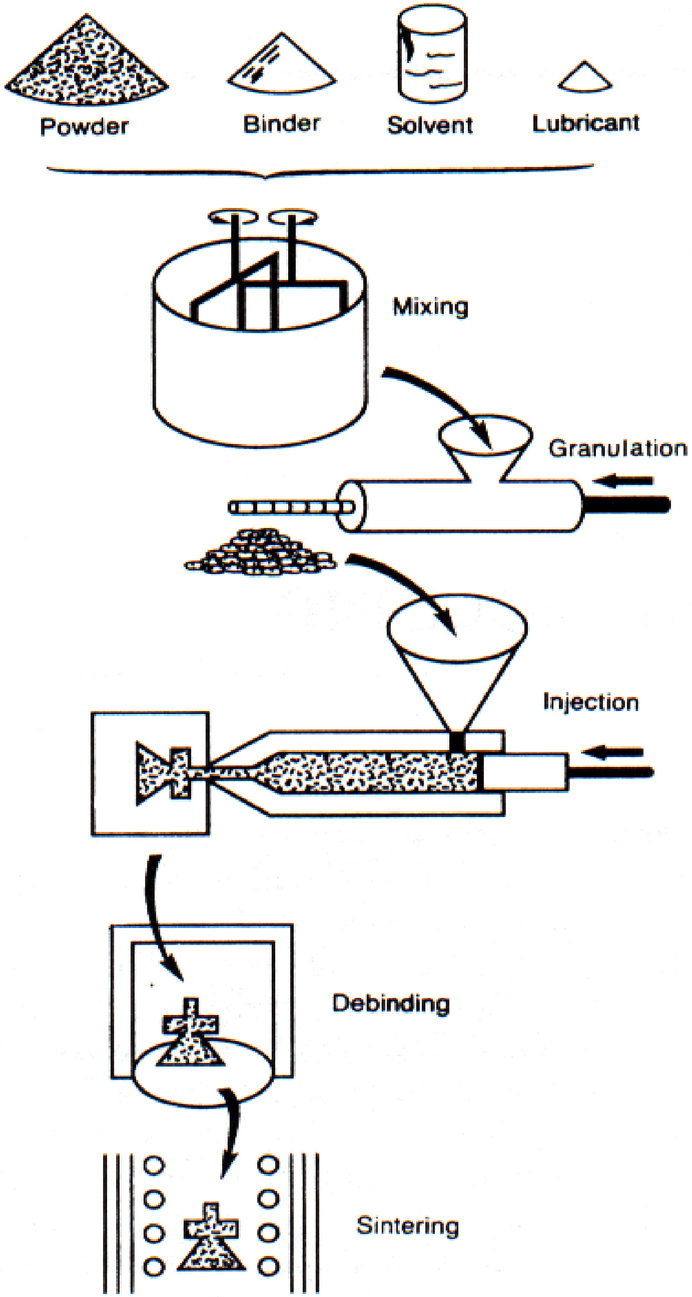


FIGURE 13.20 Extruded ceramic shapes.

Mixture

- Powder ground to appropriate size
- Organic binders
- Plasticizers (similar to above)
- Liquid phase (water or organic)
- Coagulant (typical, but not always)
- Lubricant to reduce shear pressure
- Bodies are elastic-plastic in nature

Large Scale Production - Acumentrics



- Injection molding is similar but the extrudate is injected into a shape, and then removed.

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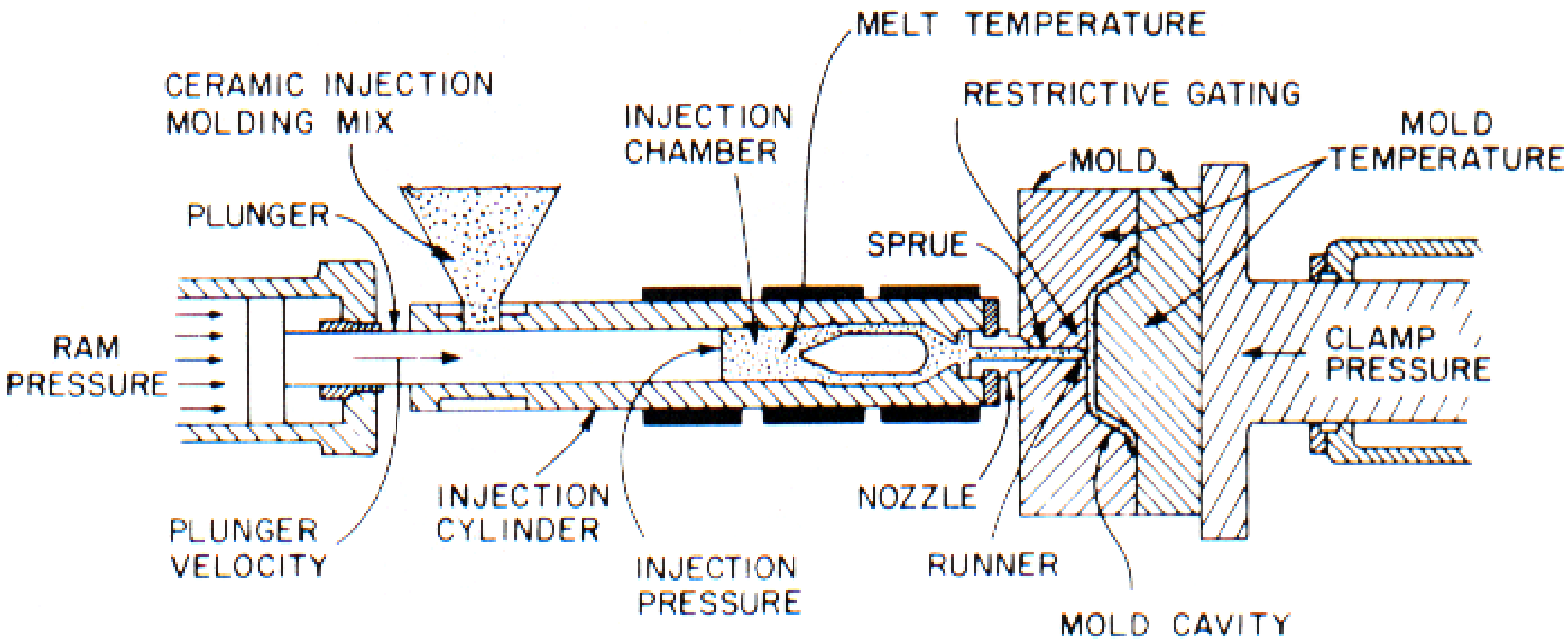
Plunger Type Injection Molding Machine



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Binder Systems Used

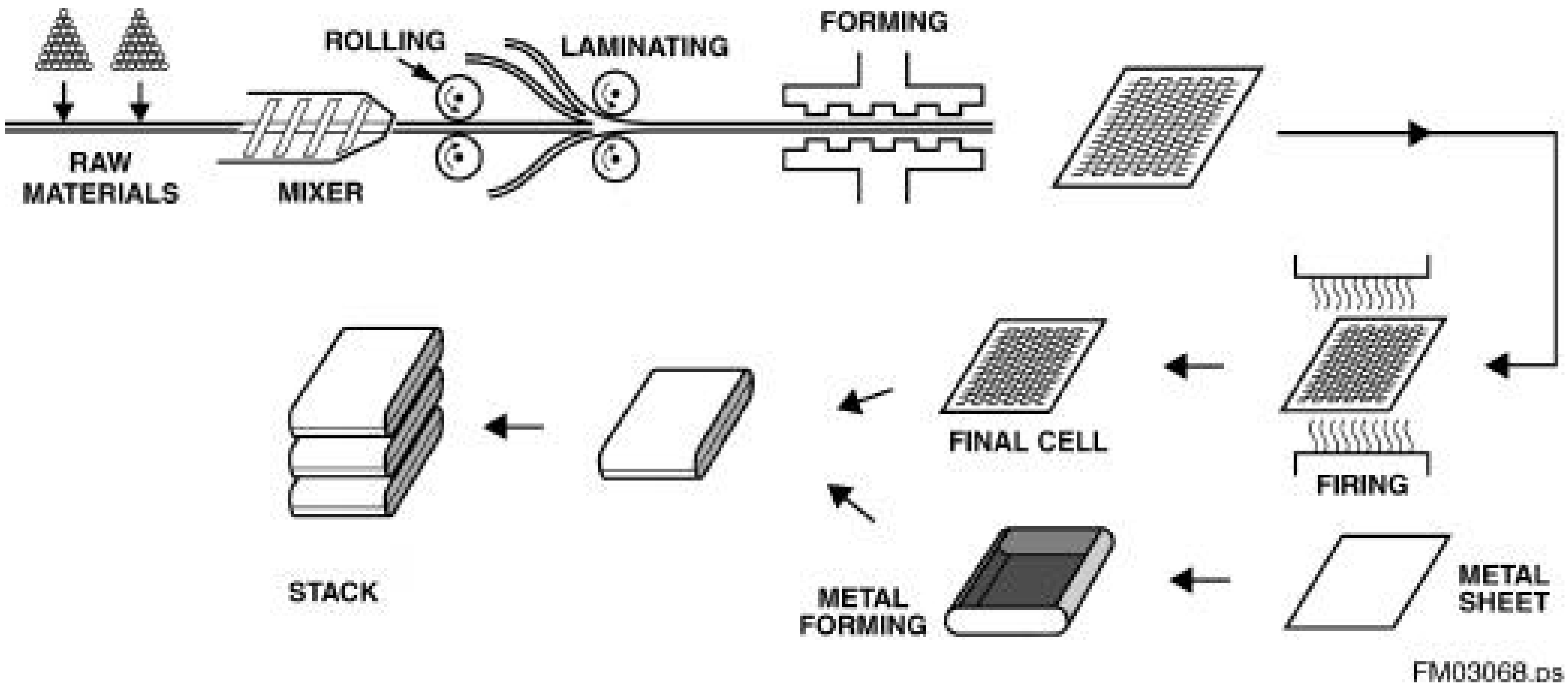
- Many binder system contains more than one compound for better rheology; viscosity < 10^5 mPa.s on molding
- Burning off these organics is an important work afterwards

Table 24.1 Binder Systems for Injection Molding (wt %)

Type	Binder #1/Binder	#2 Solvent/Plasticizer	Lubricant
Wax	Paraffin wax (70%) Microcr. wax (20%)	Methyl ethyl ketone (10%)	—
Resin	Polypropylene (67%) Microcr. wax (22%)	(Molten wax)	Stearic acid (11%)
Resin	Polystyrene (45%) Polyethylene (5%)	Vegetable oil (45%)	Stearic acid (5%)
Epoxy	Epoxy resin (65%) Paraffin wax (25%)	(Molten wax)	Butyl stearate (10%)
Aqueous	Methylcellulose (4%)	Water (96%)	

Source: R. M. German, *Powder Injection Molding*, Metal Powder Industries Federation, Princeton, NJ, 1990.

Calendar Rolling



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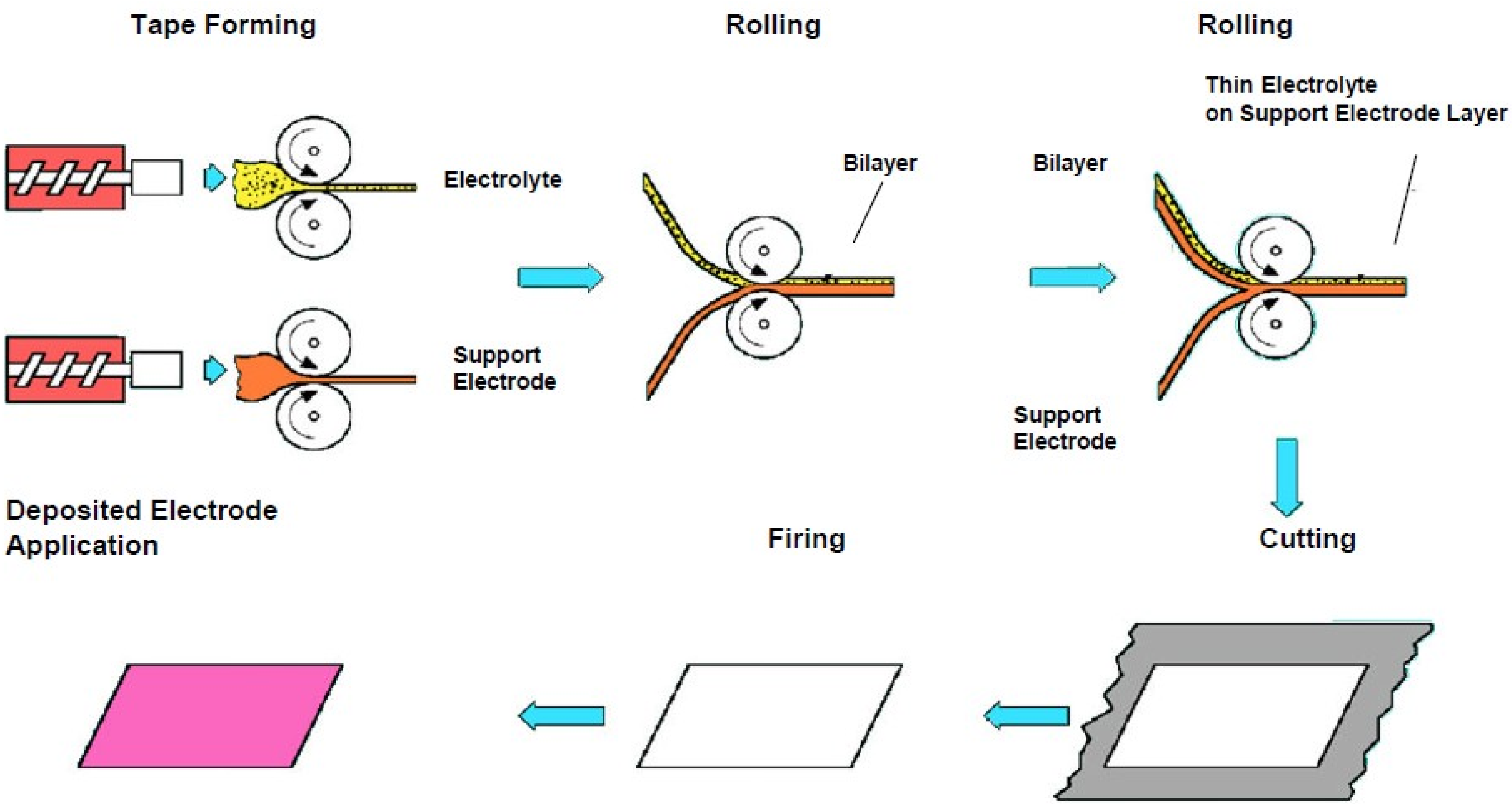
Tape Calendaring



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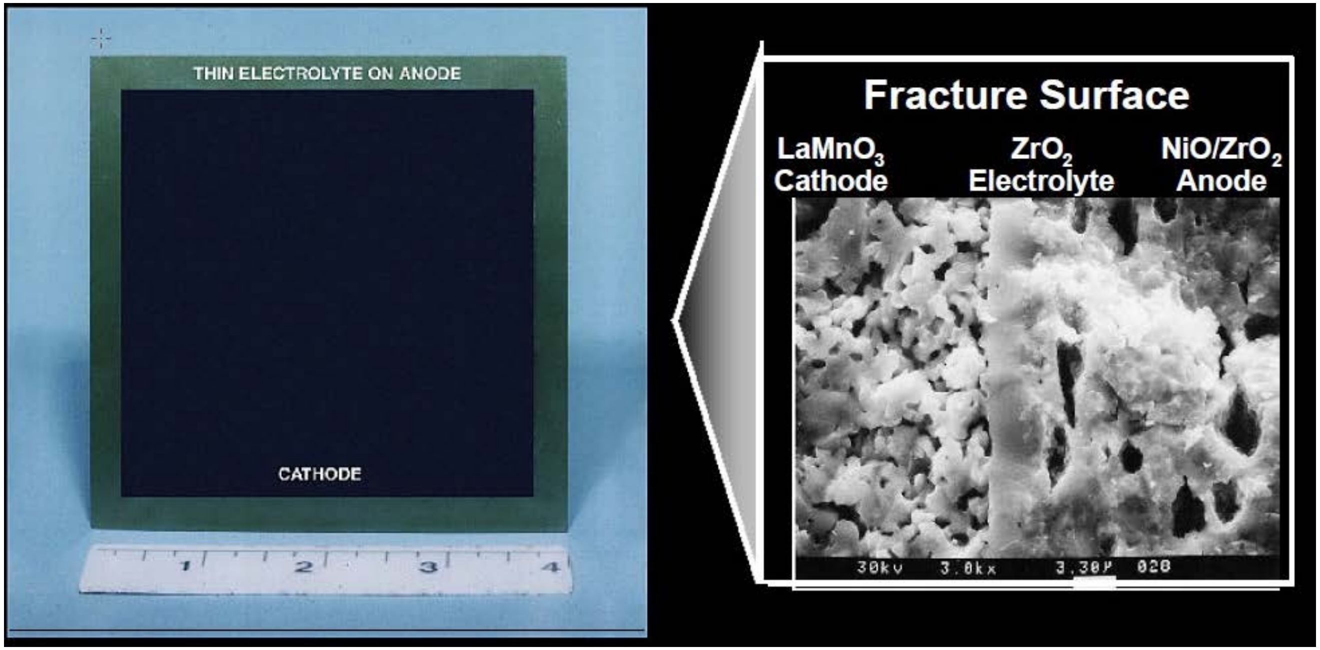
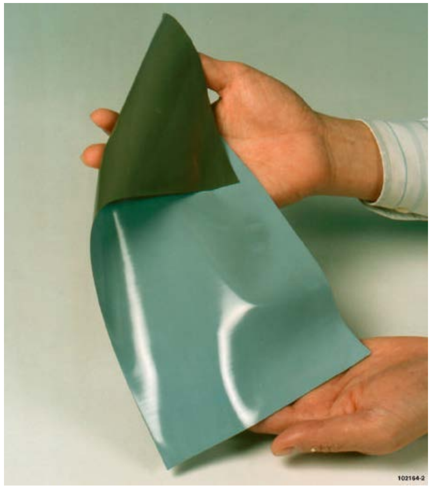
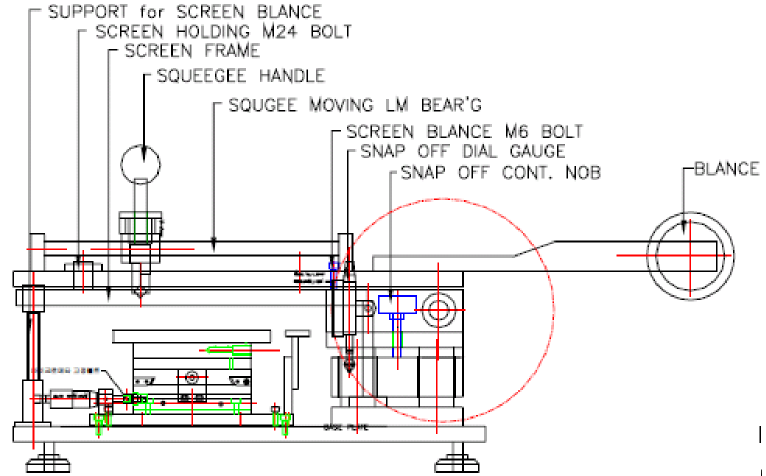
Cells Produced Via Extrusion and Rolling





Introduction- Screen Printing

- Cost-effective route
- Mass production
- Easy to make thin layers



X. Ge, Journal of Power Sources, 159, 1048-1050 (2006)

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Dip Coating Tubes

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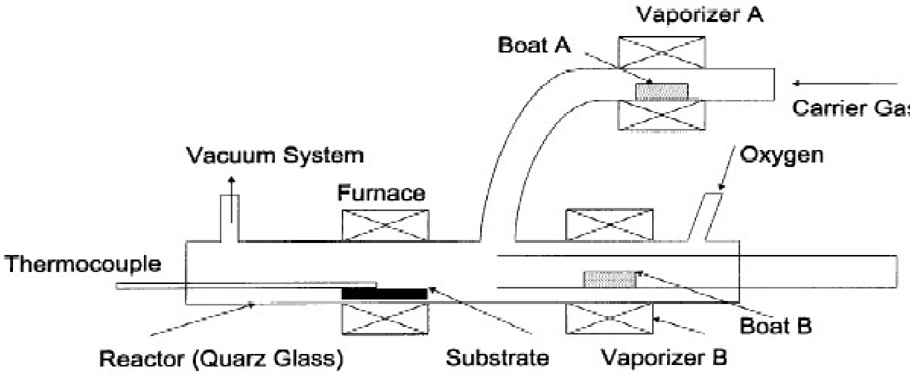
CVD/EVD

- There are two main chemical deposition techniques:
  - Chemical Vapor Deposition (CVD) and
  - Electrochemical Vapor Deposition (EVD).
- CVD is a chemical process in which one or more gaseous precursors form a solid material by means an activation process.
- EVD is a modified CVD process, originally developed by Westinghouse.

Chemical Vapor deposition

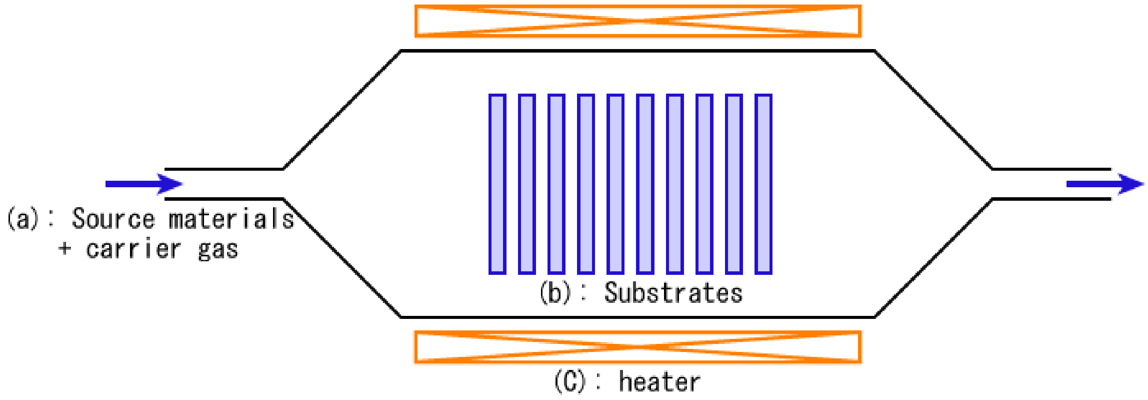
- The reactant vapors are (1) transported to the surface of a substrate and (2) adsorbed on the substrate surface where (3) the chemical reaction leads to a solid product for (4) crystal growth.
- Halogen compounds such as ZrCl and YCl, metal-organic compounds such as metal alkoxides or β-diketones have been used as precursor materials.



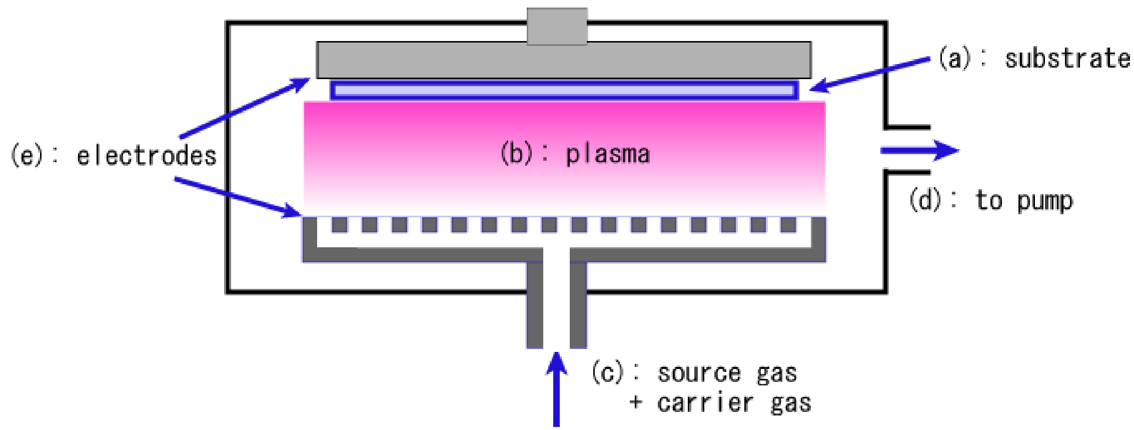
Schematic diagram of a CVD apparatus for preparation of YSZ films

Other CVD Techniques

Hot-Wall thermal CVD



Plasma assisted CVD



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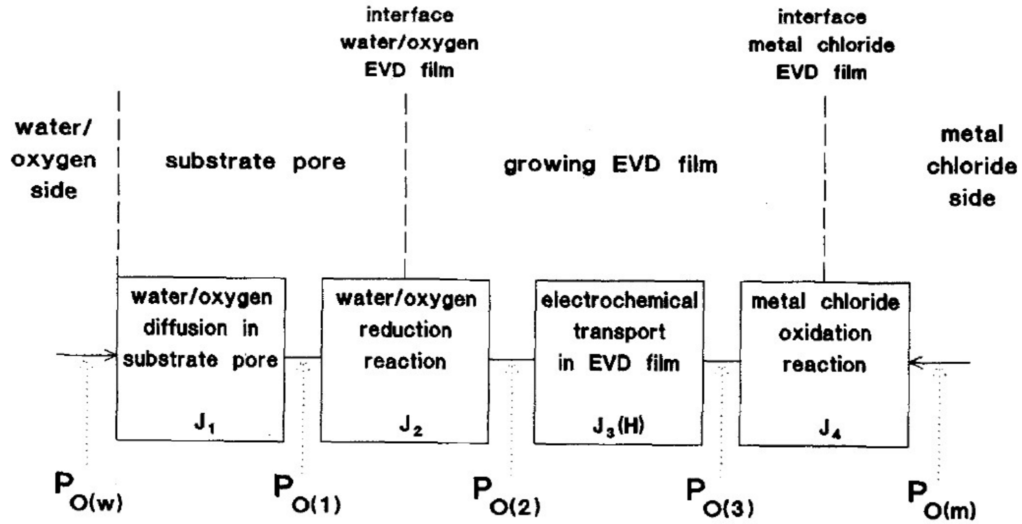
Electrochemical vapor deposition

- EVD is a two-step process:
  - The first step involves involves pore closure by normal CVD type reaction between the reactant metal chloride vapors and water vapor or oxygen.
  - Film growth via electrochemical potential gradient across the film.
  - Oxygen reacts with the metal chloride vapors to form metal oxide.
- Good for producing uniform and gas tight layers



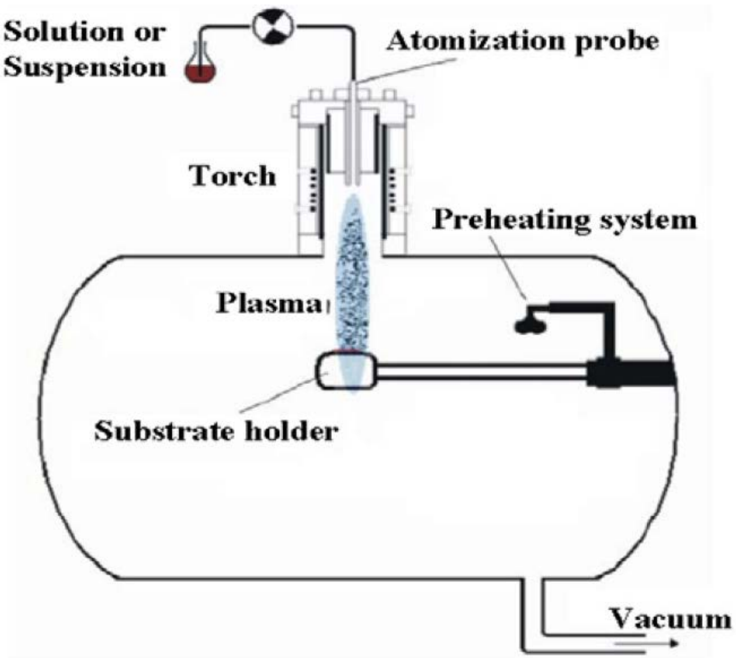
4 Stages of EVD.
(First stage is similar to CVD)

Plasma Spray

- Plasma Spray technology:
  - a suspension or solution of precursor components is fed to an induction plasma torch
  - directly gas atomized into the plasma through an atomization probe.
  - The whole inflight process (atomization, drying, and melting associated with or without chemical reactions) occurs in approximately 10 ms.
  - The powders are either collected for further application or directly deposited onto a substrate.

Plasma Spray of GDC

- Cerium nitrate hexahydrate and gadolinium nitrate hexahydrate used
- Dissolved into water to prepare a solution
- Plasma Spray



Sintering

Green Body → **Densification** (ΔT) → Component

- Rearrangement of the powder particles
- Densification of the green body (decrease of porosity)
- Coarsening of the grains (grain growth)

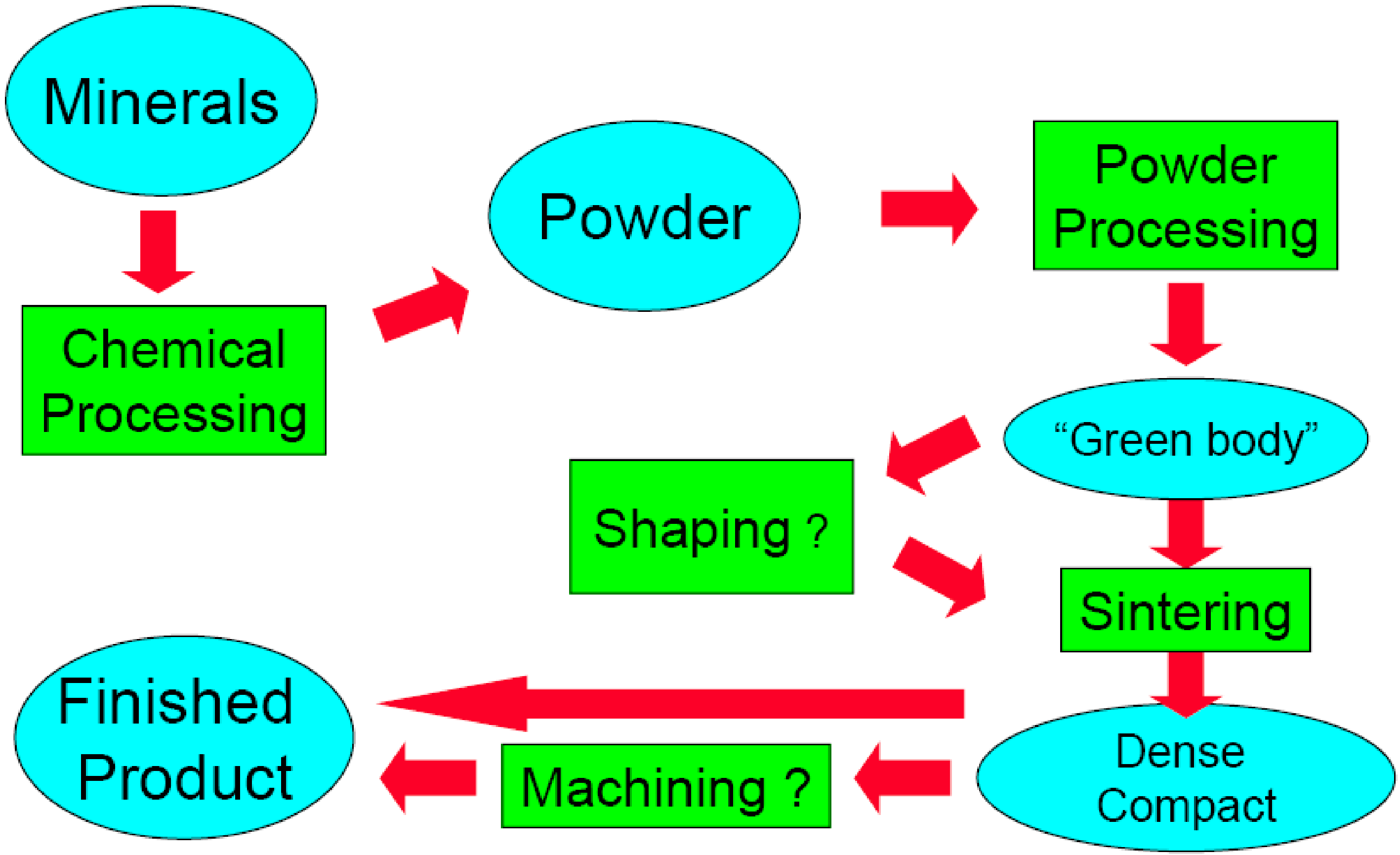
Driving force = Reduction of the free surface energy

surface-E (powder system) > grain boundary-E (dense body)

Sintering of Ceramics – Diffusion Limiting

- Because of their high melting points, ceramics are sintered
- Feedstock is usually a powder
- Powder handling and powder processing are required
- General overview of techniques is shown over

Overview

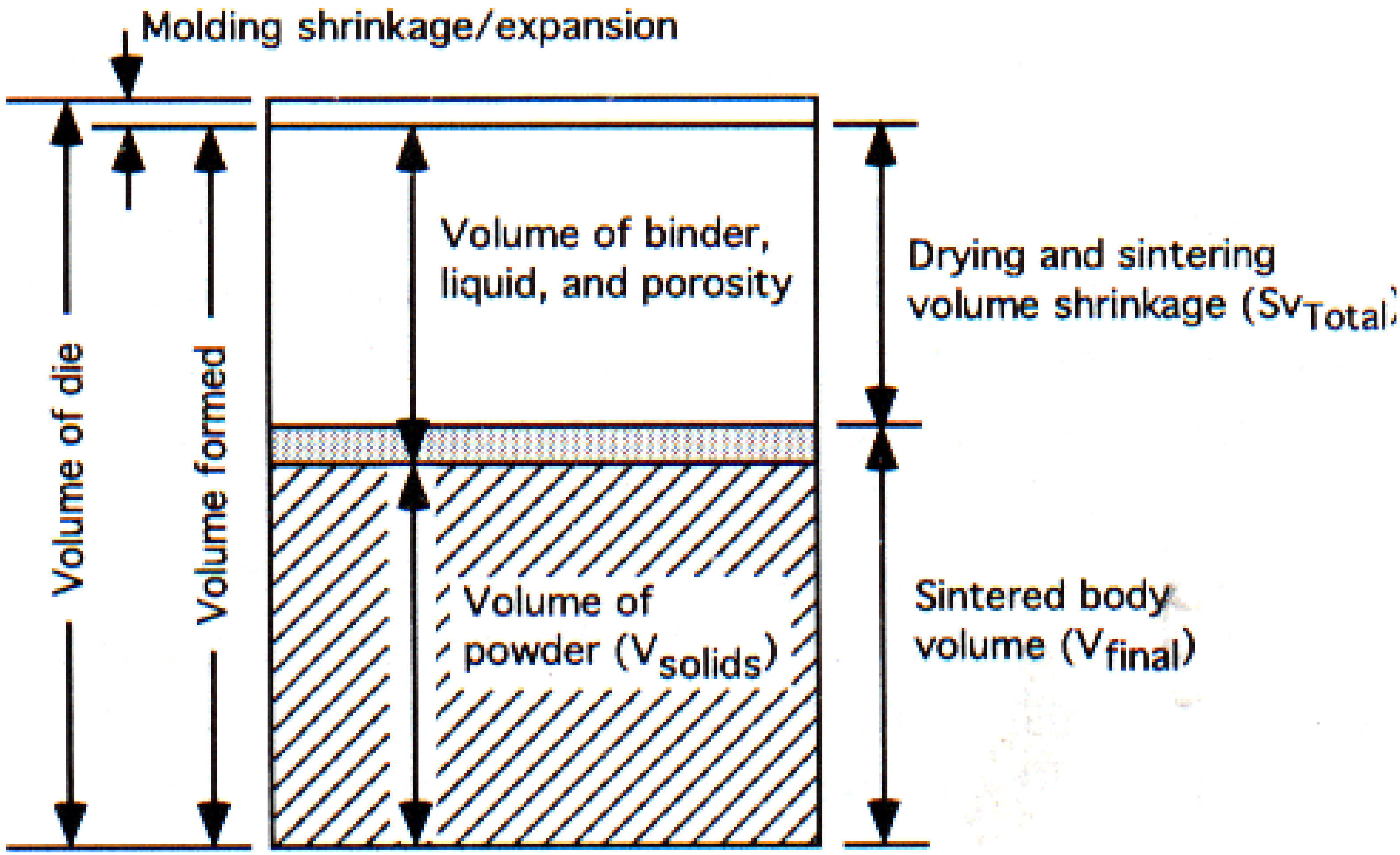


Minerals
Chemical Processing
Powder
Powder Processing
"Green body"
Shaping ?
Sintering
Dense Compact
Machining ?
Finished Product

Key Steps

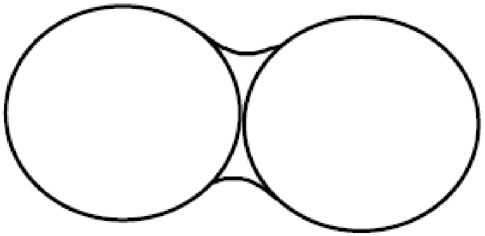
- Powder synthesis
- Powder handling
- Green body formation
- Sintering of green body
- Final machining and assembly

•Shrinkage may not be isotropic!



Green Body Formation

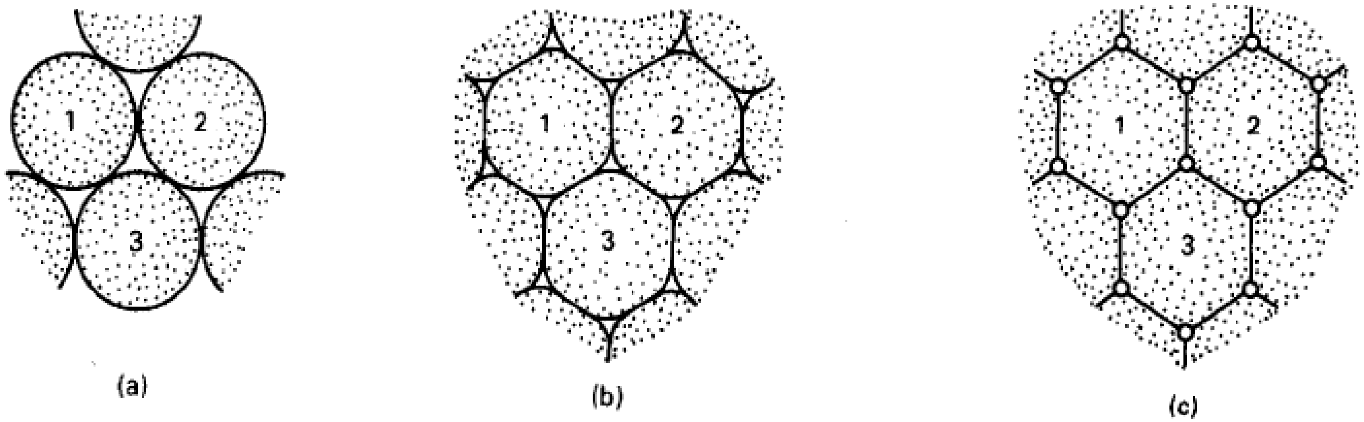
- In the presence of water vapor, liquid condenses in negative curvature regions and holds particles together
- Can also mechanically press to get rough particles to "interlock"
- Can add polymer binders and lubricants
- Can reach this stage from slipping



Sintering

- This is the conversion of a ceramic green body into a solid by heating
- Process consists of mass transfer deforming the ceramic powder, filling interparticular voids and causing overall shrinkage of the compact
- Process is thermally activated and controlled by diffusion

Sintering



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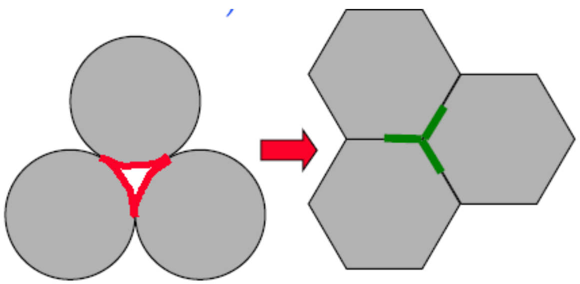
Sintering Driving Forces

- Sintering is driven by reduction in surface energy
- Two surfaces (green body) replaced by one (lower energy) grain boundary (sintered solid)
- Driving force is approximately:
  - Surface energy/volume of particle

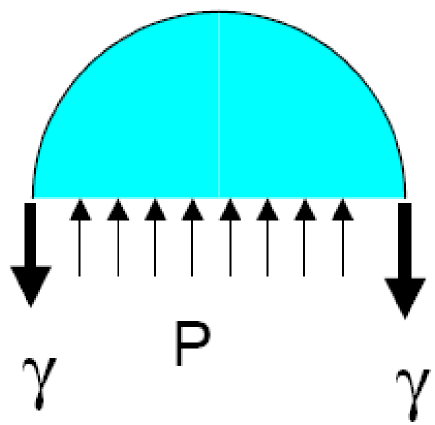


$$E/V \approx \frac{\gamma(4\pi r^2)}{(4\pi r^3/3)} = \frac{3\gamma}{r}$$

  - A typical ceramic has a surface energy of $1 Jm^{-2}$.
  - Thus the driving force for a $1\mu m$ diameter ceramic powder is approx. 3 MJm^{-3}

Surface Curvature Driving Forces

- Surface curvature (pressure) is the dominant driving force for sintering of ceramics
- The surface tension of a curved surface induces an internal change in gas pressure
- $P\pi r^2 = \gamma 2\pi r$
- $P = 2\gamma/r$



Surface Curvature Driving Forces

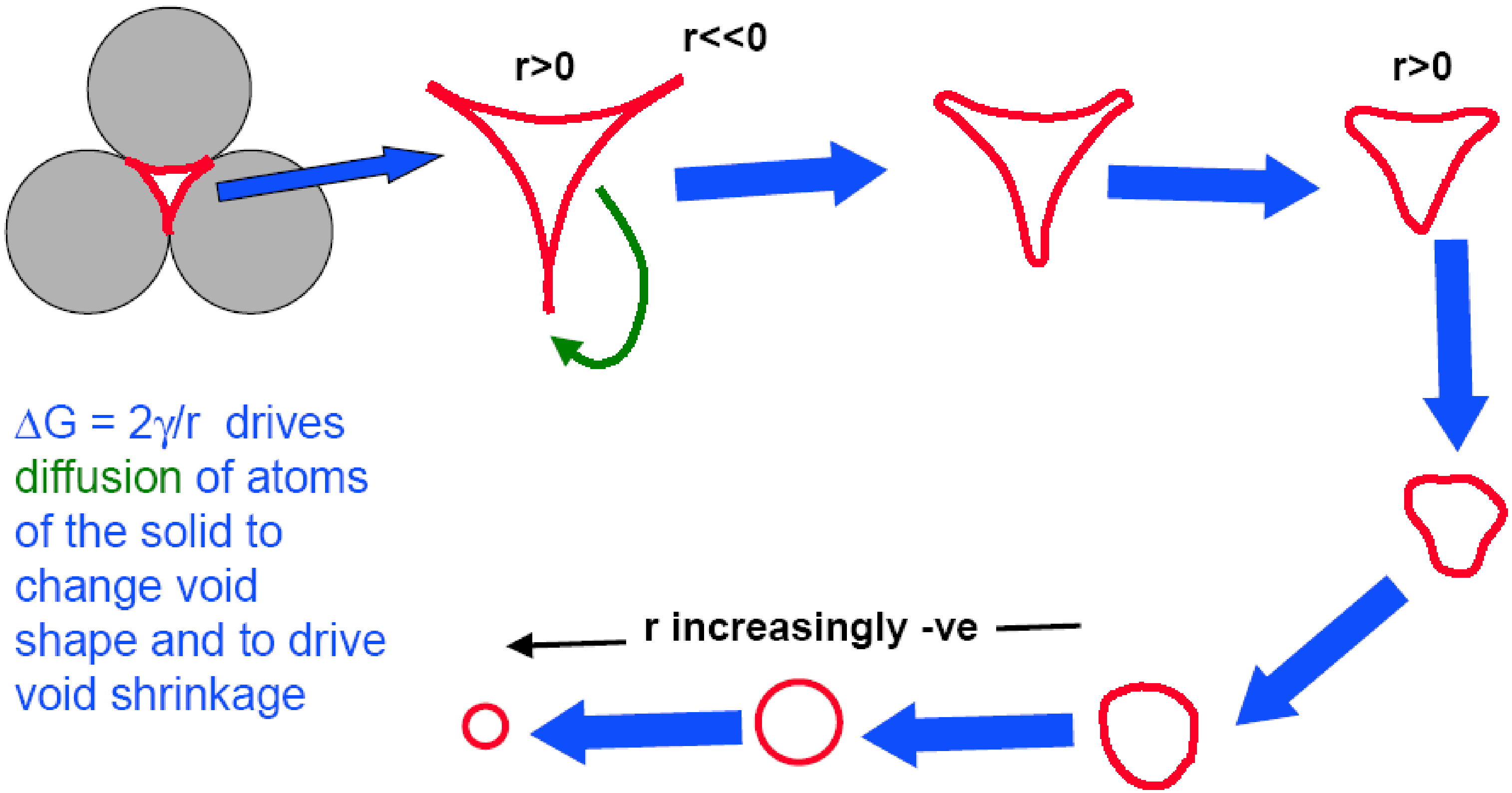
- In solid state there is an equivalent change in free energy/volume
- Viz:

$$\frac{dG}{dV} = \frac{dG}{dr} \cdot \frac{dr}{dV}$$

$$= \frac{dG}{dA} \cdot \frac{dA}{dr} \cdot \frac{dr}{dV}$$

$$= \gamma \cdot \frac{8\pi r}{4\pi r^2} = \frac{2\gamma}{r}$$

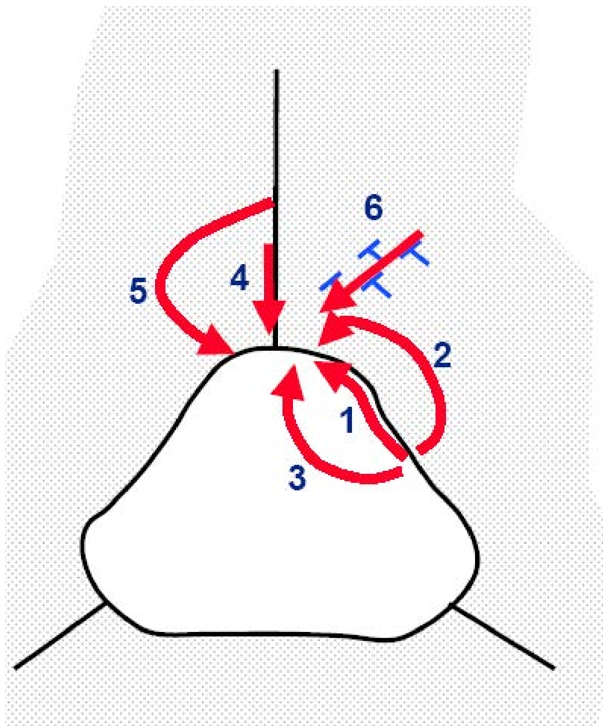
Surface Curvature Changes in Sintering



$\Delta G = 2\gamma/r$ drives diffusion of atoms of the solid to change void shape and to drive void shrinkage

Matter Transport in Sintering

	Path	From	To
1	Surface Diffusion	Surface	Neck
2	Lattice Diffusion	Surface	Neck
3	Vapour Transport	Surface	Neck
4	Grain Boundary Diffusion	Grain Boundary	Neck
5	Lattice Diffusion	Grain Boundary	Neck
6	Lattice Diffusion	Dislocations	Neck



N.B. Only 4,5,6 → densification

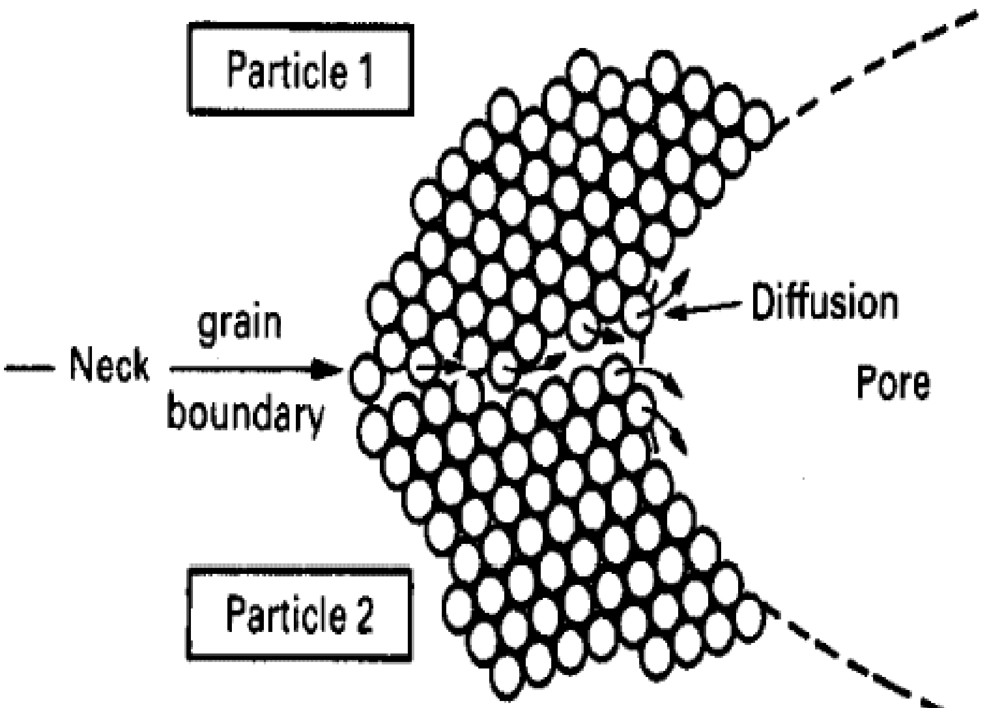
Densification

- Sintering mechanisms 1-3 do not lead to void shrinkage; they merely redistribute matter to minimize the curvature/surface area of the voids
- Mechanisms 4-6 take matter to the voids to fill them up, and give a density increase.
- Mechanism 4 (diffusion from the grain boundary forming between the particles to the neck) is usually the most effective

Sintering at the Atomic Level

- Densification occurs by the atoms diffusing from the grain boundary to the void surface so filling it up.
- Grain boundary is automatically “loose” and gives fast diffusion.
- Because matter is removed from the grain boundary, the powder particles approach and densification occurs

Sintering at the Atomic Level



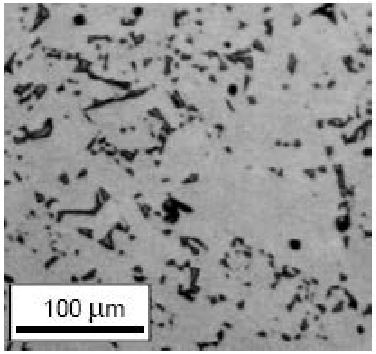
Speeding up Sintering

- Apply and external pressure; allows the particle approach to do the work (HIP, Hot pressing)
- Add sintering aids which coat particles. Choose a material with a rapid diffusion – often ones which form a glassy phase, of even a liquid, providing diffusional “short cut”
  - Silicates added to alumina
  - Glassy phases formed in traditional ceramics
    - Can ruin high temperature properties, though.

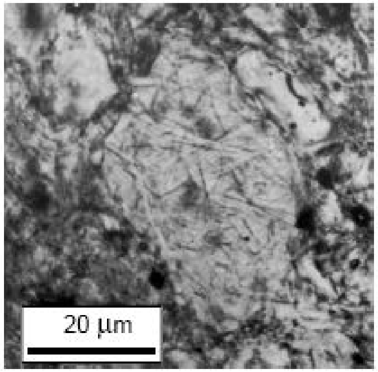
Liquid Phase Sintering

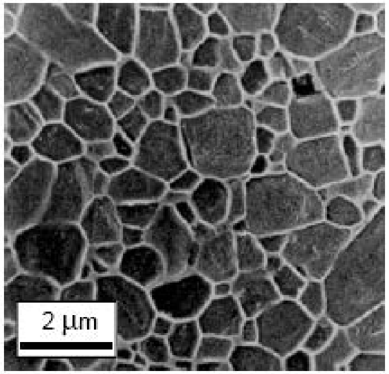
- If there is sufficient glass-forming sintering aid it may fully melt and wet the higher melting point constituents.
- The liquid then draws the solid together by the action of viscous flow driven by capillary pressure.
- Very important in traditional ceramics

Liquid Phase Sintering



remnant silicate glass at boundaries in 95% debased alumina





mullite crystals growing in feldspar (low m.p.) in whiteware

recrystallised YAG glass at boundaries in liquid-phase sintered SiC

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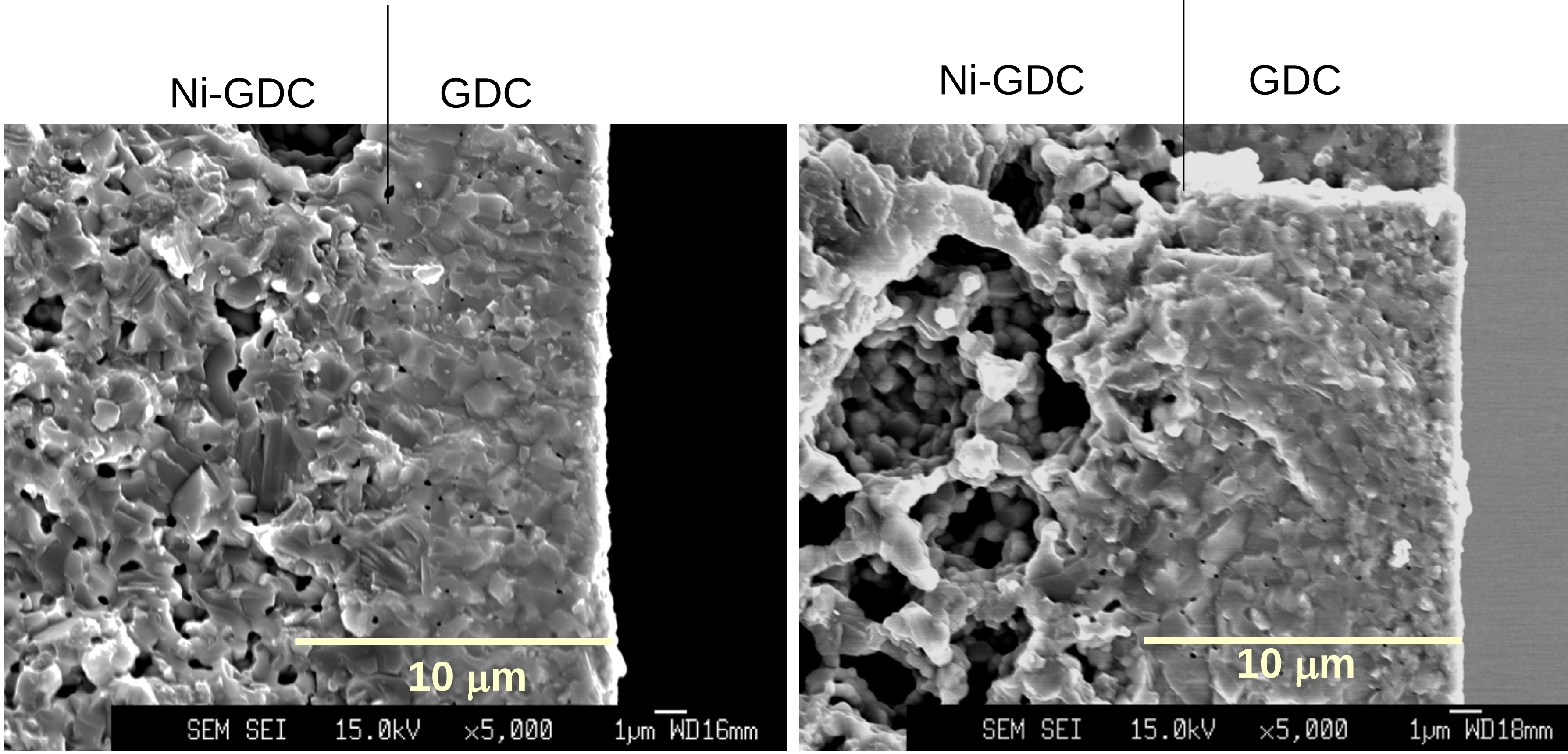
Microstructure of Anode and Electrolyte

PMMA 10 %

PMMA 40 %



SEM images of the cross-section between the electrolyte and the anode

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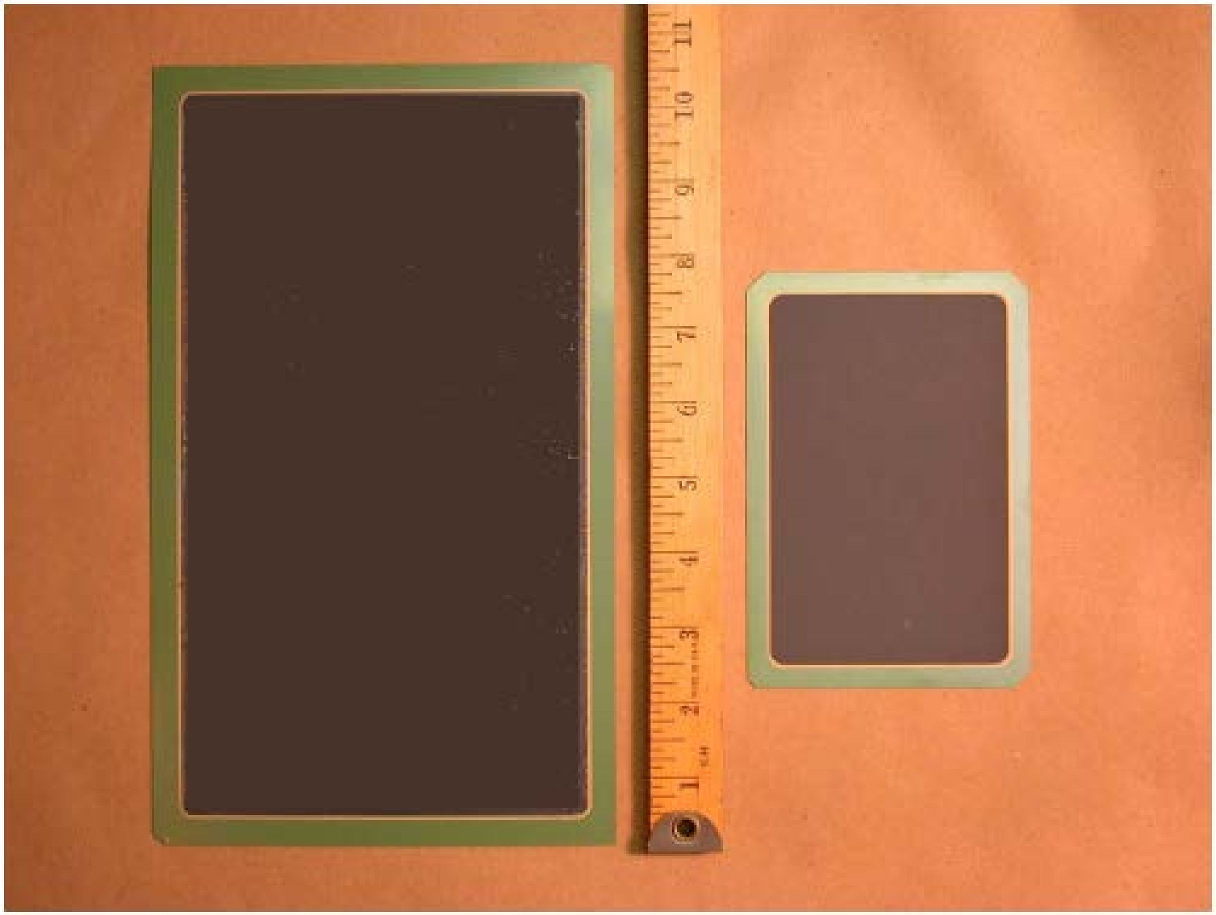
Cell and Stack Development Scale Up

Full-Scale

Full active area repeating unit for stack –for design and performance optimization

Scale-Up of Cell Active Area



Thank You !