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Ceramics: A General Overview

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ECerS Summer School 2015
June 17, 2015

MatSE
MATERIALS SCIENCE AND ENGINEERING
COLLEGE OF EARTH AND MINERAL SCIENCES

WE ARE:


Pennsylvania
Maryland
New Jersey
THE PENNSYLVANIA · STATE · UNIVERSITY
Penn State University Park

PENNSTATE 1855

WE ARE …

- Located in University Park, PA
- 17,000 faculty and staff
- 100,000 students
- Over $800 million in research spending[1]
- Largest student-run philanthropic organization, "THON" has raised over $114m for pediatric cancer research and patient care since 1973
- Known internationally for our football, ice cream and materials research!


Ph.D. student, Amra Tabakovic, examines fluorescent dyes encapsulated in nanoparticles.

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[1] FY2012

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MatSE @ Penn State

- 59 Faculty, Associated Faculty, and Research Associates
- 230 Undergraduate Students
- 150 Graduate Students
- 13 Interdisciplinary Research Centers (10 are NSF IUCRC)

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MatSE @ Penn State

- #8 ranked undergraduate program in U.S. [1]
- #11 ranked graduate program in U.S.[1]
- #1 in materials research spending [2]
- $73m in materials related research [2]
- $11m/year in research expenditures

[1] U.S. News & World Report 2014

[2] NSF FY2012

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Research Centers

- Battery and Energy Storage Technology Center
- Center for 2-Dimensional and Layered Materials
- Center for Dielectrics and Piezoelectrics
- Center for Innovative Materials Processing Through Direct Digital Deposition (CIMP-3D)
- Center for Innovative Sintered Products
- Center for Nanomedicine and Materials
- Center for Nanoscale Science (NSF MRSEC)
- Center on Optical Wireless Applications
- Center for Solar Nanomaterials
- Center for the Study of Polymeric Systems
- Electrochemical Engine Center
- Electrochemical Technologies Program
- International Center for Actuators and Transducers

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Research Centers

- Center for Nanomedicine and Materials (CNM)
- Center for Nanoscale Science (NSF MRSEC)
- Center on Optical Wireless Applications (COWA)
- Center for Solar Nanomaterials
- Center for the Study of Polymeric Systems (CSPS)
- Electrochemical Engine Center
- Electrochemical Technologies Program
- International Center for Actuators and Transducers (ICAT)

Millennium Science Center / MRI

Materials Research Institute (MRI)

MRI is a catalyst for multidisciplinary education and innovations in materials encompassing

- 5 Colleges
- 15 Departments
- 200+ Faculty
- 100 Researchers
- 800+ Graduate students
- 40,000 sq ft quiet labs shielded from vibration/electromagnetism
- 10,000 sq ft Class 1000/100 clean rooms
- 4,000 sq ft Collaborative space

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Millennium Science Center / MRI

Facilities include:

Nanofabrication Laboratory

Piezoelectric and pyroelectric complex oxides, epitaxial graphene devices and research, atomic layer deposition, lithography on curved surfaces, complimentary characterization techniques

Materials Characterization Laboratory

Fully-staffed, open access, analytical research facility

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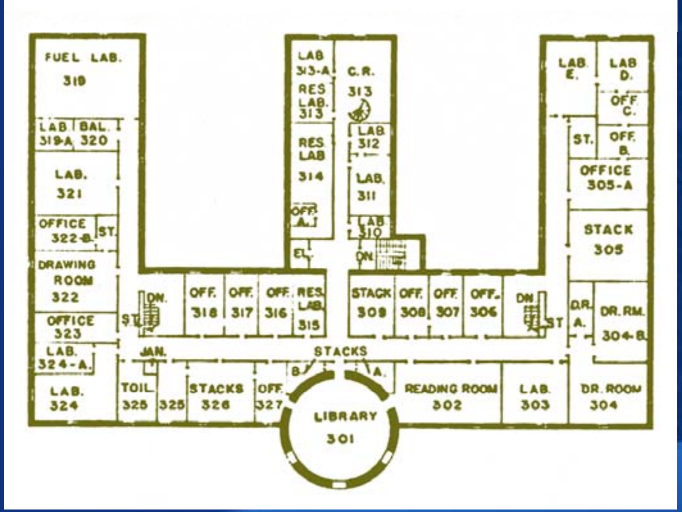
Steidle Building

Home to

- Faculty, Staff, Departmental offices
- Teaching labs, Computer lab
- Conference rooms
- Student meeting/common areas
- Advanced Processing Lab
- Mechanical Testing Lab



Built in 1929, last remodel 1940
image at left shows current footprint
(3rd floor)

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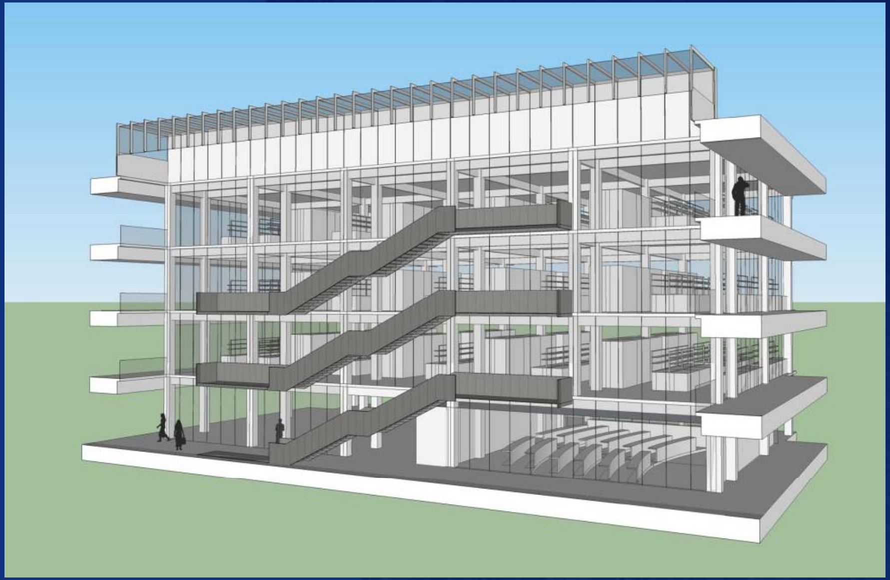
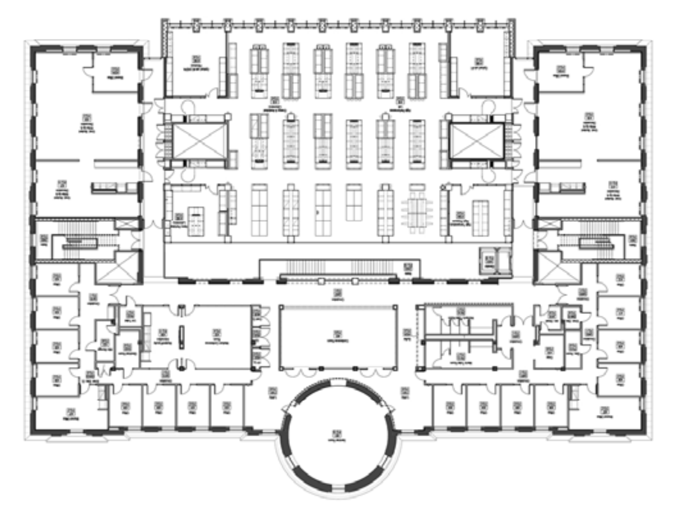
Steidle Building: Renovations



Renovations began in 2014!

- New glass atrium will span center of building, creating expansive lab space linked by central stairway
- Greatly expanded conference facilities, student meeting and study areas
- New auditorium classroom and computer lab
- New main entrance at rear of building



New floorplan shows central atrium replacing the 1940 addition

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Steidle Building: Renovations

Renderings of new 1st floor main lobby Area (above) exterior of new main entrance at what is currently rear of Building (left)

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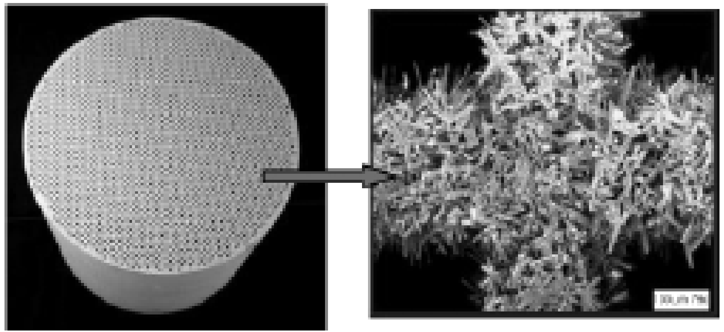
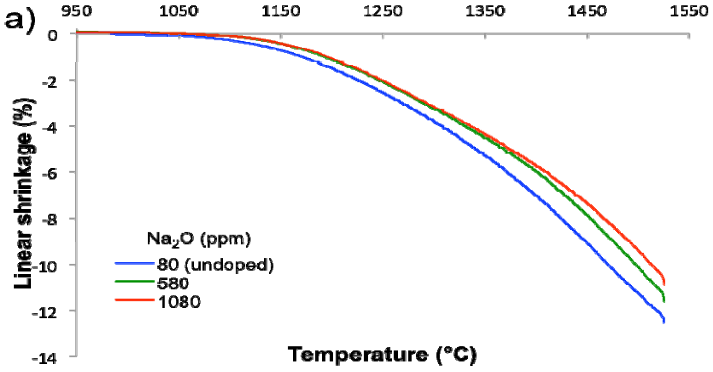
Ceramic Processing Research at Penn State

- Transparent YAG for laser gain media

- Macro-porous acicular mullite for diesel particulate filters

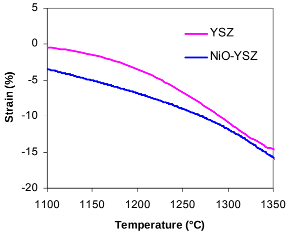


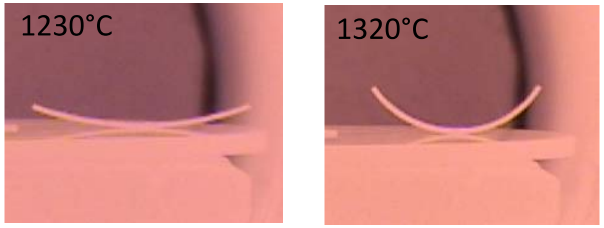
- The effect of dopants/impurities on the sintering of alumina



Ceramic Processing Research at Penn State

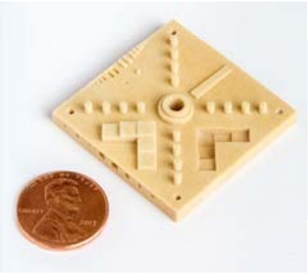
- Constrained sintering of layered ceramics (e.g., MLCC, SOFC)



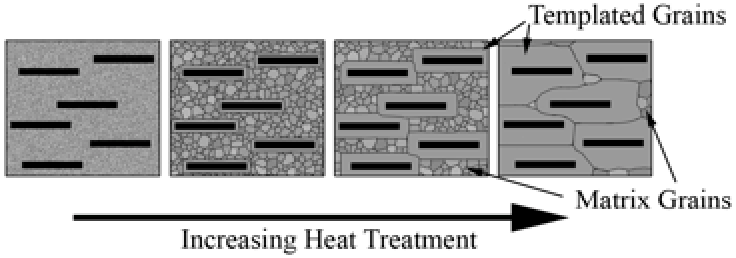


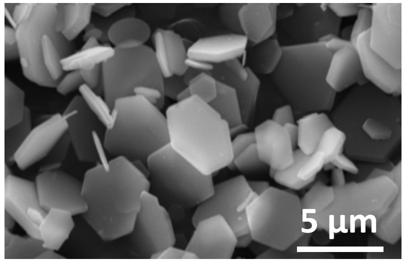
Curvature of bilayer samples due to sintering strain rate mismatch

- Additive manufacturing of glasses and ceramics



- Templated grain growth of ceramics for structural and piezoelectric applications



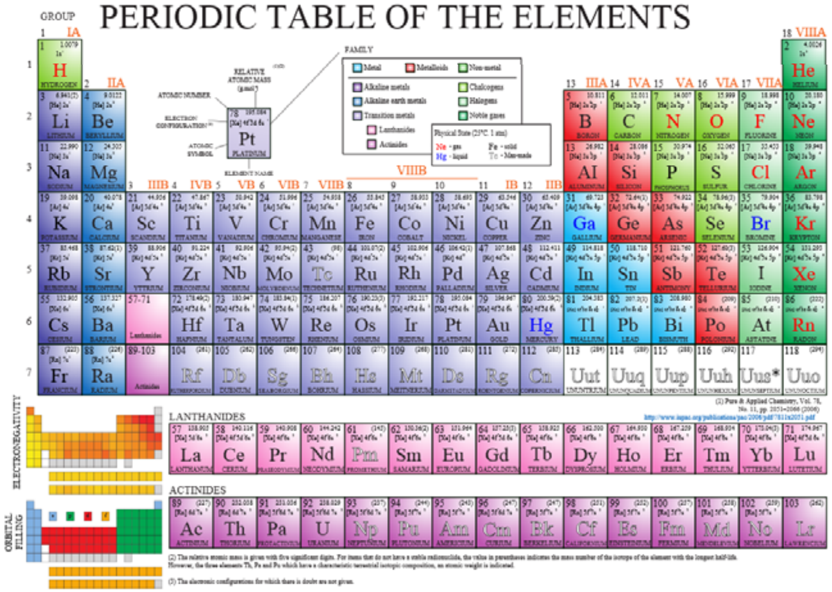


Outline

- What are ceramics?
- How are ceramics different from metals and polymers?
- Ceramic processing
- Microstructure-processing-property relationships

Ceramics are ….

- Nonmetallic, inorganic materials
- Typically metal oxides, carbides, borides and/or nitrides
  - Examples include monolithic ceramics:
    - Al_2O_3, Al_4C_3, AlN, AlON
    - SiC, Si_3N_4, SiAlON
    - PMN-PT, $BaTiO_3$
    - TiO_2, TiB_2, TiC
  - As well as composites:
    - SiC whisker reinforced Al_2O_3
    - C or SiC fiber reinforced SiC
- Ionically and covalently bonded
- Crystalline



Applications of Ceramics

"Classification of High Technology Ceramics by Function"
Kenny, and Brown
Bulletin of American Ceramic Society
Vol. 62, No. 5, (1983)
*Reprinted by permission of the American Ceramic Society.

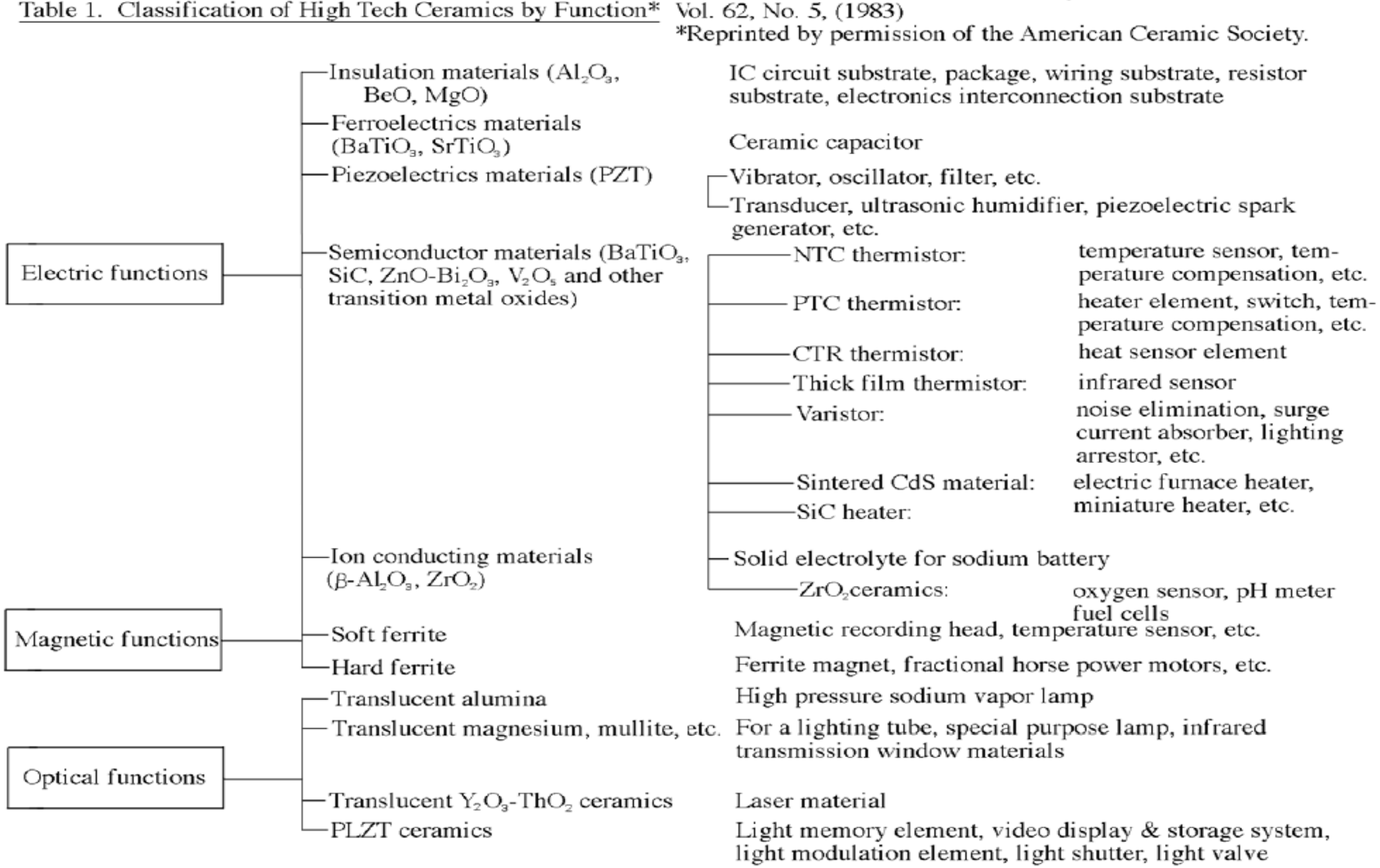
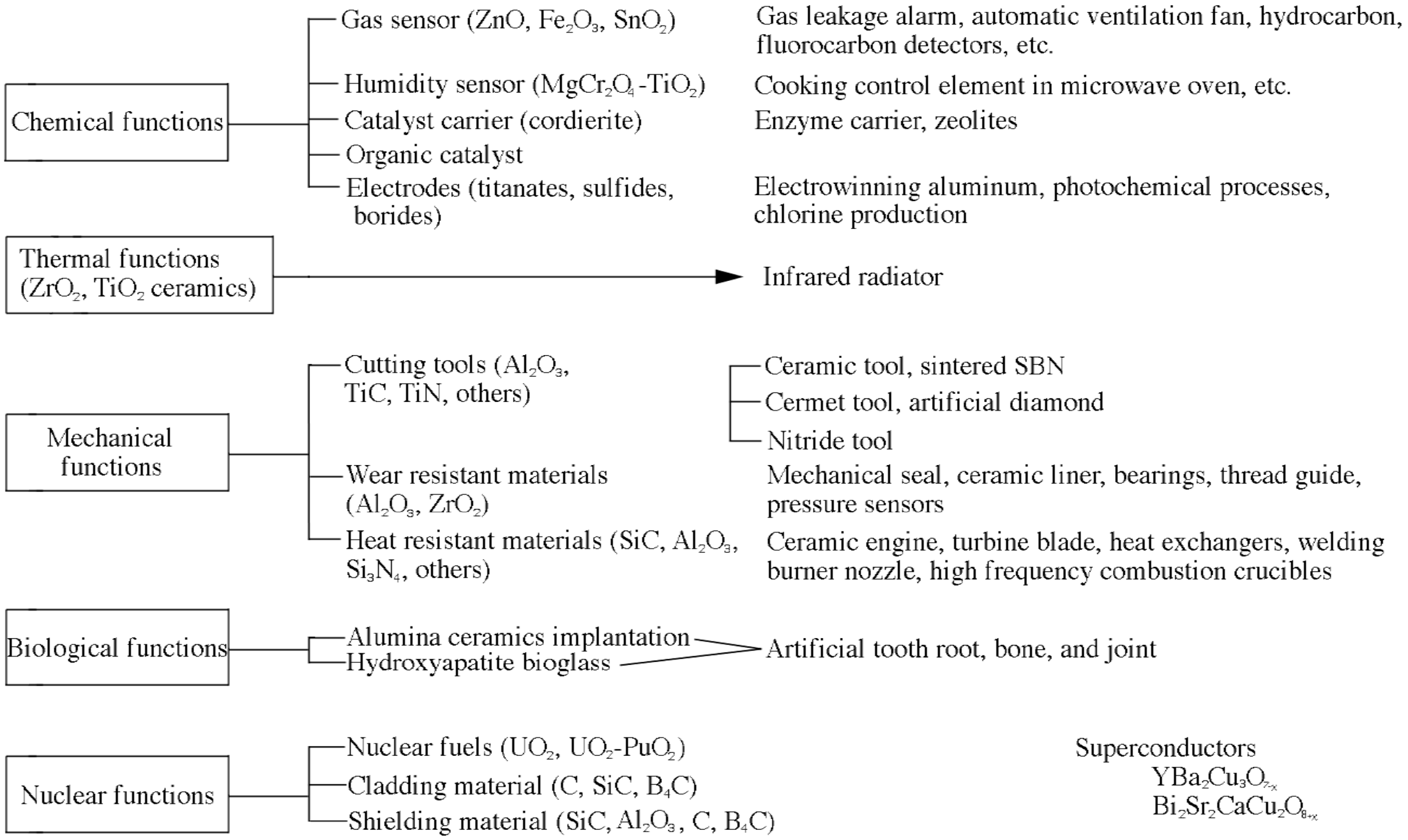


Table 1. Classification of High Tech Ceramics by Function*

- Electric functions
  - Insulation materials (Al_2O_3, BeO, MgO): IC circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate
  - Ferroelectrics materials ($BaTiO_3$, $SrTiO_3$): Ceramic capacitor
  - Piezoelectrics materials (PZT)
    - Vibrator, oscillator, filter, etc.
    - Transducer, ultrasonic humidifier, piezoelectric spark generator, etc.
  - Semiconductor materials ($BaTiO_3$, SiC, ZnO-Bi_2O_3, V_2O_5 and other transition metal oxides)
    - NTC thermistor: temperature sensor, temperature compensation, etc.
    - PTC thermistor: heater element, switch, temperature compensation, etc.
    - CTR thermistor: heat sensor element
    - Thick film thermistor: infrared sensor
    - Varistor: noise elimination, surge current absorber, lighting arrestor, etc.
    - Sintered CdS material: electric furnace heater,
    - SiC heater: miniature heater, etc.
  - Ion conducting materials (β-Al_2O_3, ZrO_2)
    - Solid electrolyte for sodium battery
    - ZrO_2ceramics: oxygen sensor, pH meter fuel cells
- Magnetic functions
  - Soft ferrite: Magnetic recording head, temperature sensor, etc.
  - Hard ferrite: Ferrite magnet, fractional horse power motors, etc.
- Optical functions
  - Translucent alumina: High pressure sodium vapor lamp
  - Translucent magnesium, mullite, etc.: For a lighting tube, special purpose lamp, infrared transmission window materials
  - Translucent Y_2O_3-ThO_2 ceramics: Laser material
  - PLZT ceramics: Light memory element, video display & storage system, light modulation element, light shutter, light valve

Applications of Ceramics



- Chemical functions
  - Gas sensor (ZnO, Fe_2O_3, SnO_2) — Gas leakage alarm, automatic ventilation fan, hydrocarbon, fluorocarbon detectors, etc.
  - Humidity sensor ($MgCr_2O_4$-TiO_2) — Cooking control element in microwave oven, etc.
  - Catalyst carrier (cordierite) — Enzyme carrier, zeolites
  - Organic catalyst
  - Electrodes (titanates, sulfides, borides) — Electrowinning aluminum, photochemical processes, chlorine production
- Thermal functions (ZrO_2, TiO_2 ceramics) → Infrared radiator
- Mechanical functions
  - Cutting tools (Al_2O_3, TiC, TiN, others)
    - Ceramic tool, sintered SBN
    - Cermet tool, artificial diamond
    - Nitride tool
  - Wear resistant materials (Al_2O_3, ZrO_2) — Mechanical seal, ceramic liner, bearings, thread guide, pressure sensors
  - Heat resistant materials (SiC, Al_2O_3, Si_3N_4, others) — Ceramic engine, turbine blade, heat exchangers, welding burner nozzle, high frequency combustion crucibles
- Biological functions
  - Alumina ceramics implantation
  - Hydroxyapatite bioglass
  - → Artificial tooth root, bone, and joint
- Nuclear functions
  - Nuclear fuels (UO_2, UO_2-PuO_2)
  - Cladding material (C, SiC, B_4C)
  - Shielding material (SiC, Al_2O_3, C, B_4C)

Superconductors
$YBa_2Cu_3O_{7-x}$
$Bi_2Sr_2CaCu_2O_{8+x}$

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*Adapted from Ref. 1. Vol. 62, No. 5 (1983) (Kenny and Bowen) Bull. Am. Ceram. Soc.

New Ceramics and Applications in the Past 20 Years

- Thermoelectrics
- Solid state lighting
- High Tc superconductors
- Laser gain media
- Ultrahigh temperature materials
- Ultrahard materials
- Solid oxide fuel cells

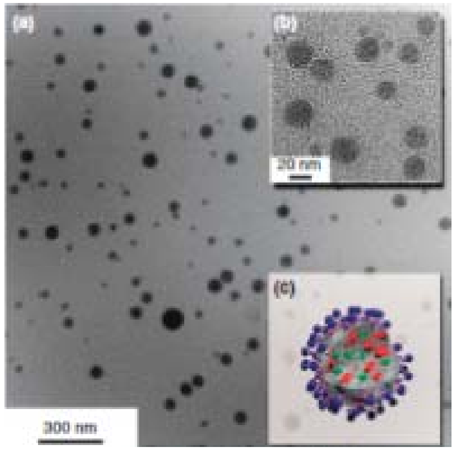
Bioceramic Applications

Smileinthecity.com

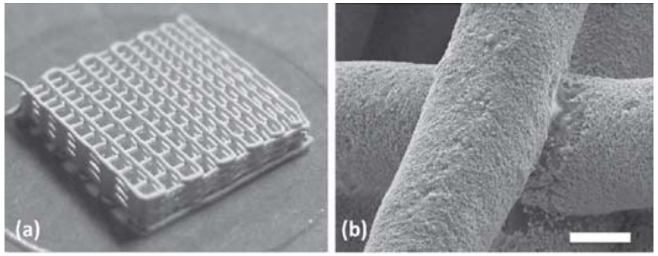
- Example applications:
  - Hip and dental implants (e.g., ZrO_2) – high relative density, hardness, wear resistance, toughness
  - Bone scaffolding (e.g., hydroxyapatite) – low relative density, micro- and macro-porous
  - Nano-composite particles for drug delivery (e.g., calcium phosphate) – core shell architectures

Bonesmart.org

- Bioceramic material requirements:
  - Biocompatible and non-toxic
  - Either stable or bioabsorbable
  - Bioactive



Tabakovic et al., WIREs Nanomed. and Nanobiotech, **4** (2012)



Sun et al, Adv. Healthcare Maters., **1** (2012)

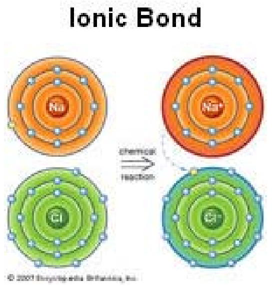
Characteristics of Advanced Ceramic Products

- Composition
  - Simple : Al_2O_3, Si_3N_4, TiC
  - Multicomponent(aka mixed metal oxides) : $BaTiO_3$, $Pb_{1-x}La_x(Zr_yTi_{1-x/4})O_3$, $Na_2O{\cdot}11Al_2O_3$
  - Composites : ZrO_2-Al_2O_3, Co-WC, SiC_w-$3Al_2O_3{\cdot}2SiO_2$
- Microstructure
  - Equiaxed or anisotropically-shaped grains
  - Fine grain size < 10 μm
  - Dense (>95% of theoretical)
- Fabrication
  - Product shape and dimensional stability
  - As little shrinkage as possible during component ‘drying’
- Densification
  - As low a temperature and for as short a time as possible
  - High green density of particulate system (i.e., as-formed) to limit sintering shrinkage
  - Shrinkage (<18% linear during sintering)

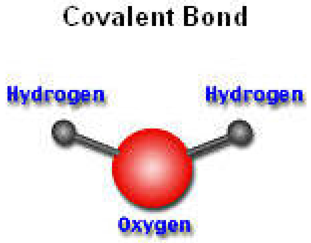
Ceramics vs. Metals and Polymers

Ceramics	Metals	Polymers
ZrO_2	Zn	$(C_2H_4)_n$ - polyethylene
$Bi_2Sr_2CaCu_2O_{8-x}$	Pt	$(C_{10}H_8O_4)_n$ – polyethylene terephthalate
B_4C	Fe	$C_{2n}H_{4n+2}O_{n+1}$ - polyethylene glycol
$SrTiO_3$	Al	$(C_2H_6OSi)_n$ – polydimethylsiloxane
Si_3N_4	NiTiNOL	$(C_6H_{10}O_5)_n$ - cellulose
PLZT	Ti	$(C_2F_4)_n$ - PTFE
UO_2	Ni	$(C_2H_3Cl)_n$ - polyvinylchloride
$Y_{3-x}Gd_xFe_5O_{12}$	Au	$[NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO]_n$ – nylon 6,6
$MgAl_2O_4$	Mn	

Ceramics vs. Metals vs. Polymers: Bonding

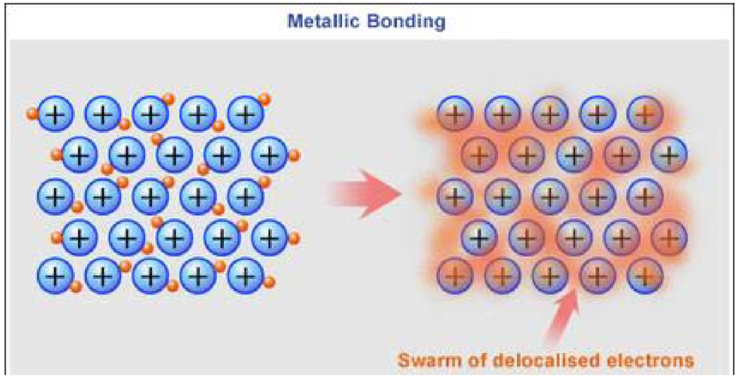


- Ceramics
  - Ionic bonding – metal to nonmetal bonds
    - Electrons transferred from metal to nonmetal
    - Bond strength dependent on valence of each ion and relative ionic radius
  - Covalent bonding – two nonmetals
    - Electrons shared between atoms
    - Bond strength scales with number of shared electrons
  - Bonds yield:
    - High elastic modulus, hardness, melting point
    - Low thermal expansion, toughness, electrical and thermal conductivity
    - Good chemical stability



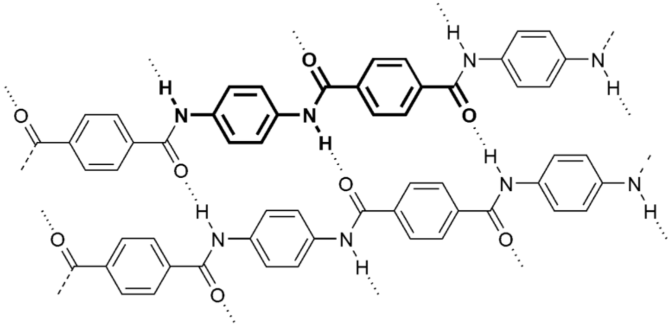
http://ceramics.org/learn-about-ceramics/structure-and-properties-of-ceramics

Ceramics vs. Metals vs. Polymers: Bonding



http://mypchem.wikispaces.com/Metallic+Bonding

- Metals
  - Metallic bonding
    - Electrons move freely between atoms
    - Relatively weak bonds
  - Bonds yield:
    - Ductility, high electrical and thermal conductivity
    - Low corrosion resistance



http://commons.wikimedia.org/wiki/File:Kevlar_chemical_structure.png

- Polymers
  - Covalent bonding – within chains
  - Intermolecular bonding – between chains
    - Van der Waals, hydrogen, dipole-dipole
  - Bonds yield:
    - Elasticity and chemical resistance
    - Low melting point, strength, electrical and thermal conductivity
  - Most polymers have a glass transition temperature above which they are elastic, below which they act like a glass

http://ceramics.org/learn-about-ceramics/structure-and-properties-of-ceramics

Ceramics vs. Metals vs. Polymers: Properties

Property	Ceramic	Metal	Polymer
Hardness	Very High	Low	Very Low
Elastic modulus	Very High	High	Low
Thermal expansion	High	Low	Very Low
Ductility	Low	High	High
Corrosion resistance	High	Low	Low
Wear resistance	High	Low	Low
Electrical conductivity	Depends on material	High	Low
Density	Low	High	Very Low
Thermal conductivity	Depends on material	High	Low
Magnetic	Depends on material	High	Very Low

Note: For general comparison only; specific properties depend on the material's specific composition and how it is made.

http://ceramics.org/learn-about-ceramics/structure-and-properties-of-ceramics

Ceramic Processing

- OR –

How to go from

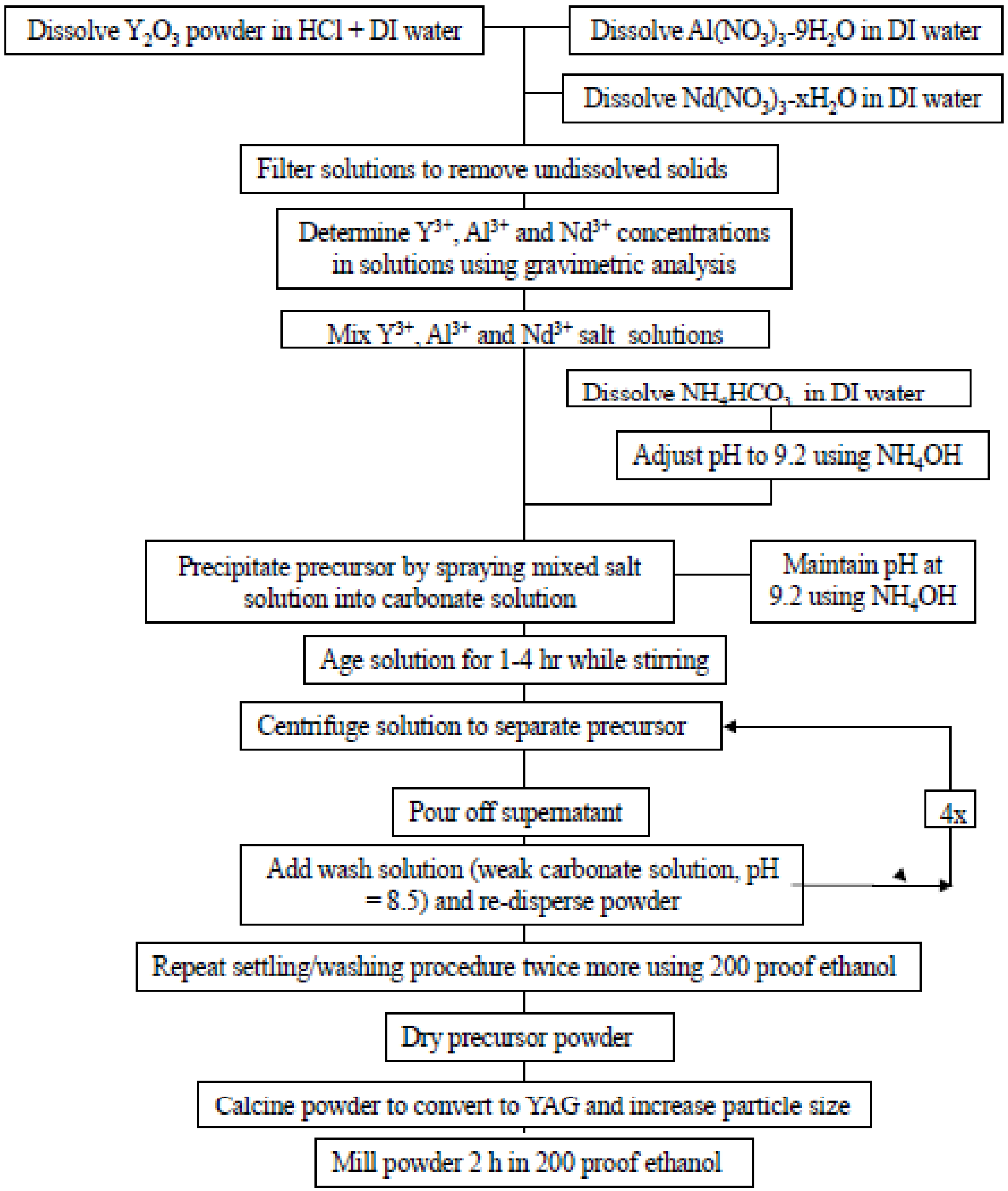
Here to Here

Ceramic Powder Synthesis

- Beneficiated ores
  - Bauxite – Bayer-process Al_2O_3
  - Clays – kaolinite, porcelain
- Solution synthesis using metal salts
  - Al_2O_3 synthesis from alkoxides
  - Co-precipitation of YAG from $Al(NO_3)_3$ and $YCl_3 \cdot 6H_2O$
- Solid state reaction of mixed powders
  - Calcination (i.e., heat treatment) of powder mixtures (e.g., $Si_3N_4 + Al_2O_3 + AlN \rightarrow SiAlON$)
- Vapor phase synthesis
  - Spray pyrolysis

Solution Synthesis of Ceramic Powders

Solution synthesis of Nd-doped $Y_3Al_5O_{12}$



Dissolve Y_2O_3 powder in HCl + DI water

Dissolve $Al(NO_3)_3$-$9H_2O$ in DI water

Dissolve $Nd(NO_3)_3$-xH_2O in DI water

Filter solutions to remove undissolved solids

Determine Y^{3+}, Al^{3+} and Nd^{3+} concentrations in solutions using gravimetric analysis

Mix Y^{3+}, Al^{3+} and Nd^{3+} salt solutions

Dissolve NH_4HCO_3 in DI water

Adjust pH to 9.2 using NH_4OH

Precipitate precursor by spraying mixed salt solution into carbonate solution

Maintain pH at 9.2 using NH_4OH

Age solution for 1-4 hr while stirring

Centrifuge solution to separate precursor

Pour off supernatant

4x

Add wash solution (weak carbonate solution, pH = 8.5) and re-disperse powder

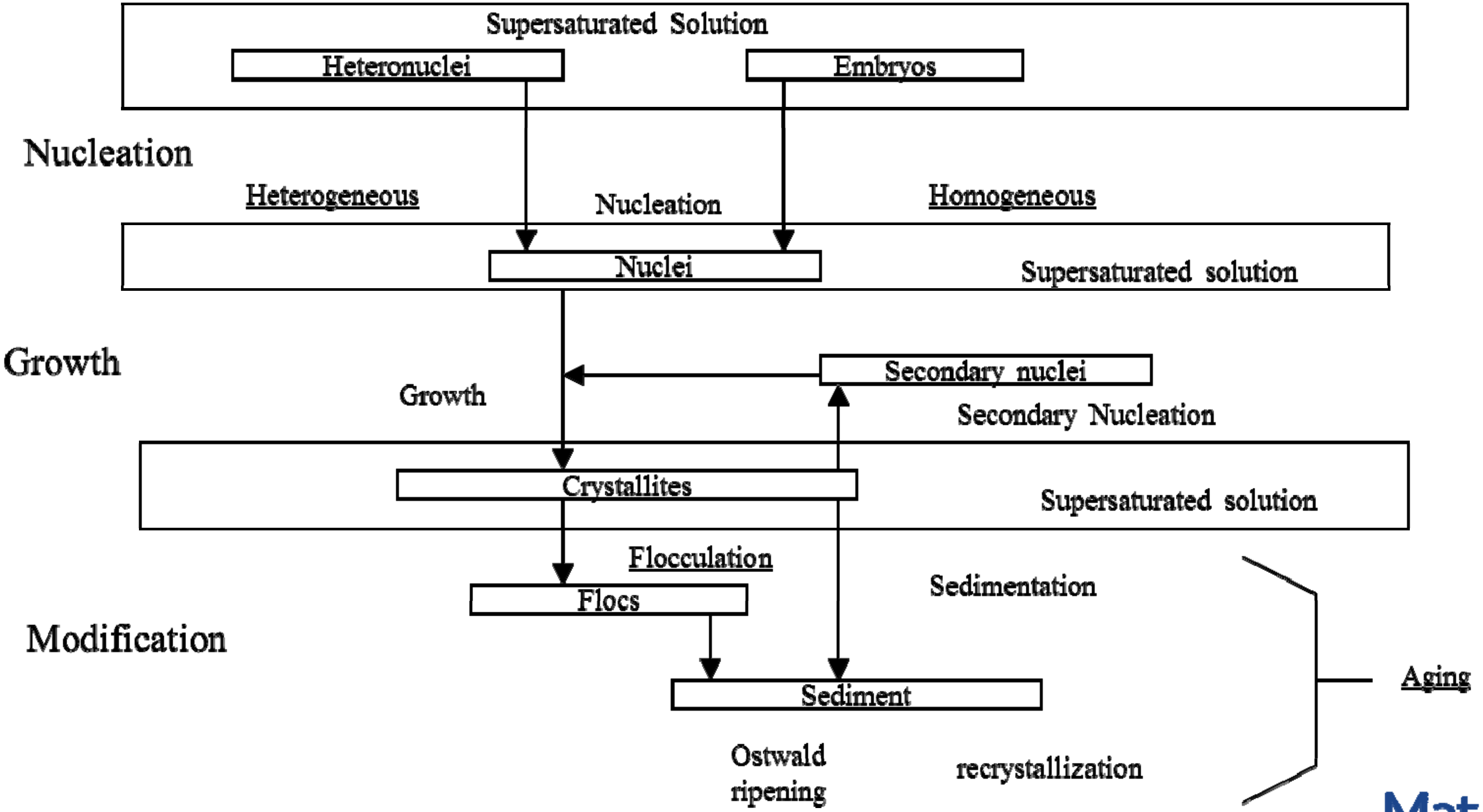
Repeat settling/washing procedure twice more using 200 proof ethanol

Dry precursor powder

Calcine powder to convert to YAG and increase particle size

Mill powder 2 h in 200 proof ethanol

Particle Precipitation Steps



Supersaturated Solution

Heteronuclei

Embryos

Nucleation

Heterogeneous

Nucleation

Homogeneous

Nuclei

Supersaturated solution

Growth

Secondary nuclei

Growth

Secondary Nucleation

Crystallites

Supersaturated solution

Flocculation

Sedimentation

Flocs

Modification

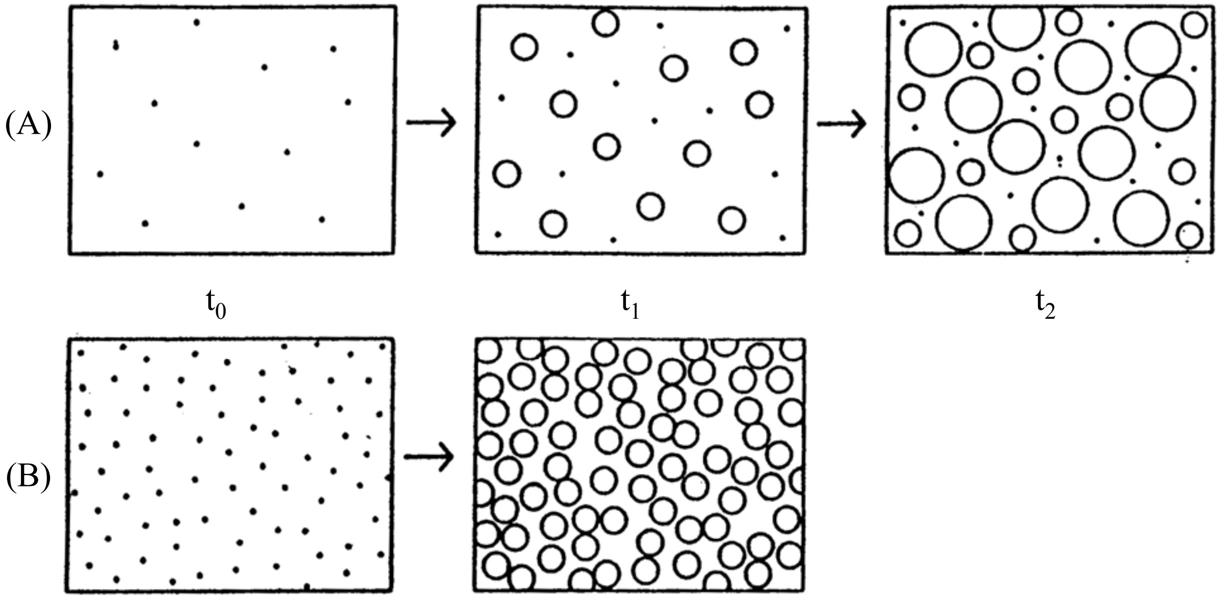
Aging

Sediment

Ostwald ripening

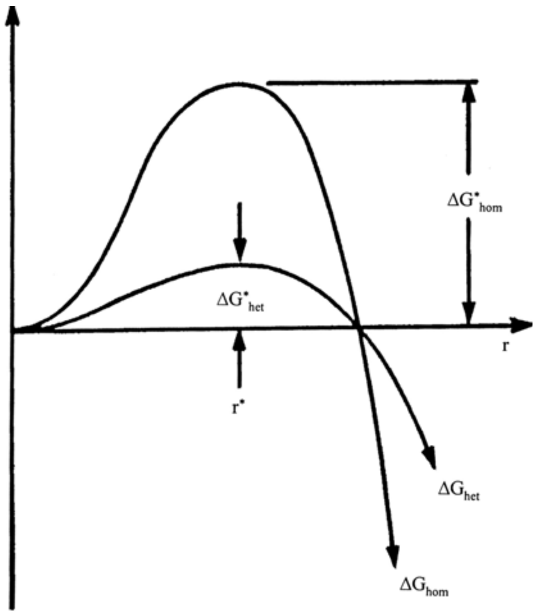
recrystallization

Heterogeneous vs. Homogeneous Nucleation



- Schematic microstructure evolution for conditions of:
- (A) constant nucleation rate (unseeded system)
- (B) site saturation, nucleation rate ≈ 0 (seeded system)

- Energy barriers associated with homogeneous nucleation (ΔG^*_{hom}) and heterogeneous nucleation (ΔG^*_{het}) at critical radius r^*.



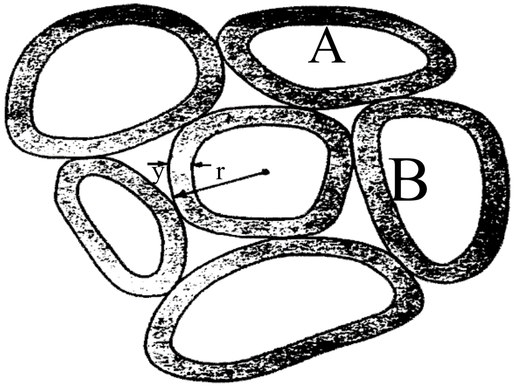
Solid State Reaction

A parabolic rate law is often observed for kinetic processes in which the rate limiting step is mass transport through the reaction zone $t^{1/2}$ relation.

(1) let $y = (KDt)^{1/2}$

y = thickness of product layer
t = time
K = configurational constant
D = diffusivity
r = particle radius

(2) $V = 4/3\pi\,(r - y)^3$ - volume unreacted
(3) $V = 4/3\pi r^3\,(1 - \alpha)$ α = volume fraction reacted



Schematic representation of reaction-product layers forming on surface of particles in powder mixture.

Combine equations (2) & (3)

(4) $$y = r\left(1 - \sqrt[3]{1-\alpha}\right)$$ - a relation between particle size, thickness, and vol. fraction reacted.

Combine equations (1) & (4) **Jander Equation**. KD = Reaction rate constant (diffusion limited)

(5) $$\left(1 - \sqrt[3]{1-\alpha}\right)^2 = \left(\frac{KD}{r^2}\right)t$$

$$K' = \text{slope} = \frac{KD}{r^2}$$

$$K' = \frac{KD}{r^2} = KD_{\circ}\exp\left\{\frac{-Q}{RT}\right\}$$

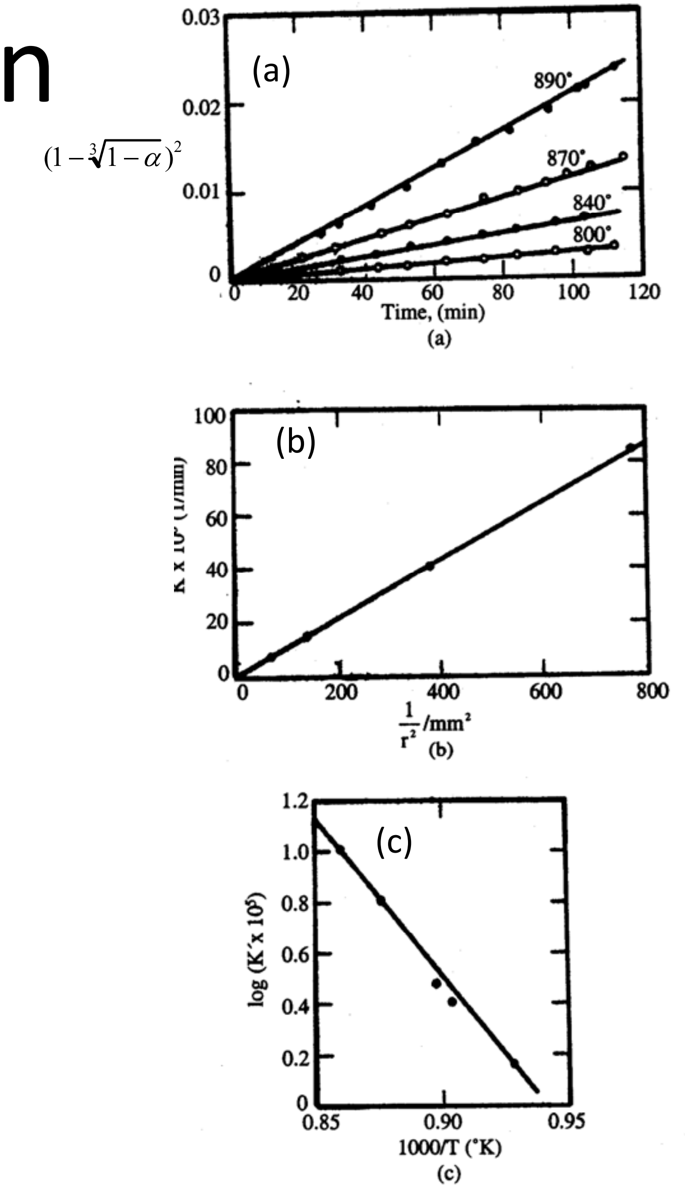
Assumes (1) parabolic rate law
(2) no molar volume change; consequently only valid for initial stage of reaction
(3) Arrhenius relation

W. Jander, Z. Anorg. Allg. Chem., 163, 1 (1927).

Solid State Reaction

- By plotting
- (1) $(1-\sqrt[3]{1-\alpha})^2$ vs. t can establish $\frac{KD}{r^2}$
- (2) K vs. $1/r^2$ can validate dependence of K on $1/r^2$
- (3) From Arrhenius equation: $K' = K'_\circ \exp\left[-Q/RT\right]$
- can establish and verify diffusional nature of process
- (where Q = Activation Energy)

- Solid reaction between silica and barium carbonate showing (a) time dependence, (b) particle-size dependence, and (c) temperature dependence of reaction rate. From W. Jander, Z. Anorg. Allg. Chem., 163, 1 (1927).



Solid State Reaction

(1) Valid for small Δy

(2) Ignores changes in molar volume between products and reactants

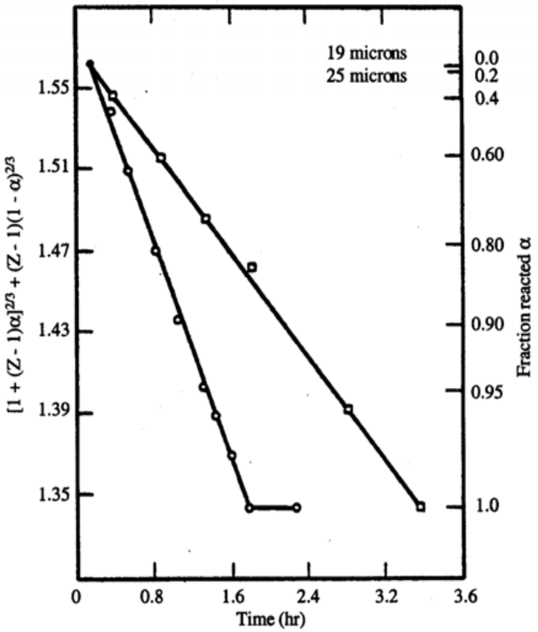
Correction for These Two Oversimplifications Yields:

$$[1+(z-1)\alpha]^{2/3}+(z-1)(1-\alpha)^{2/3}=2+(1-z)\left(\frac{KD}{r^2}\right)t$$

(R.E. Carter, J. Phys. Chem. 34, 2010 1961) and 1137 (1961))

z = volume of particle formed per unit volume of a spherical particle consumed.

Plot: $[1+(z-1)\alpha]^{2/3}+(z-1)(1-\alpha)^{2/3}$



Reaction between ZnO and Al_2O_3 to form $ZnAl_2O_4$ at 1400˚C in air (two spherical particle sizes

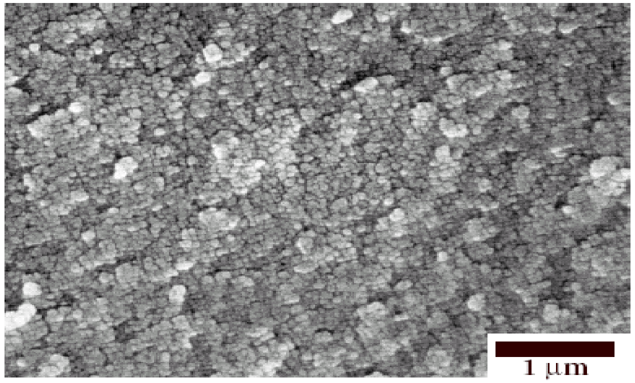
Powder Conditioning

- Granulation
- Calcination:
  - Phase formation/solid state reaction
  - Phase transformation (e.g., γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$)
  - Decomposition of precursor species (e.g., carbonates, nitrates in source material salts)
  - Increasing particle size – Ostwald ripening
  - Removing impurities
- Size separation
- Milling
  - Size reduction
  - Homogeneous mixing of powders and slurries
  - Addition of processing aids

Calcination

- Annealing process during which chemical/physical changes occur
  - Best to avoid the occurrence of these changes during sintering
  - Large volume changes during reaction and/or weight loss due to evolution of gases can disrupt evolving microstructure
- Potential reactions/outcomes
  - Phase formation/solid state reaction
  - Phase transformation (e.g., γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$)
  - Decomposition of precursor species (e.g., carbonates, nitrates in source material salts)
  - Increasing particle size – Ostwald ripening
  - Removing impurities
  - Crystallization

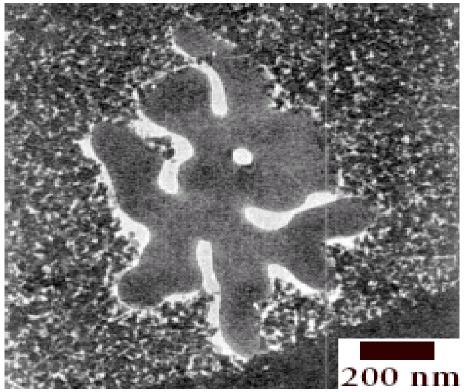
Calcination – Phase Transformation



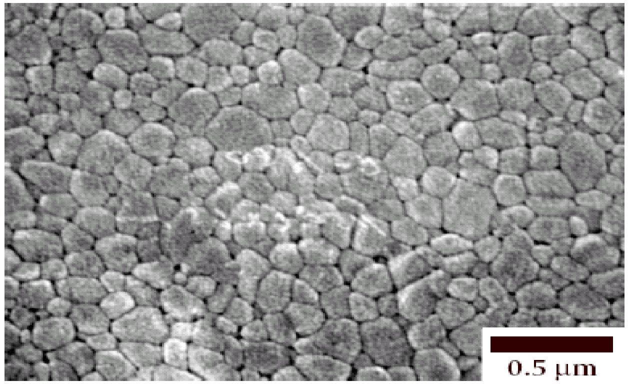
Boehmite gel – physically and chemically homogeneous

Transformation of boehmite (AlOOH) to $\alpha\text{-}Al_2O_3$:

$$\gamma\text{-AlOOH} \xrightarrow{450^\circ C} \gamma\text{-}Al_2O_3 \xrightarrow{900^\circ C} \theta\text{-}Al_2O_3 \xrightarrow{1200^\circ C} \alpha\text{-}Al_2O_3$$



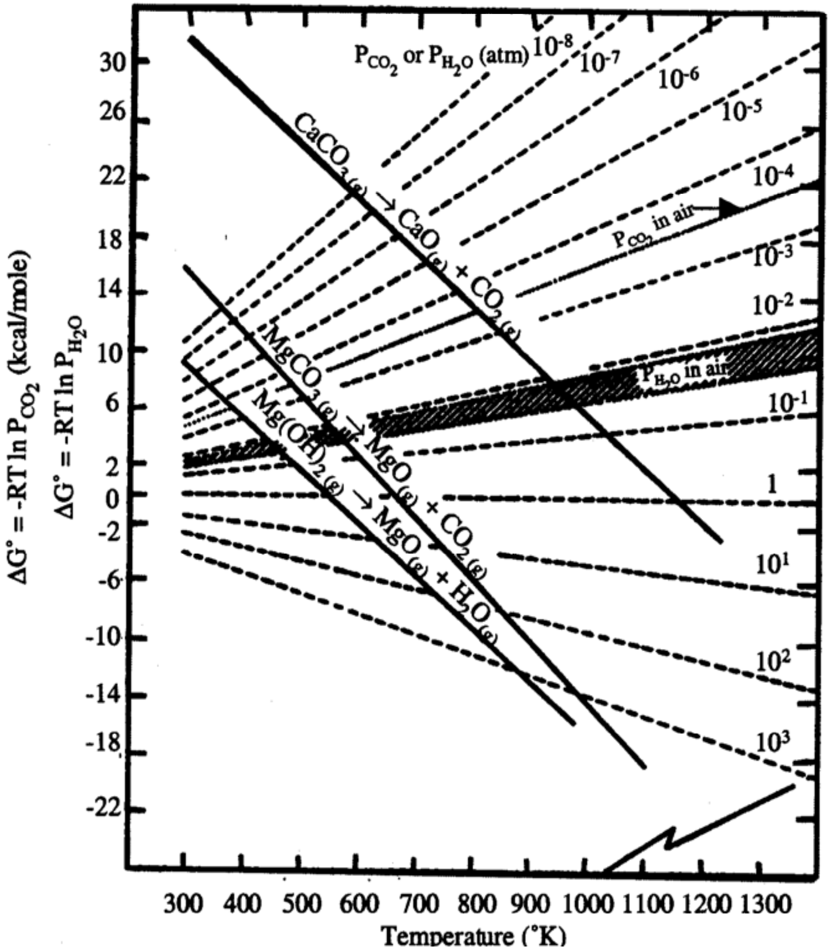
After calcination - unseeded



After calcination– seeded (1 wt% $\alpha\text{-}Al_2O_3$ seeds)

Calcination - Decomposition

- Precursor metal salts react with atmosphere to form metal oxides
- Relatively large volume changes occur – want this process to happen
- Ellingham diagrams useful for predicting atmospheric conditions where decomposition will occur

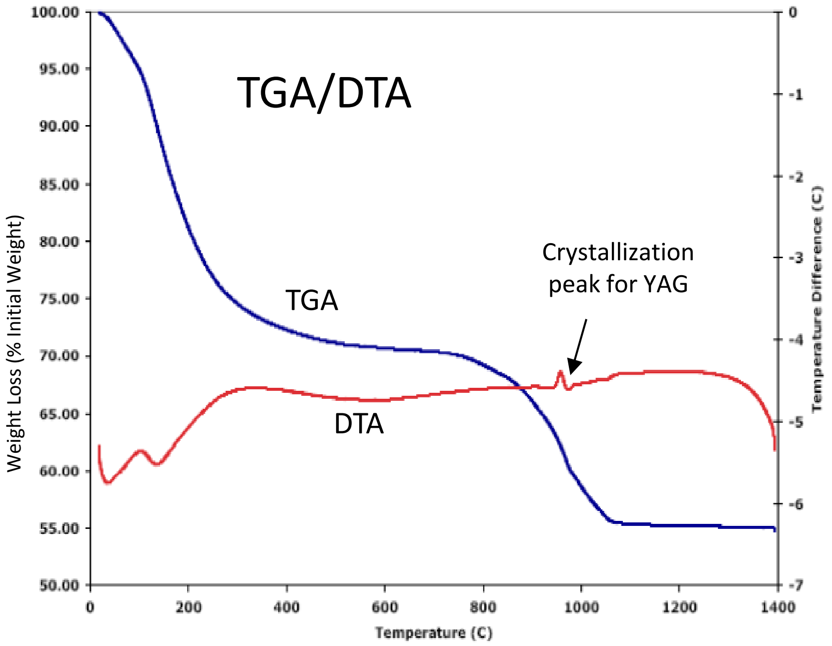


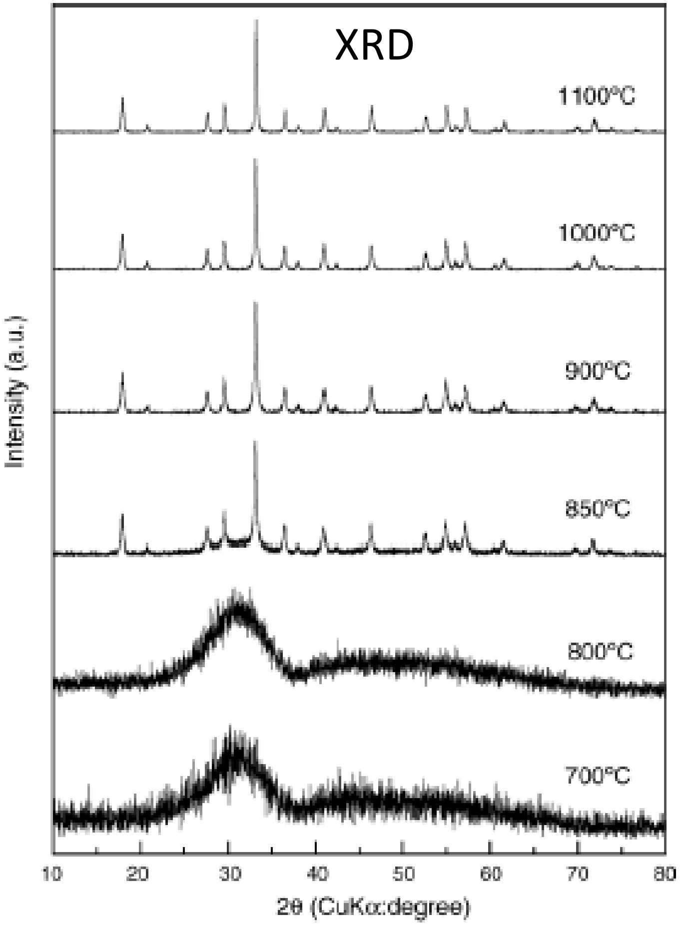
$p_{CO_2} = 10^{-1}$ atm

T = 1025 K
= 752 °C

Kingery et al., Introduction to Ceramics, Wiley, 1976

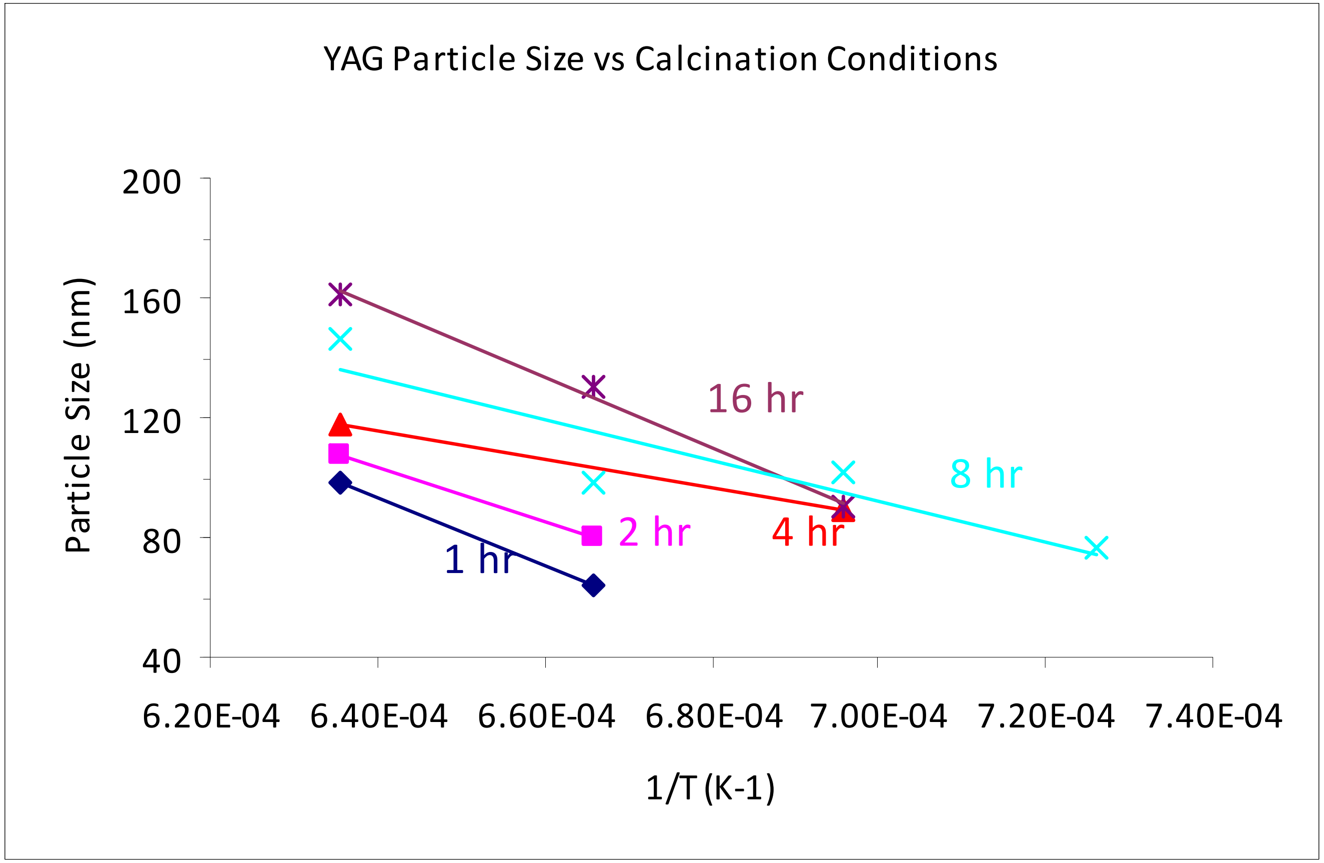
Calcination - Crystallization





Calcination of co-precipitated $YCl_3{\cdot}6H_2O + Al(NO_3)_3$ to form $Y_3Al_5O_{12}$

Calcination – Particle Growth



Characterization of Ceramic Powders

Why Characterize Powders?

- To learn more about what we are working with
- To confirm the supplier's specifications
- To maintain reproducibility during processing
- To determine the physical characteristics of the powder (e.g., particle size distribution, surface area)
- Information can be used to establish, interpret, or forecast processing/fabrication/sintering/Relations
- To generate a database from which processing controls can be developed

What Parameters Should be Measured?

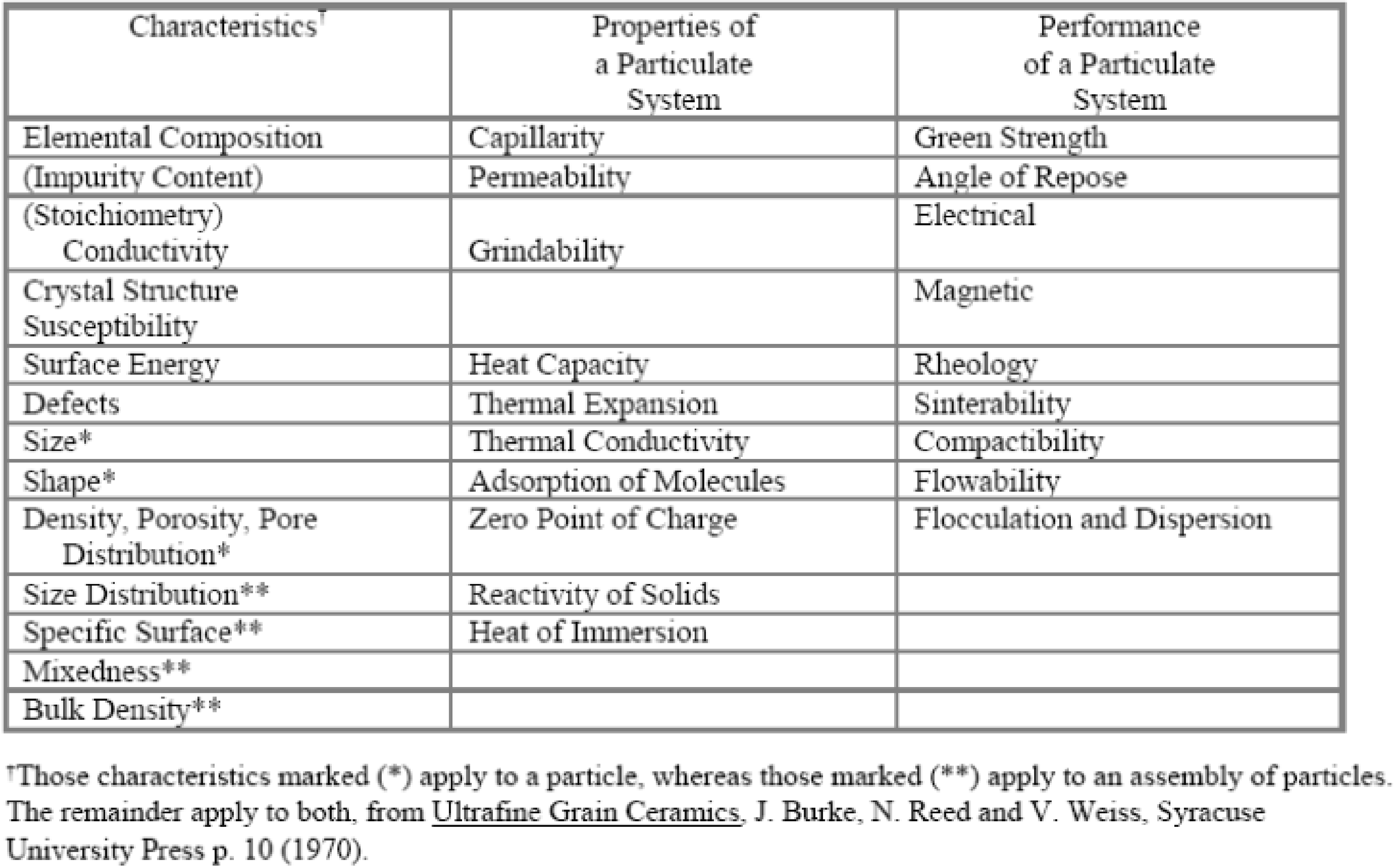
It is not possible to measure all of these attributes. Therefore, one must measure those which are the most useful for control. For example,

1. During processing - trying to attain a specific surface area of minimum particle (e.g., calcining, grinding).

2. In the final microstructure - making sure all particles are less than a specific size.

3. Its application - the powder itself may be the product (e.g., catalysis).

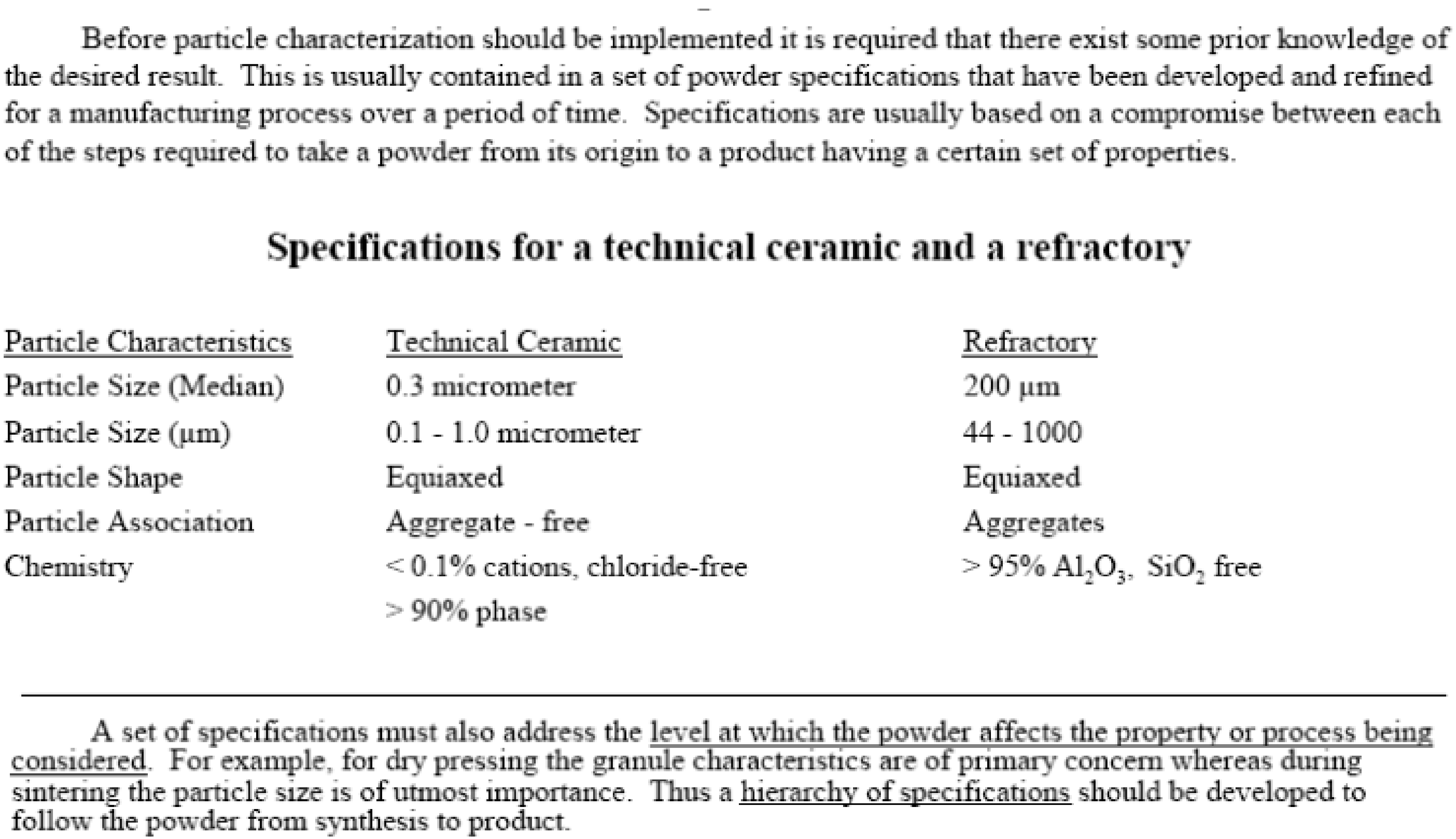
Powder Characteristics



Characteristics†	Properties of a Particulate System	Performance of a Particulate System
Elemental Composition	Capillarity	Green Strength
(Impurity Content)	Permeability	Angle of Repose
(Stoichiometry) Conductivity	Grindability	Electrical
Crystal Structure Susceptibility		Magnetic
Surface Energy	Heat Capacity	Rheology
Defects	Thermal Expansion	Sinterability
Size*	Thermal Conductivity	Compactibility
Shape*	Adsorption of Molecules	Flowability
Density, Porosity, Pore Distribution*	Zero Point of Charge	Flocculation and Dispersion
Size Distribution**	Reactivity of Solids	
Specific Surface**	Heat of Immersion	
Mixedness**		
Bulk Density**		

†Those characteristics marked (*) apply to a particle, whereas those marked (**) apply to an assembly of particles. The remainder apply to both, from Ultrafine Grain Ceramics, J. Burke, N. Reed and V. Weiss, Syracuse University Press p. 10 (1970).

Powder Specifications



Before particle characterization should be implemented it is required that there exist some prior knowledge of the desired result. This is usually contained in a set of powder specifications that have been developed and refined for a manufacturing process over a period of time. Specifications are usually based on a compromise between each of the steps required to take a powder from its origin to a product having a certain set of properties.

Specifications for a technical ceramic and a refractory

Particle Characteristics	Technical Ceramic	Refractory
Particle Size (Median)	0.3 micrometer	200 µm
Particle Size (µm)	0.1 - 1.0 micrometer	44 - 1000
Particle Shape	Equiaxed	Equiaxed
Particle Association	Aggregate - free	Aggregates
Chemistry	< 0.1% cations, chloride-free > 90% phase	> 95% Al_2O_3, SiO_2 free

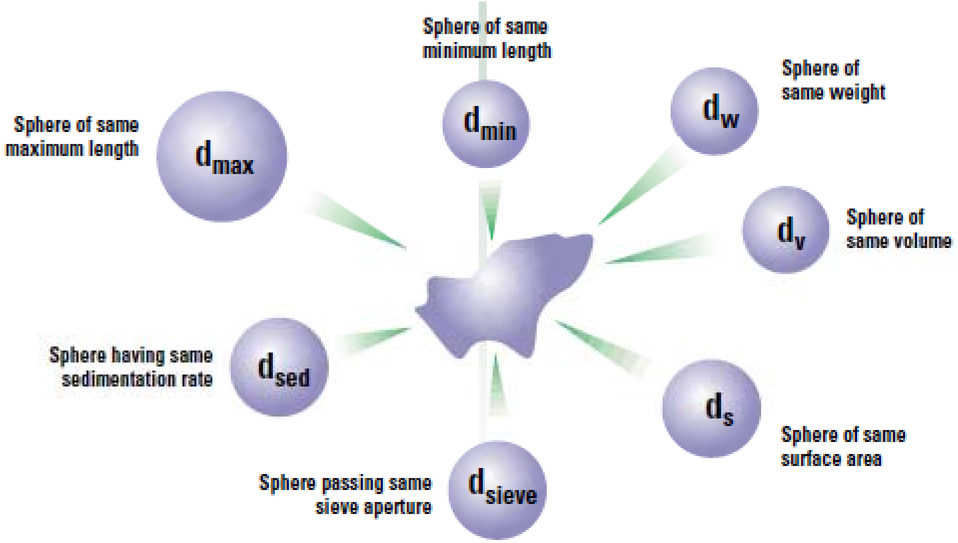
---

A set of specifications must also address the level at which the powder affects the property or process being considered. For example, for dry pressing the granule characteristics are of primary concern whereas during sintering the particle size is of utmost importance. Thus a hierarchy of specifications should be developed to follow the powder from synthesis to product.

Particle Size Measurement Techniques

- D_{proj}
  - Sieving
  - Quantitative microscopy
  - Light scattering
- D_v
  - Particle motion
    - Brownian
    - Sedimentation
  - Electrical resistance
  - Acoustic spectroscopy
- D_s
  - Gas adsorption

It is important to know how each technique works to know how to interpret the results



Different Methods for Particle Size Analysis

Method	*Diameter*	*Frequency*	*Size Range (μm)*	*Comments*
Dry Sieving	d_{proj}	weight	>38	Electrostatic charge <50 μm
Wet Sieving	d_{proj}	weight	5-100	
Optical Microscopy	d_{proj}	number	1-100	Orientation dependent
SEM	d_{proj}	number	0.1-100	Electrical charging
FESEM	d_{proj}	number	0.02-10	Electrical charging
TEM	d_{proj}	number	0.005-0.05	Sample preparation dependent
Light Scattering	d_{proj}	number	0.01-3000	Dilute suspensions
Sedimentation	d_v	weight	0.1-300	Brownian motion limited
Centrifugation	d_v	weight	0.01-50	Excellent for 0.1-1 μm
Electrical Resistance	d_v	number	0.04-250	Coincidence
Acoustic Spectroscopy	d_v	weight	0.05-100	Need "perfect" powders
Surface Area	d_s		<100	

Particle Packing

Significance of Particle Packing:

(1) Controls the green density
(2) Controls the fired density
(3) Influences microstructural development
(4) Controls the degree of shrinkage
(5) Influences ceramic/organic formulations

Volume Fraction Shrinkage $= \dfrac{V_b - V_s}{V_b} = \dfrac{1/\rho_b - 1/\rho_s}{1/\rho_b} = 1 - \dfrac{\rho_b}{\rho_s}$ where

V = specific volume (cm^3/g)
ρ = density
b = bulk
s = sintered

Packing Density:

- the same as the bulk or apparent density
- the volume occupied by powder irrespective of how it got there
- highly variable parameter as it is dependent on many other factors
- must be knowledgeable of particle characteristics to interpret its significance

Tap Density:

- highest density obtained by tapping or vibrating the powder

Specific Volume:

- inverse of the density $V = 1/\rho$

Relative Density: (or packing factor)

- the ratio of the packing density to the theoretical particle density (ρ_o) e.g. solids fraction $= \rho_b/\rho_o$ and the void fraction $= 1 - \rho_b/\rho_o$

Forming of ceramics

Colloidal Dispersions

- Slip casting (colloidal filtration)
- Tape casting
- Pressure filtration

Plastic Forming

- Extrusion (mechanoplasticity – plasticity due to stress and shape retention upon removal of stress – characteristic of clay-based systems)
- Injection molding (thermoplasticity – deformation enabled by heating and retained during cooling)

Dry Forming

- Uniaxial pressing
- Isostatic pressing
- Roll compaction
- Lamination

Additive manufacturing

- Powder bed systems
  - Polymer jetting
  - Selective laser melting
- Fused deposition modeling
- Stereolithography

Many factors including dispersion rheology, degree of saturation and fabrication stresses must be controlled to form a green ceramic that possesses high green density, sufficient green strength and plasticity for subsequent processes. Because advanced ceramics seldom use clay, plasticity is usually obtained by using organic additives.

Dry Pressing

- Definition: “process by which ceramic powders are consolidated inside a cavity into a predetermined shape through the use of an applied pressure”
- Most widely used high-volume forming process for ceramics
- Low cost
- Easily automated
- Relatively simple shapes
- Uniform die filling critical – controlled agglomeration advantageous

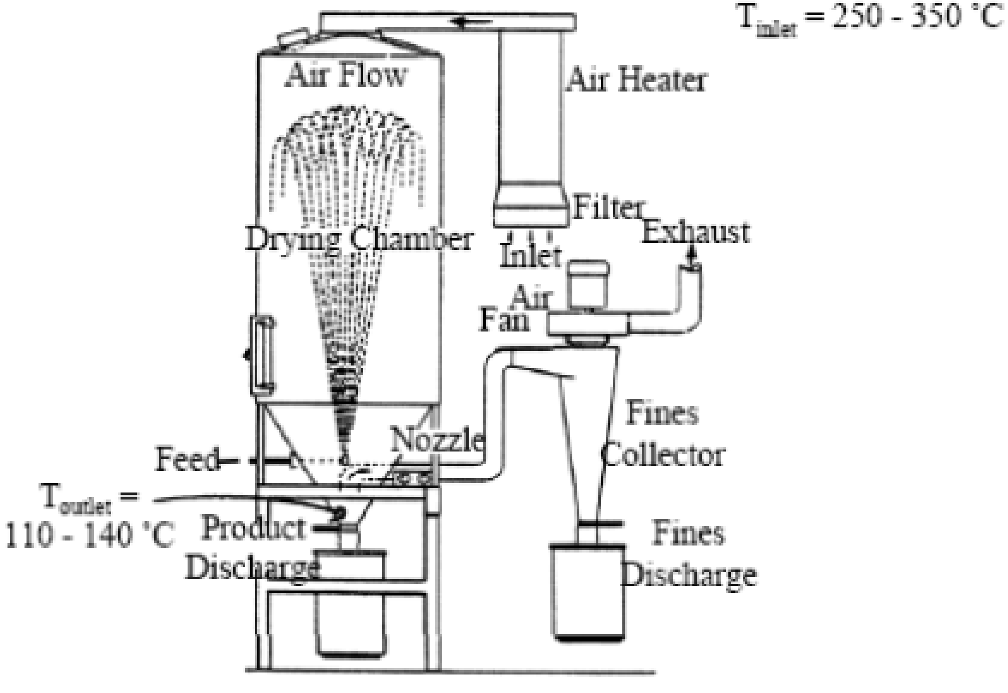
Spray Drying
(Controlled Agglomeration)

Reasons for granulating

1) Improve powder flow characteristics
2) To produce uniform pressed microstructure through control of powder flow and density
3) Reduce dust during shipping
4) Improve consistency and uniformity of batching (e.g., glass)

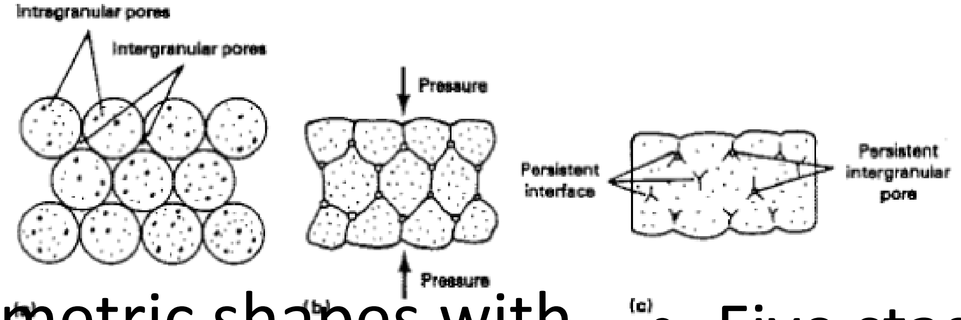
Methods of Granulation

1) Spray Drying
2) Agitation (e.g., disc pelletizer, drum, cone)
3) Compaction (briquetting, compaction, extrusion)



Granulation

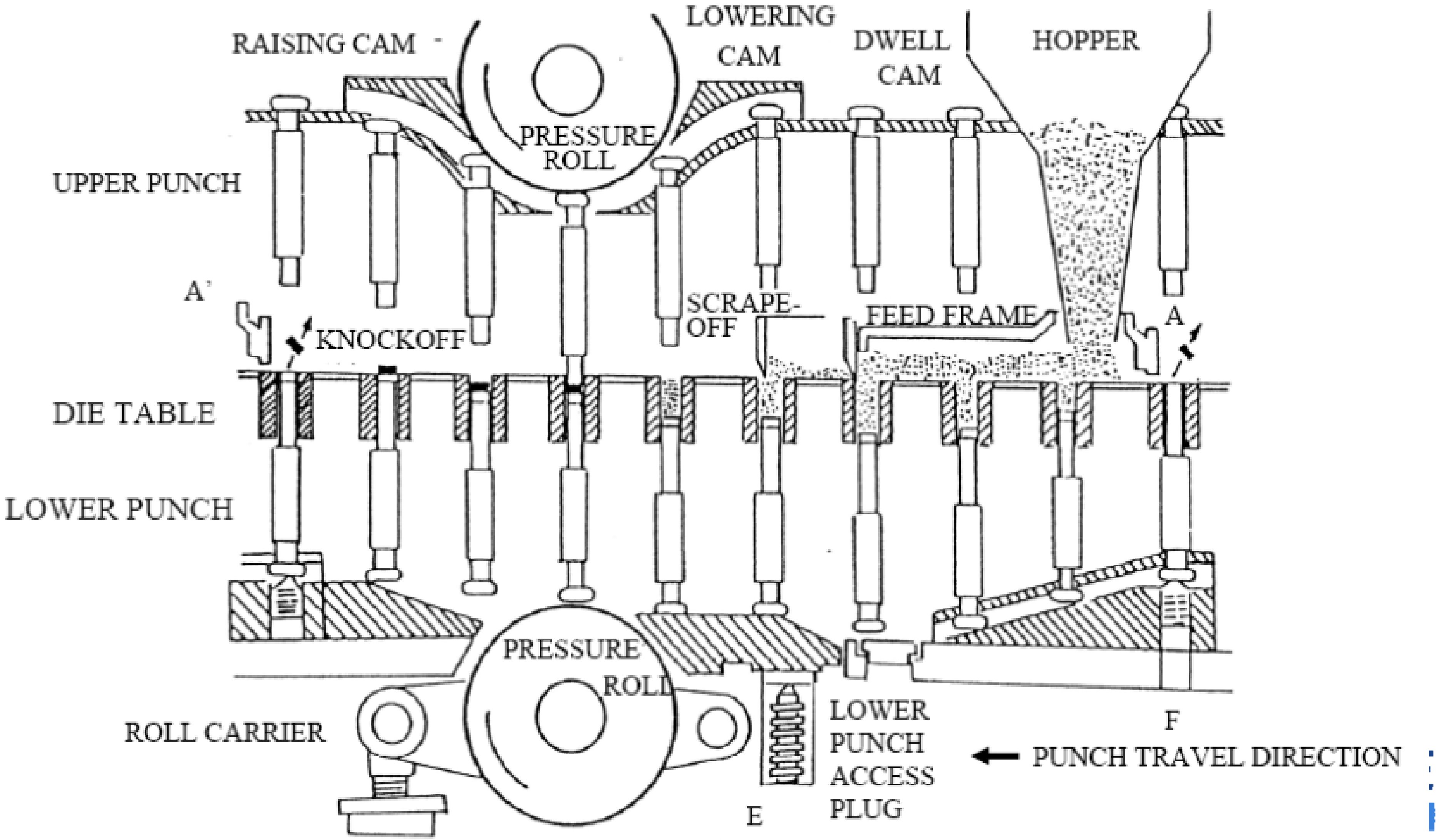
Uniaxial Pressing



- Simple geometric shapes with vertical punches
- Through-holes and surface topography possible
- Applications:
    - cutting tools
    - refractories
    - seal rings
    - grinding wheels
- Used alone or coupled with subsequent CIP

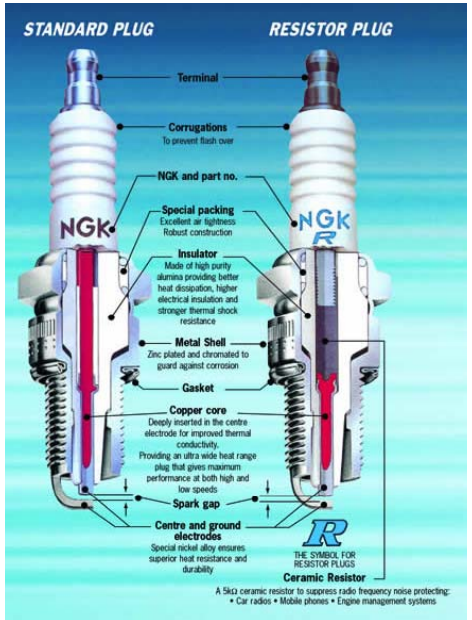
- Five stages
    - Die fill
    - Transitional restacking
        - <10 MPa
    - Low flow and fragmentation
        - 50-100 MPa
    - Bulk compression
        - 50-200 MPa
    - Springback

Rotary Dry Pressing



Isostatic Dry Pressing

- Increased shape complexity available relative to uniaxial pressing
- Uniform densities achieved due to isostatic pressure
- Pressures:
  - Dry bag – up to 275 MPa
  - Wet bag – up to 690 MPa
- Applications
  - spark plug insulators
  - dinnerware
  - power line insulators
  - sodium vapor lamp tubes (alumina)



Colloidal Processing

- Slurries or pastes are made by dispersing powders in a liquid with the organics necessary to give the unfired (i.e. green) parts the desired properties
- Aqueous (i.e. water-based) or non-aqueous (e.g. methanol, toluene, etc.)
- Organic additives:
  - Surfactants – alter interface energy between powder and liquid to allow wetting
  - Dispersants – prevent particles from flocculating
  - Binders – impart strength to green parts
  - Plasticizers – lower glass transition temperature of binder

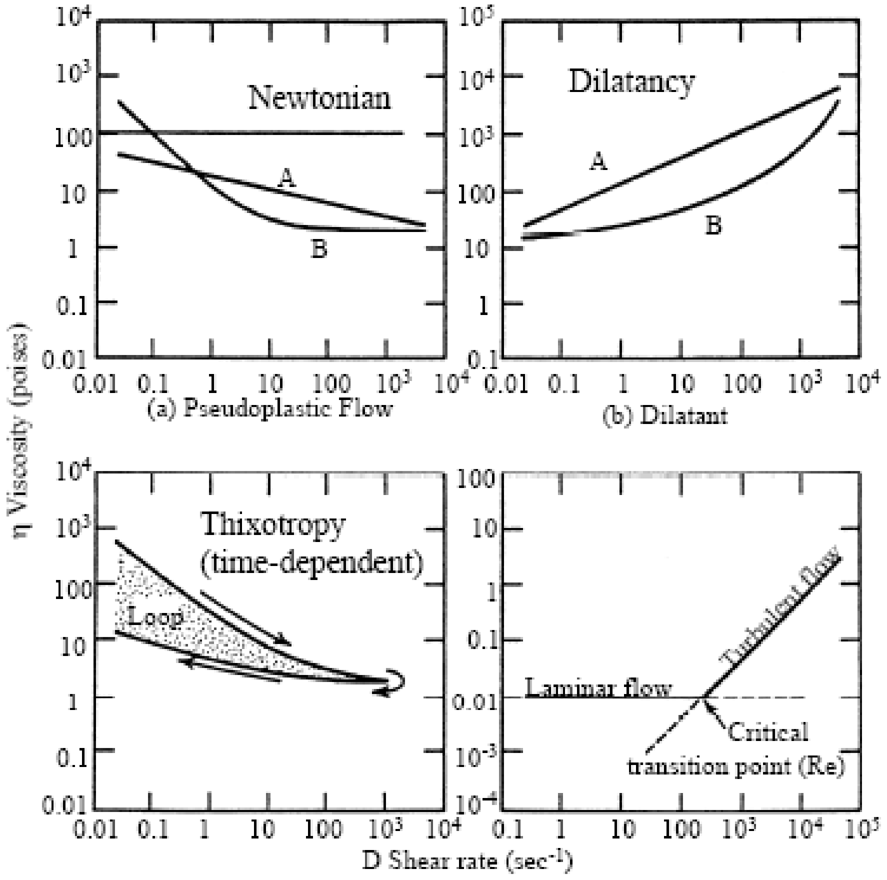
Organic binder selection criteria

1. Non-contaminating (no free C, Na^+, K^+, Cl^- etc.)
2. Chemically compatible with the dispersion
3. Physically compatible with the system - Particularly important for emulsion polymers
4. Within viscosity requirements for forming and/or processing
5. Sufficient plasticity/deformability/flexibility
6. Adequate mechanical properties after forming
7. Decomposes/pyrolyses in a controlled manner

Polymer characteristics

- Degree of polymerization (no. of repeat units)
- Molecular weight = DP x weight of monomer or repeat units
- Molecular weight distribution
- Glass transition temperature
- Degree of crystallinity
- Crosslinking
- Branching
- Vapor pressure
- Melting temperature

Fluid (Slurry) Behavior



(a) Pseudoplastic Flow

(b) Dilatant

(c) Thixotropic loop

(d) Laminar vs. Turbulent Flow

$\eta = \tau/\gamma$

η = viscosity

τ = shear stress

γ = shear rate

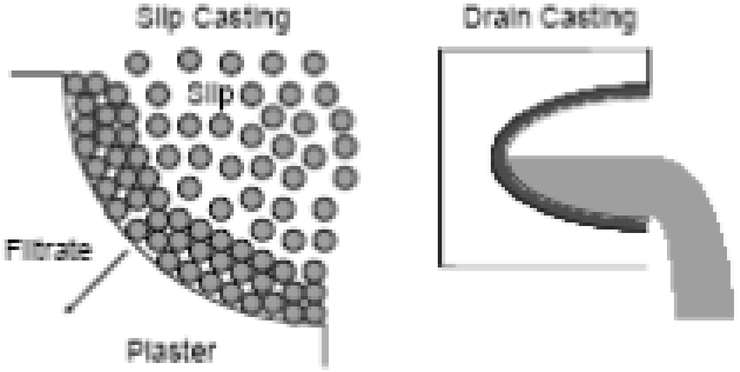
1 centipoise = 10^{-2} P (= 1 mPa·s)
water at 20 °C

Apparent Viscosity* - viscosity quoted for a specific set of experimental parameters [Shear Rate]

Viscous behavior is a function of:

- pH
- solids loading
- additives
  - surfactants or wetting agents
  - dispersants (same as deflocculants)
  - binders

Slip Casting



- Slip casting is a slurry-based shaping technique
- Slips are powder suspensions which contain:
  - Ceramic powder
  - Liquid (solvent for organics)
  - Dispersant
  - Surfactant (optional)
  - Binder (optional)
- Slip casting is a filtration process

Slip Casting Process

- Slip is poured into a porous mold (plaster or polymer)
- Capillary forces (~0.1-0.2 MPa) in the mold pull the liquid into the mold from the slip
- The powder particles are drawn towards the mold walls and gradually build up into a consolidated layer or filter cake
- Several techniques have grown out of this concept

- Advantages:
  - –Complex shapes can be produced
  - –Low tooling costs
- Disadvantages
  - –Long cycle times
  - –Labor intensive
  - –Limited dimensional control
  - –Requires large work areas

Slip Casting

Techniques

- Drain casting
  - Used to make hollow parts
  - Pour out remaining slip when desired wall thickness is obtained
- Solid casting
  - As filter cake thickens, the slip level recedes
  - Additional slip is poured into the mold until the part is solid
- Pressure and vacuum casting
  - Externally-applied pressure (4.0 MPa) increases the kinetics of the filtration process
  - Speeds the entire process
- Centrifugal casting
  - Applied pressure generated by centrifugal force
  - Used for tube shapes, especially for making porous membranes
  - Porous mold not necessary

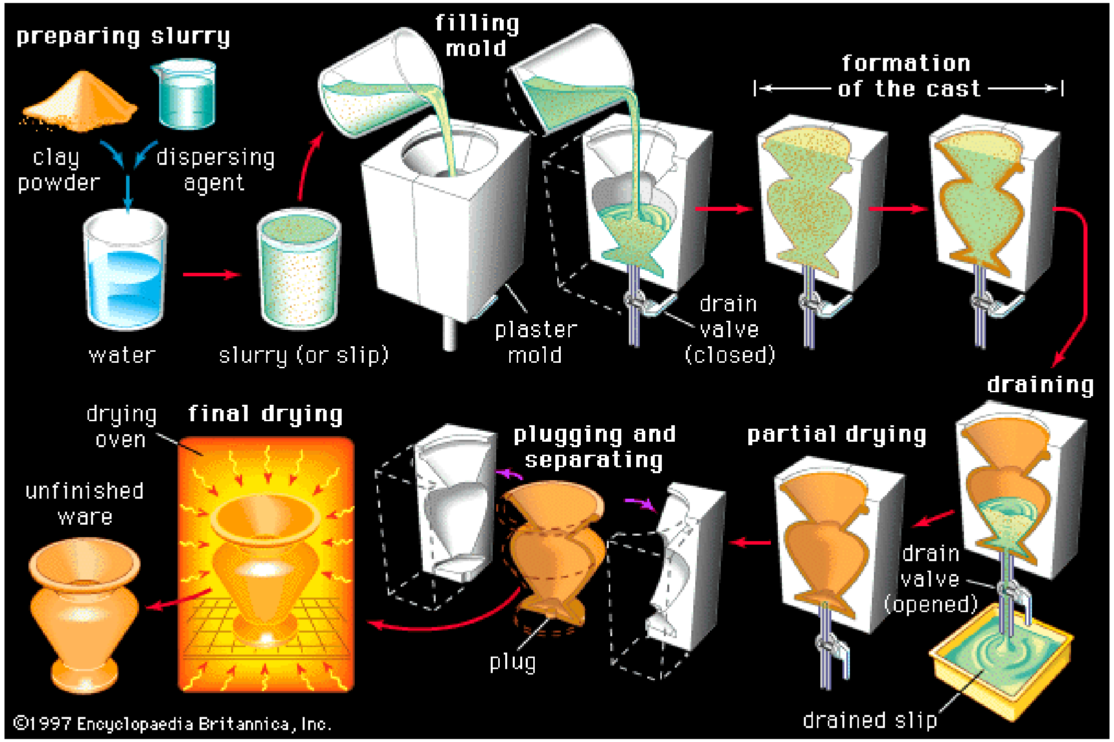
Applications

- Traditional ceramics:
  - China/stoneware
  - Artware
  - Sanitaryware
  - Crucibles
- Technical/advanced ceramics:
  - Filter media
  - Structural tubing
  - Bone implants
  - Heat engine components
  - Optical components

http://www.ikts.fraunhofer.de/

Slip Requirements

- Low viscosity (<1 Pa-s)– must be pourable
- High solids loading
    - Improves kinetics of casting
    - Reduces shrinkage/cracking
- Dispersant is critical
    - Affects interparticle forces
        - Maintains particles in suspension
        - Enhances uniformity of packing and high packing density



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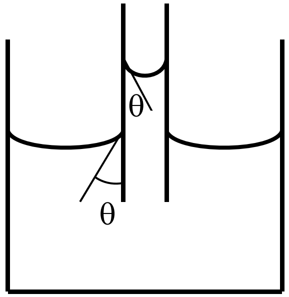
http://www.britannica.com/technology/traditional-ceramics

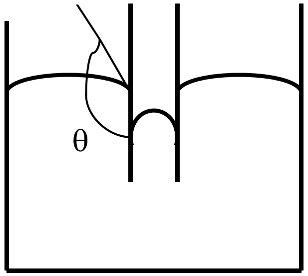
Capillarity

Capillary rise



$\theta < 90°$

Capillary depression



$\theta > 90°$

Hydrostatic Pressure

$\Delta P = \Delta\rho g h$ $\Delta\rho$ = density difference between liquid and vapor

h = height of liquid

r = radius of capillary tube

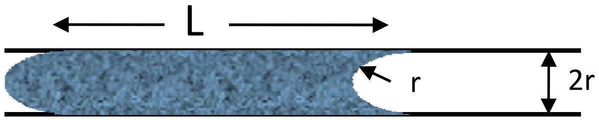
g = gravity constant

Capillarity

$$\Delta P = \frac{2\gamma_{lv}}{r}\cos\theta$$

$$\boxed{h = \frac{2\gamma_{lv}}{\Delta\rho g r}\cos\theta}$$

Capillarity in porous materials



$$\Delta P = \frac{2\gamma_{lv}}{r}\cos\theta$$ Capillary Pressure

$$\frac{V}{t} = \mu\pi\, r^2 = \frac{\Delta P\,\pi\, r^4}{8\eta L}$$ Poiseuille Eqn.

V = volume

ΔP = pressure on the system

η = viscosity

μ = average rate of flow

$$\Delta P_h = \mu\left(\frac{8\eta L}{r^2}\right)$$ hydraulics

$$\Delta P_c = \frac{2\gamma_{lv}}{r}\cos\theta$$ capillarity

$$\text{For } \Delta P_h = \Delta P_c \longrightarrow \frac{dL}{dt} = \mu = \frac{\gamma_{lv} r}{4\eta L}\cos\theta$$

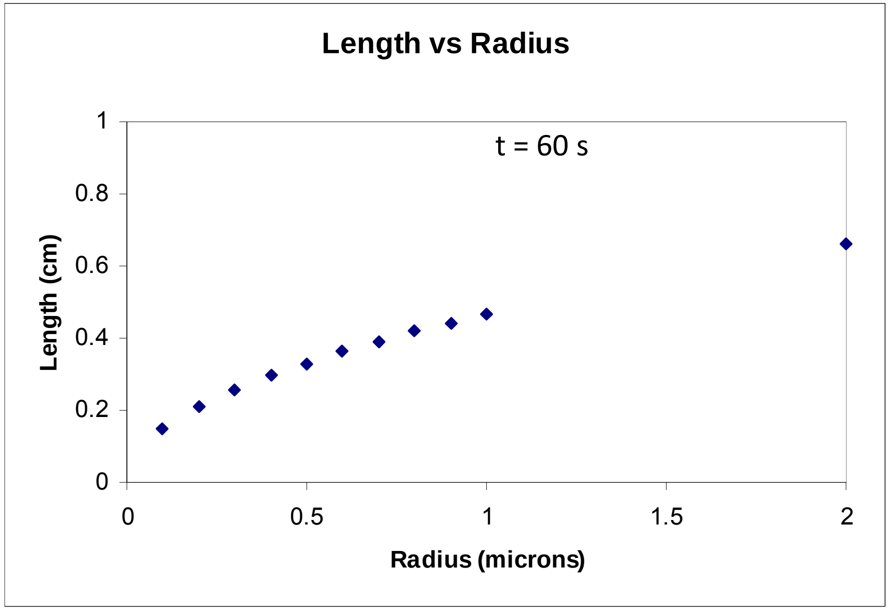
$$\boxed{L = \left(\frac{r\,\gamma_{lv}\cos\theta\, t}{2\eta}\right)^{1/2}}$$ **Rideal-Washburn eqn.**

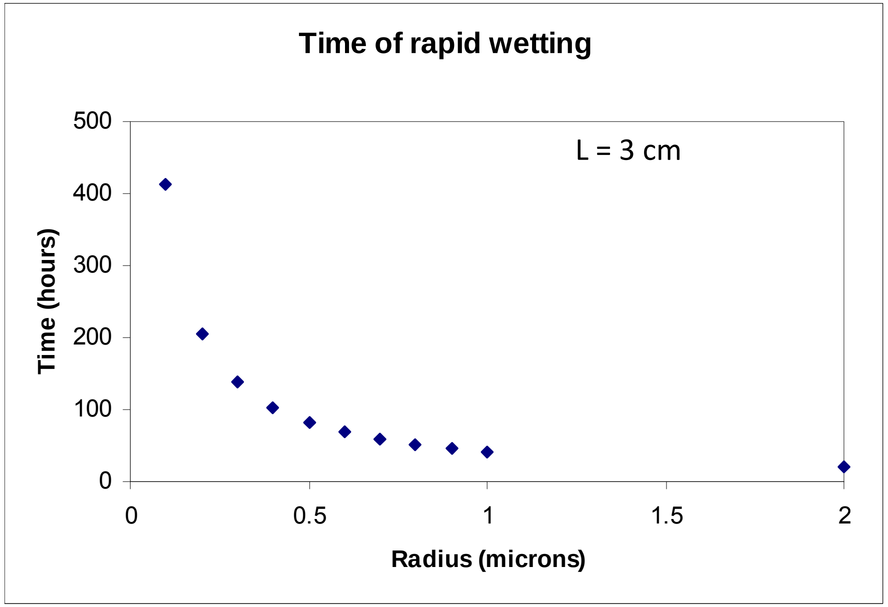
Capillarity is important for

- Slip casting
- Wetting of powders
- Wicking
- Drying
- Liquid phase sintering

Rideal-Washburn Equation

$$L = \left(\frac{r\gamma_{lv}\cos\theta\, t}{2\eta} \right)^{1/2}$$

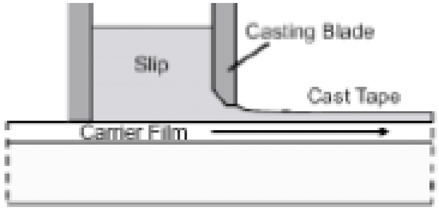


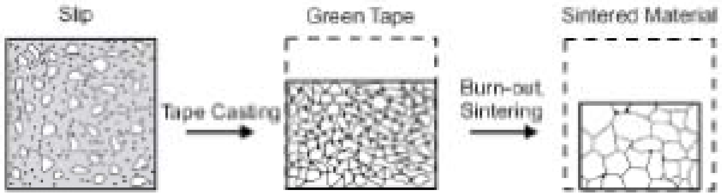


Assume water surface tension (0.0728 J/m^2), viscosity = 1 mPa·s

Tape Casting

- History – tape casting (also known as knife coating or doctor blading) was developed to test the covering power of paint formulations
- Howatt patented its use for ceramics for “High-dielectric high-insulation ceramic plates” in 1952



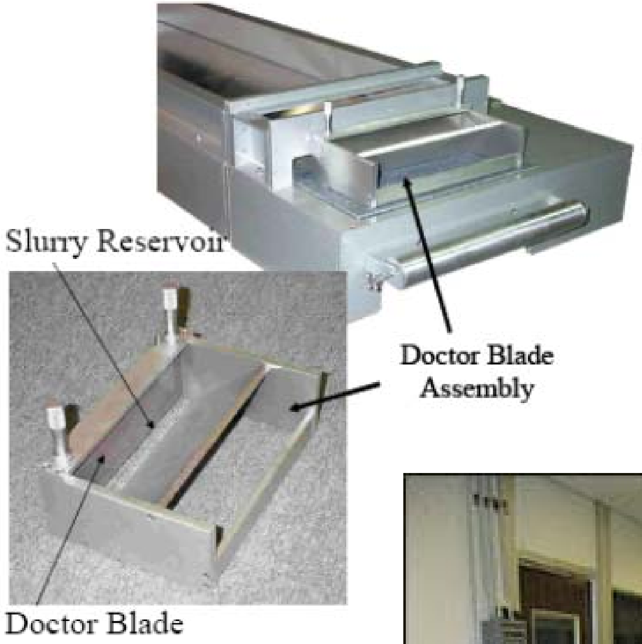


Schematic drawings of tape casting material at various steps in the process

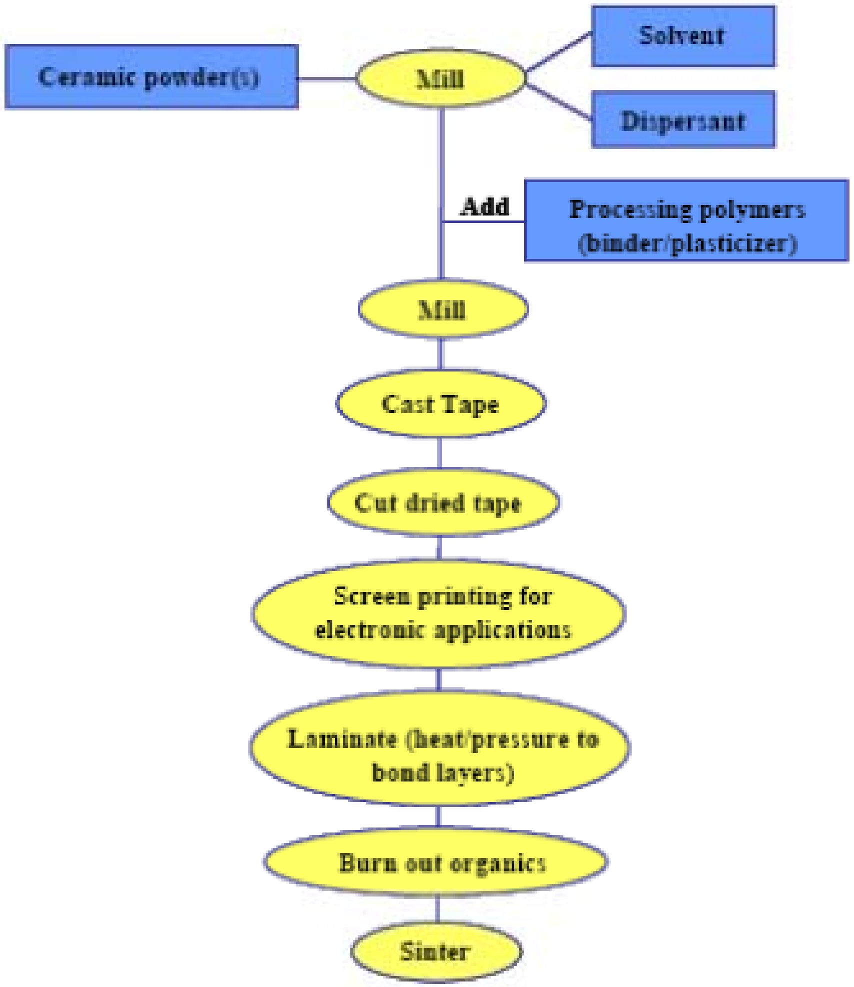
- Only way to form large area, thin (50 – 250 μm) ceramic sheets
- Applications:
  - Multilayer ceramic packaging (MLC)
  - Low temperature co-fire ceramics (LTCC)
  - Solid oxide fuel cells (SOFC)
  - Piezoelectric smart devices
  - Polyvinylidene fluoride (PVDF) battery separator films
  - Tape automated bonding (TAB) semiconductive adhesive metals
  - Ceramic membranes for microfiltration
  - Structural laminates
  - Knives

Tape Casting Slurry Characteristics

- Pseudoplastic
  - Lower viscosity during shearing under the doctor blade
  - Higher viscosity when cast so tape retains shape
- Typically organic solvents are used
  - Aqueous tapes dry too slowly for continuous casting (allows component segregation and slows production)
  - Formulations very difficult to develop



Tape Casting Process



Ceramic powder(s)

Mill

Solvent

Dispersant

Add

Processing polymers (binder/plasticizer)

Mill

Cast Tape

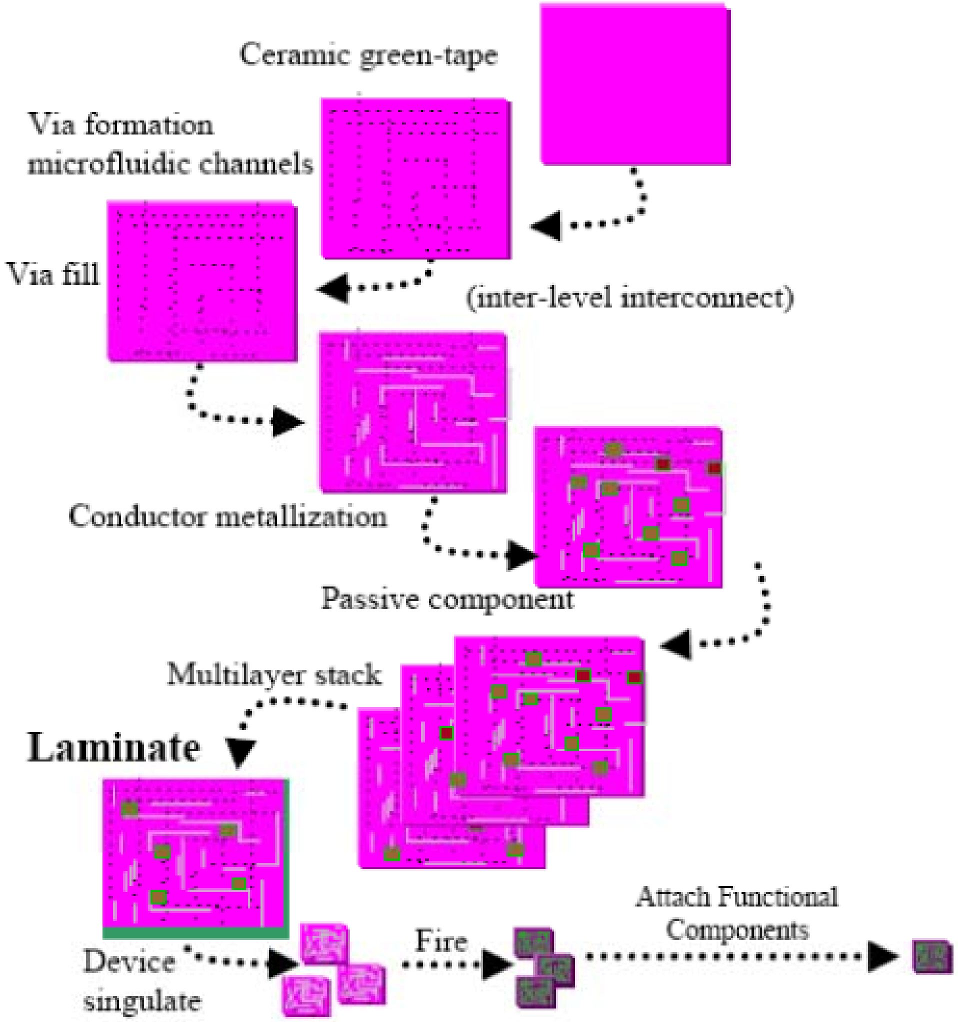
Cut dried tape

Screen printing for electronic applications

Laminate (heat/pressure to bond layers)

Burn out organics

Sinter



Ceramic green-tape

Via formation microfluidic channels

Via fill

(inter-level interconnect)

Conductor metallization

Passive component

Multilayer stack

Laminate

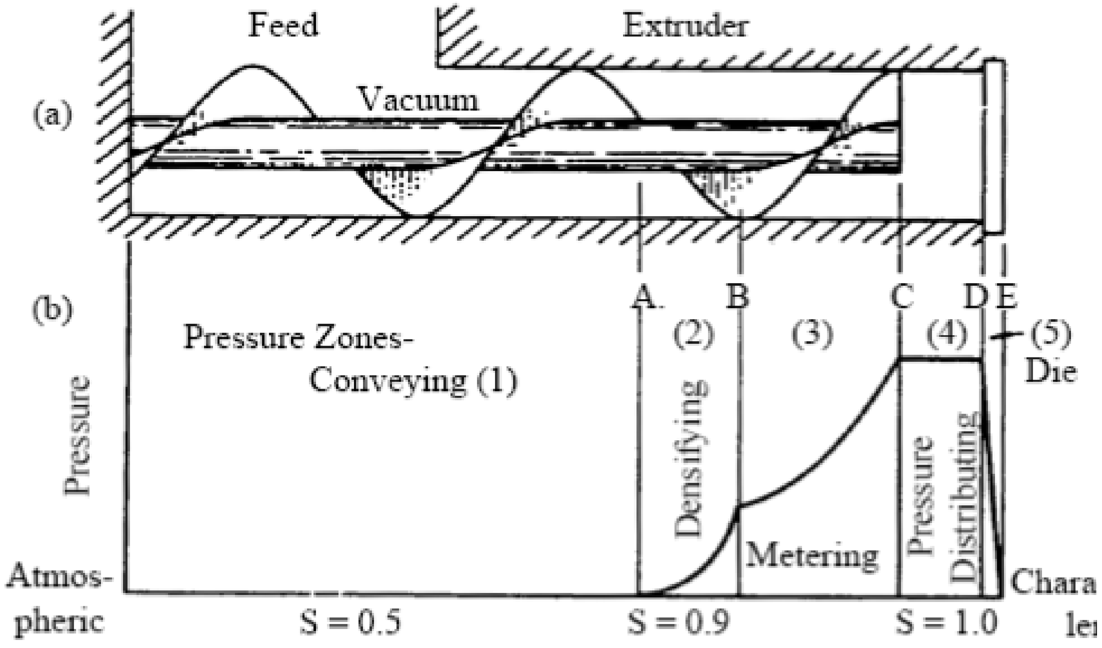
Device singulate

Fire

Attach Functional Components

Extrusion

- Extrusion paste must exhibit Bingham flow
- Viscosity dependent on:
  - Binder type
  - Volume
  - Grain size
  - Rate of shear
- 5-40 vol% organic content
- Critical paste characteristics:
  - No entrapped air
  - High solids content
  - Homogeneous mixing



Extrusion

- Parts with a high length to diameter ratio
- Applications:
    - Catalytic converters
    - Drill bits
    - Lucalox lamp tubes

Injection Molding

Advantages

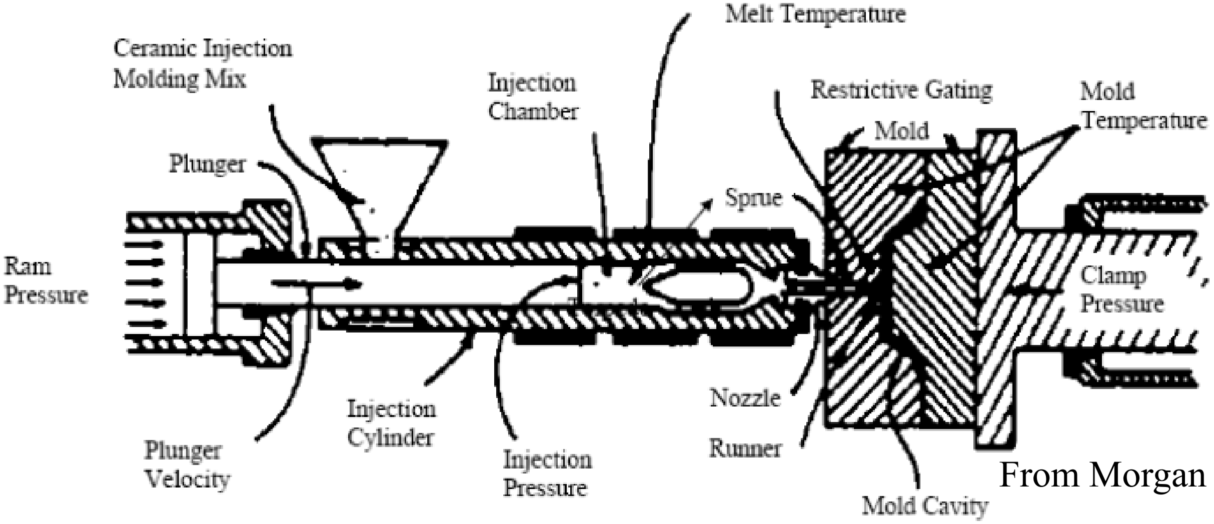
1. Automatic molding can reduce cost per part
2. Wide range of complex shapes can be molded
3. Part to part reproducibility is excellent
4. Excellent surface finish possible
5. Excellent for small complex, shapes

Disadvantages

1. Based on hydrocarbons
2. Expensive equipment - particulary the molds
3. Binder removal is difficult and time consuming

Molding Machines

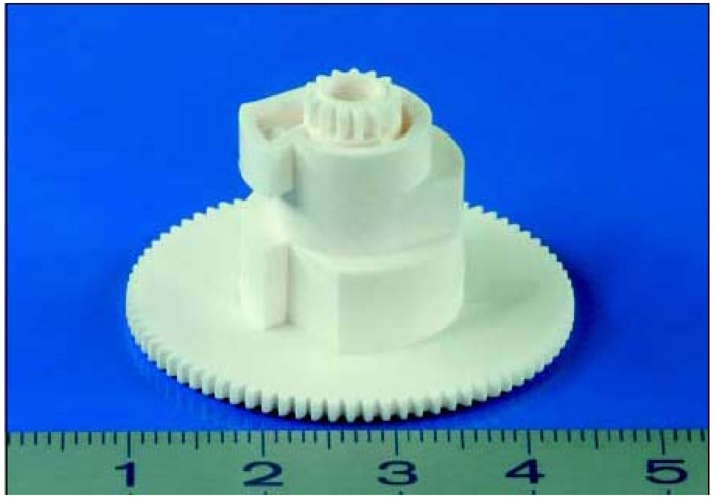
1. Ram or screw type delivery system
2. Machines are rated on the amount of organic that can be molded at a time (e.g., 4 oz., 8 oz., 4 oz. ~ 118 cm^3)



From Morgan Advanced Ceramics websi

Applications

- Screws
- Nozzles
- Cam plates (shown at right)
- Water jet assemblies
- Tape guides
- Sleeves
- Dental implants
- Orthodontic brackets



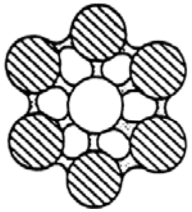
Degree of polymer saturation

Formulations for ceramic fabrication must fulfill dispersion requirements, fabrication process limitations and post-fabrication processing requirements. The volume fraction of liquid (solvent plus binder), powder and voids in a formulation is established by the forming process. Space filling during the fabrication process can be easily visualized by comparing the relative volume fractions of the components in a parameter called the degree of saturation.

Degree of Saturation (DS) = $\dfrac{\text{Volume liquid}}{\text{Volume open pores}}$

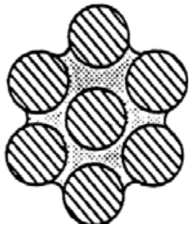
Pendular state

DS = 0.1 - 0.2



Capillary state

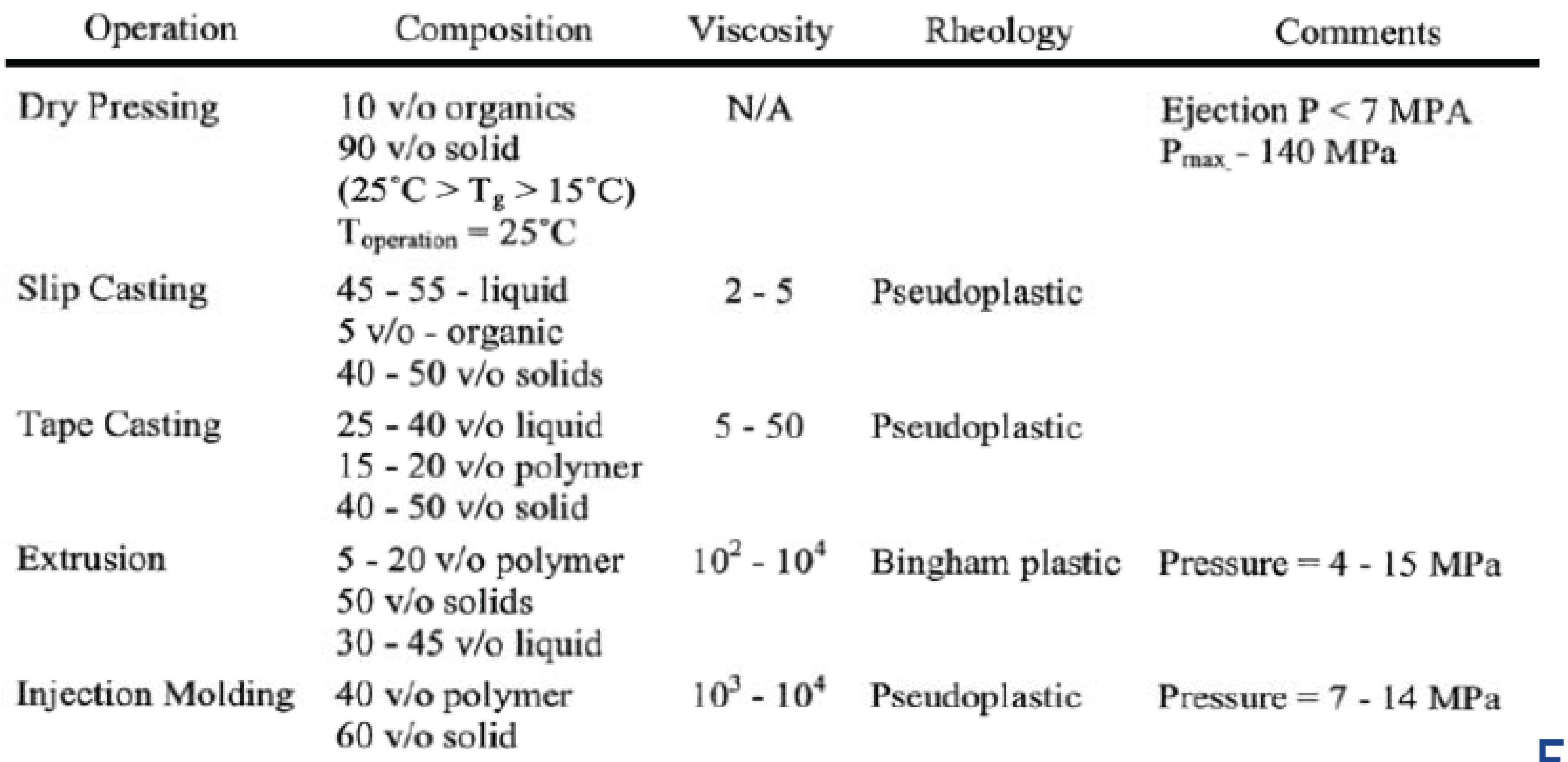
DS = 1



DS ≈ 0	Dry pressing, Isostatic pressing and Roll compaction
DS ≈ 0.3	Semidry pressing
DS ≈ 1	Extrusion, Injection molding
DS ≥ 1	Slip casting, Tape casting

Degree of Polymer Saturation (DPS) = $\dfrac{\text{Volume polymer}}{\text{Volume open pores}} = \dfrac{\text{PF}}{(1-\text{PF})}\left(\dfrac{V_{\text{polymer}}}{V_{\text{powder}}}\right)$

Comparison of Ceramic Forming Techniques



Operation	Composition	Viscosity	Rheology	Comments
Dry Pressing	10 v/o organics 90 v/o solid (25°C > T_g > 15°C) $T_{operation}$ = 25°C	N/A		Ejection P < 7 MPA P_{max} - 140 MPa
Slip Casting	45 - 55 - liquid 5 v/o - organic 40 - 50 v/o solids	2 - 5	Pseudoplastic	
Tape Casting	25 - 40 v/o liquid 15 - 20 v/o polymer 40 - 50 v/o solid	5 - 50	Pseudoplastic	
Extrusion	5 - 20 v/o polymer 50 v/o solids 30 - 45 v/o liquid	10^2 - 10^4	Bingham plastic	Pressure = 4 - 15 MPa
Injection Molding	40 v/o polymer 60 v/o solid	10^3 - 10^4	Pseudoplastic	Pressure = 7 - 14 MPa

Additive Manufacturing

All additive manufacturing techniques employ the same basic five-step process:

- Create a CAD model of the design
- Convert the CAD model to STL format
- Slice the STL file into thin cross-sectional layers
- Construct the model one layer atop another
- Clean and finish the model

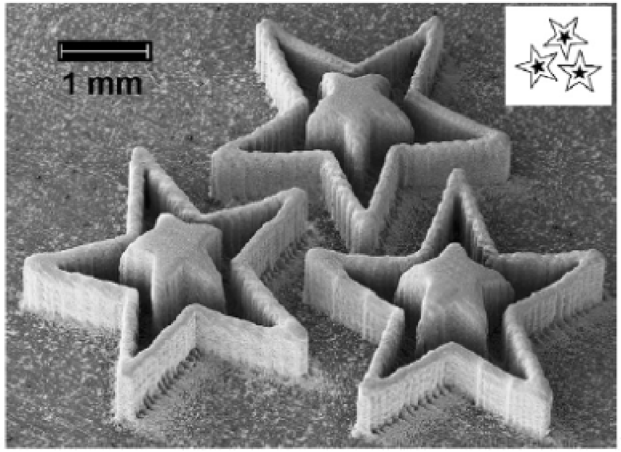
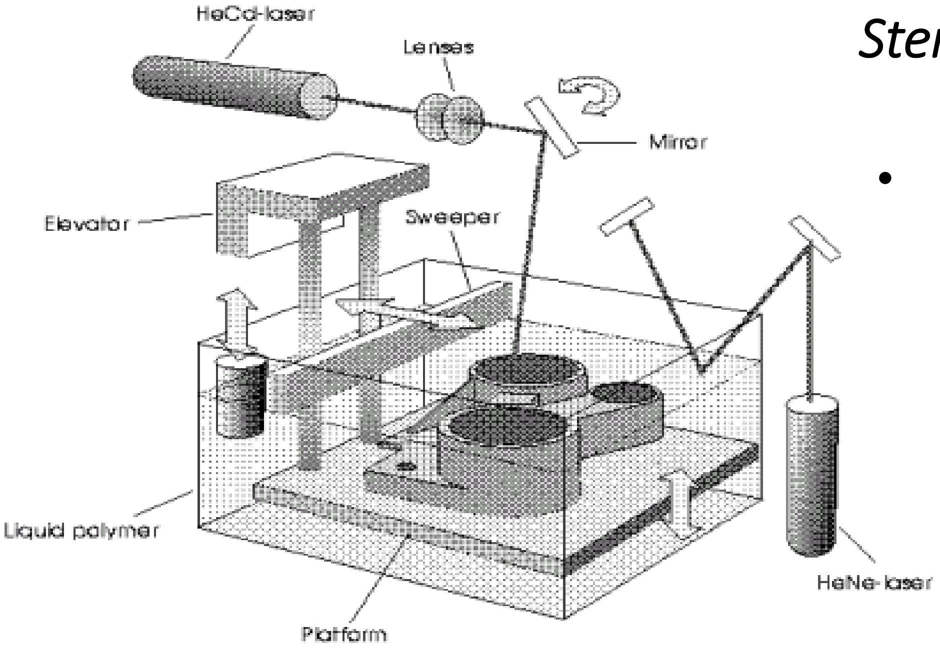


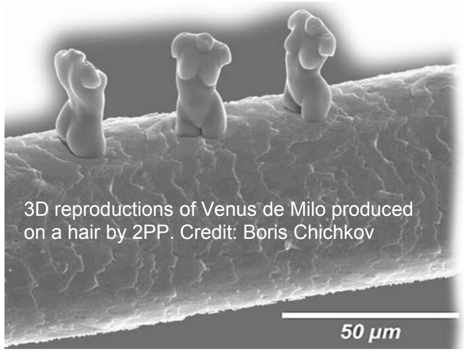
Fig. 9. SEM micrograph of a green printed ceramic structure (tilt angle = 30°) and the downscaled cross section.

Ozkul, J. Eur. Ceram. Soc., **30** (2010)

Stereolithography



- Stereolithography (SLA)
  - Epoxy resin (may contain a dispersed ceramic or metal powder) is photocured one layer at a time and the part in-process is incrementally dropped into a bath containing monomers and photoinitiators by the layer thickness to allow the next layer to be formed. UV light excites the photoinititaors and crosslinks the monomer. Most mature process.
  - Advantages: best surface finish, intricate shapes possible
  - Disadvantages: system cost, messy/potentially toxic liquids


3D reproductions of Venus de Milo produced on a hair by 2PP. Credit: Boris Chichkov

2PP – two-photon polymerization: a femtosecond laser is used to excite the photoinitiator

R. Narayan/ Bull. Am. Ceram. Soc., **88**[5] *(2009) 20-25*

Selective Laser Melting

- <u>Selective Laser Melting (SLM)</u>
  - A loose powder bed is leveled and bound by melting/sintering polymer powders or polymer-coated ceramic or metal powders in the desired geometry, layer-by-layer. The finished part is simply pulled from the loose powder bed.
  - Advantages: broad range of materials, speed
  - Disadvantages: system cost, surface finish

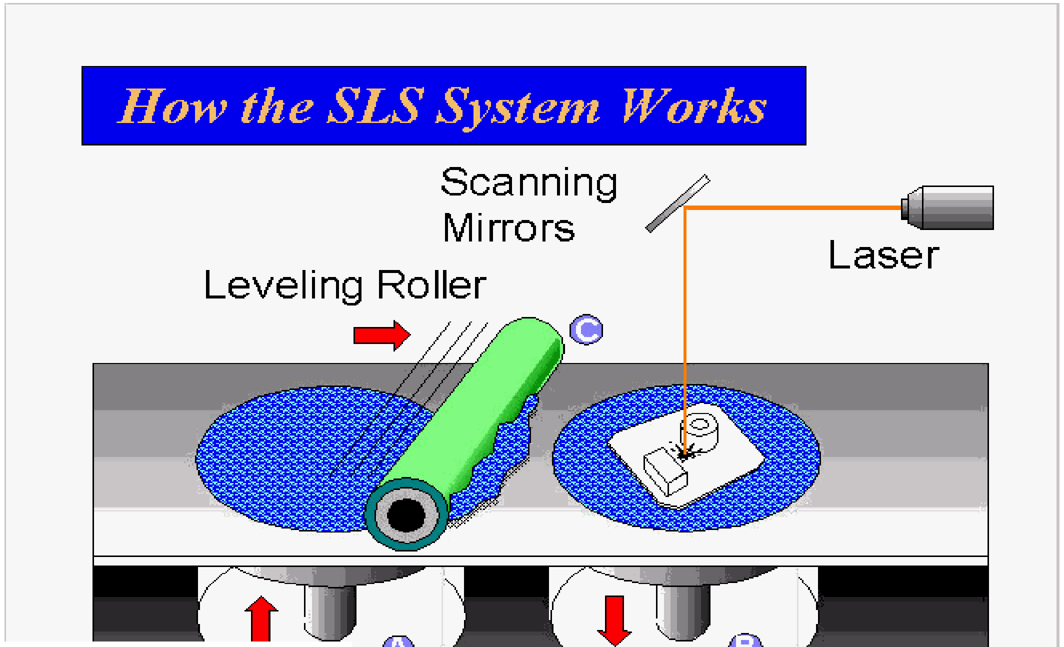


FIG. 15. Pure alumina parts processed by SLM.

Juste, J. Mater. Res., **29** (2014)

3-D Ink Jet Printing

- Ink Jet Methods
  - *Binder Deposition or Three Dimensional Printing (3DP)*
    - Build layers by ink jet printing of binder on powder bed. Lay down and level powder layer, deposit binder. Finished part is lifted from the loose powder bed.
    - Advantages: speed, decent surface finish, features down to 30 µm
    - Disadvantages: low strength/porous parts, limited materials, infiltrants expensive, no metal or ceramic parts
  - *Deposition of Ceramic Suspensions*
    - Hot melt ink jet deposits a suspension of ceramic/metal powders in a waxy thermoplastic.
    - Advantages: speed and surface finish good, parts are durable, choice of materials
    - Disadvantages: system cost

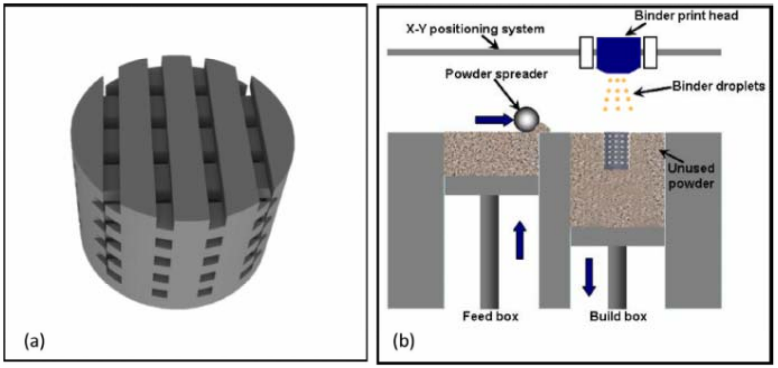
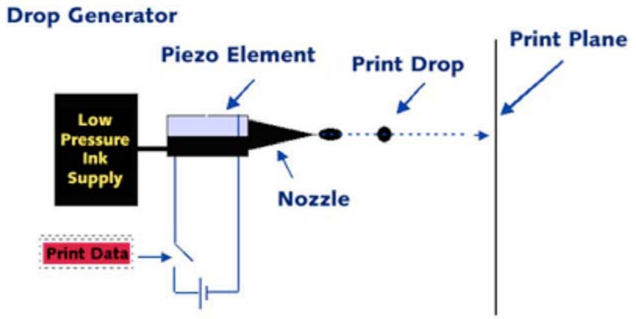


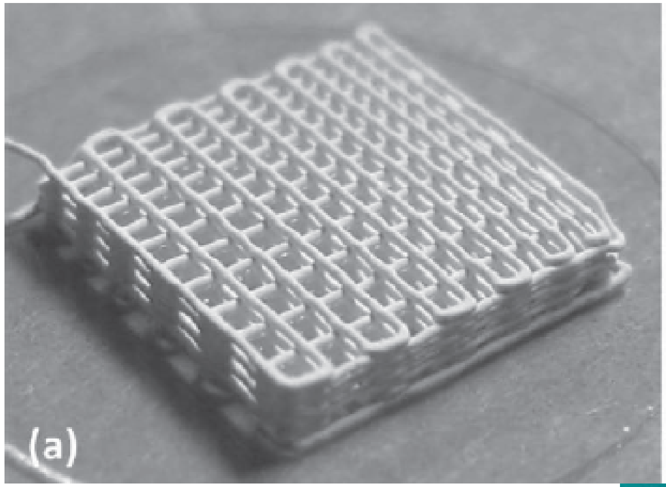
Figure 1.
(a) CAD image of a cross section of a porous scaffold. Square channels are oriented 0°/90° for subsequent layers. (b) Schematic drawing representing the 3D printing process.

Fielding et al., Dent. Mater., **28** (2012)

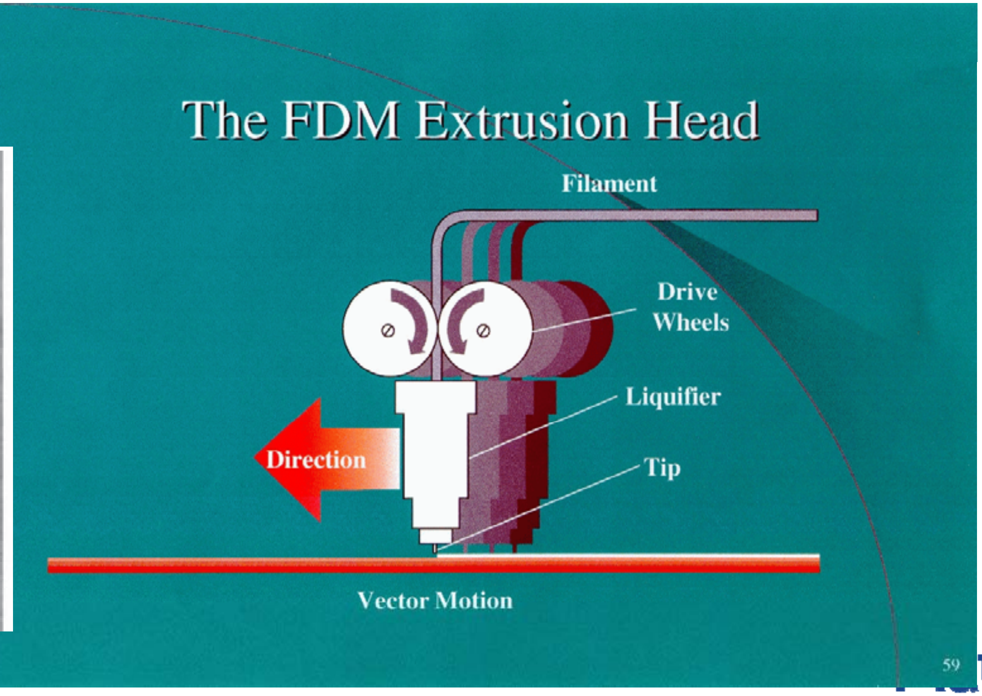


Fused Deposition Molding

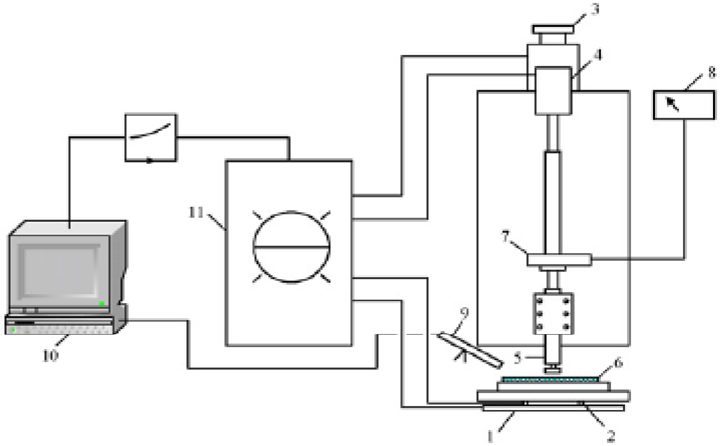
- Fused Deposition Modeling (FDM)
  - A thermoplastic (with or without ceramic or metal powders) is extruded from a small nozzle, directed by an x-y positioning device.
  - Advantages: strong parts, reliable
  - Disadvantages: slow speed



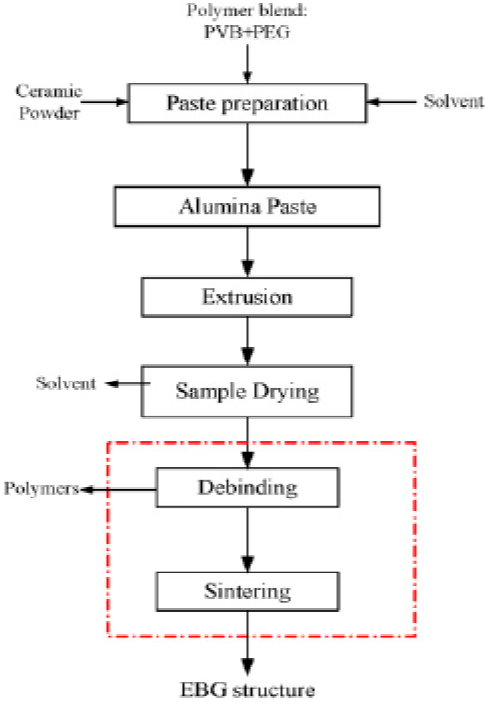
Sun et al., Adv. Healthcare Mater., **1** (2012)



Fused Deposition Molding



1. X-axis; 2. Y-axis; 3. Z-axis; 4. extrusion axis; 5. syringe; 6. substrate; 7. load cell; 8. pressure gauge; 9. camera; 10. computer and program; 11. control panel.



X. Lu et al. / Journal of the European Ceramic Society 30 (2010) 1–10

Fig. 1. Experimental set-up and process for extrusion freeforming showing three-axis table and two extruder drives.

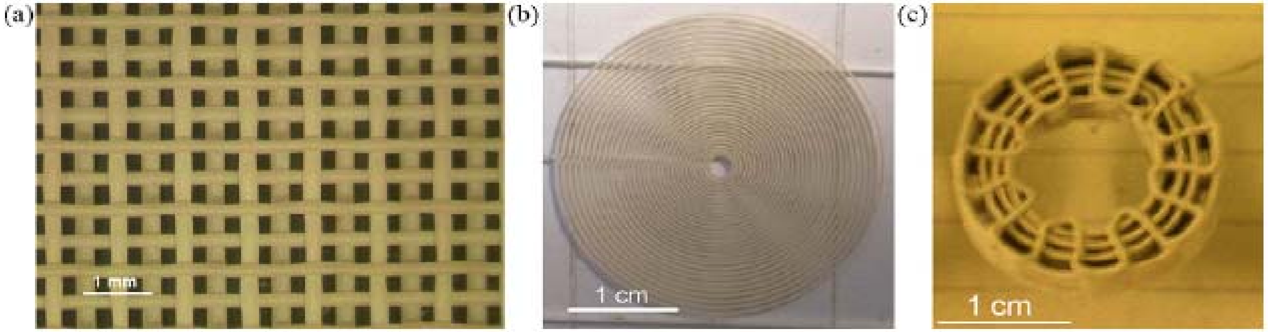


Fig. 11. Structures fabricated by extrusion freeforming: (a) periodic woodpile structure (4 layers) fabricated with LMT paste; (b) circle ring structure (2 layers) fabricated with quartz paste; (c) cylindrical structure (8 layers) with alumina paste.

Dimensional Changes – Important Design Criteria

Shrinkage or growth is often defined in terms of initial and final densities:

If dimensional changes are isotropic: $V_i = l_i^3$ and $V_f = l_f^3$

Volume shrinkage factor: $\frac{\rho_{\text{final}}}{\rho_{\text{initial}}} = \frac{w_f / V_f}{w_i / V_i}$ if $w_i = w_f$ then $\frac{V_i}{V_f}$

Linear shrinkage factor : $l_i = l_f$

$$\boxed{\frac{V_i}{V_f} = \frac{l_i^3}{l_f^3} = \left(\frac{l_i}{l_f}\right)^3 \qquad \left(\frac{V_i}{V_f}\right)^{1/3} = l_f\left(\frac{\rho_f}{\rho_i}\right)^{1/3}}$$

Organic Removal

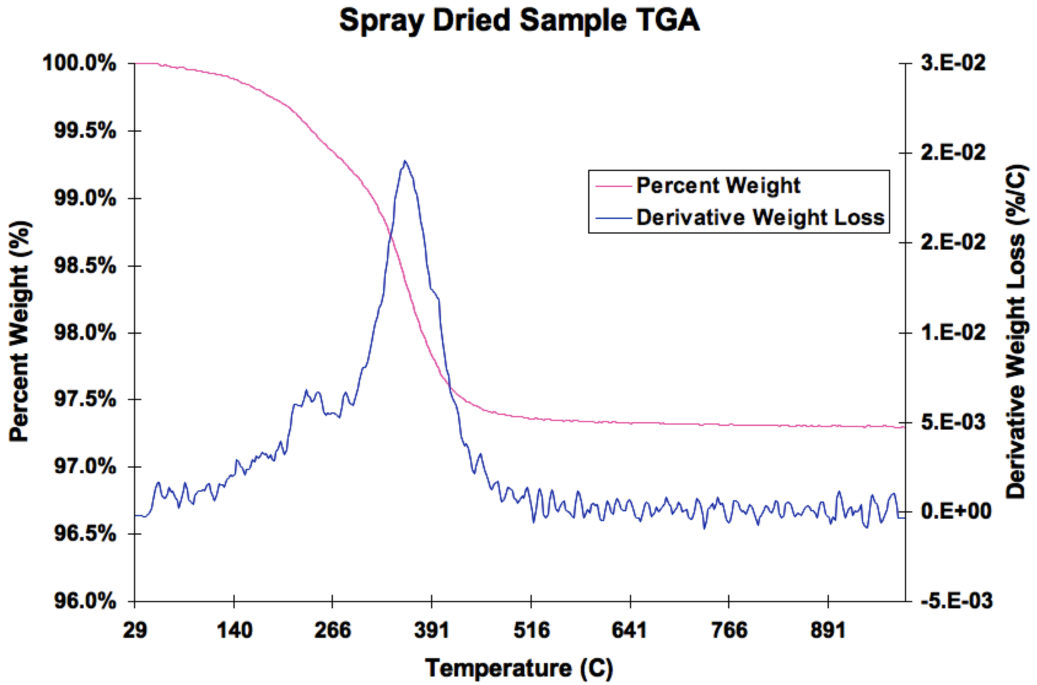
- Binder systems are developed for forming, green properties and for eventual removal
- Means of binder removal
  - Thermal degradation/decomposition
  - Chemical dissolution in solvent
- Need to remove polymer without los of shape of defect generation (e.g., swelling, cracks, large voids)
- Challenging for:
  - Large parts
  - Parts with high polymer contents (e.g., injection molding, tape casting)
  - Parts with organics requiring removal in reducing atmospheres

Thermal Binder Removal

- At least two polymers are typically used together
  - Major binder – higher MW, provides strength
  - Minor binder – lower MW, plasticizer
- On heating, polymers soften, flow and degrade and are removed as vapor
- Polymer can also be wicked out of parts (capillary forces) into a bed of fine particles
- Vapors or liquid must diffuse through pore spaces
- Most systems have gradual decomposition where minor binder is removed first, opening pore passages for removal of major binder

Determination of Organic Removal Conditions

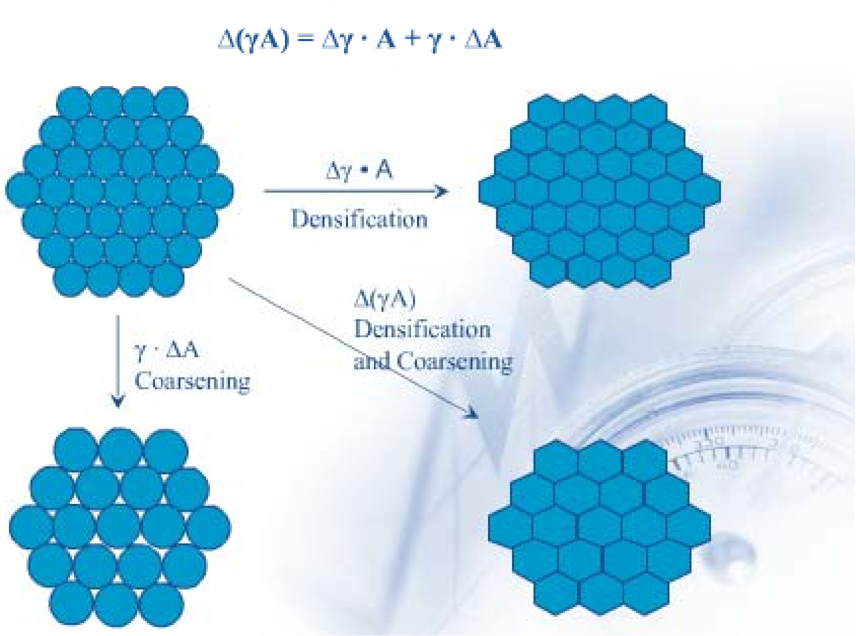
- Thermogravimetric analysis (TGA)
- Measure weight loss as a function of temperature (and atmosphere)
- Potential weight loss sources:
  - Adsorbed water
  - Organic processing aids
    - Dispersant
    - Binder
    - Plasticizer
  - Unreacted artifacts of powder synthesis
    - Carbonate
    - Nitrate
    - Etc.



Sintering

Sintering is the result of a thermodynamic driving force and a transport mechanism

Sintering* is the heat treatment of a particle mass, or high surface area powder, that results in a strength increase, reduction in surface area and, usually, densification.



$$\text{Driving Force} = A_{sv}\gamma_{sv} - A_{ss}\gamma_{ss}$$

$$\frac{\text{Driving Force}}{\text{volume}} = \frac{6\rho_b}{d\rho_o}\gamma_{sv}$$

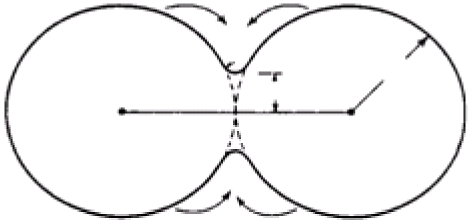
where ρ_b = bulk density
ρ_o = theoretical Density
d = particle diameter

From a driving force argument we conclude - the finer the particle size, the greater its densification. The system will attempt to lower its total surface area by either reducing A_{sv} (i.e. sintering) and/or reducing A_{ss} (i.e. grain growth).

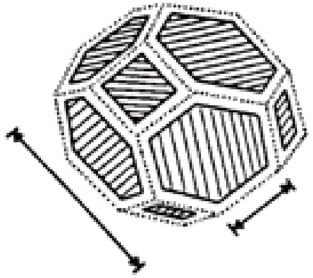
Sintering Stages

An approximate division of the microstructure at various stages of densification to make the geometry of diffusion mathematically tractable. (Coble)

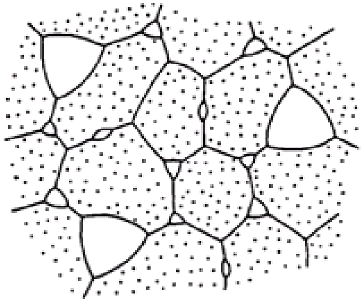
1. Initial Stage - continuous porosity and contacts between particles (< 65% density)



2. Intermediate Stage - continuous pore channels at grain edges (65 - 92% density)

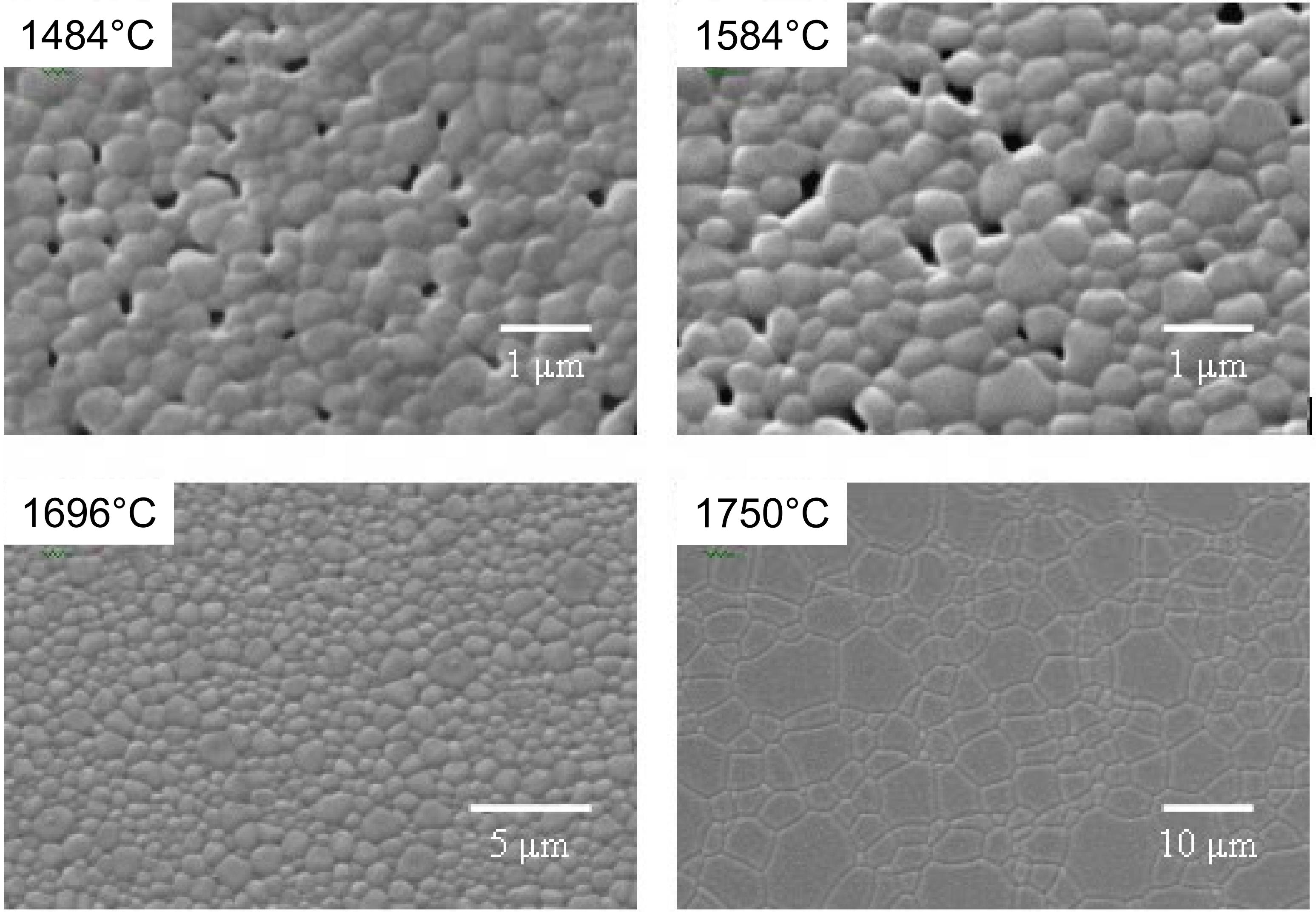


3. Final Stage - isolated pores on the grain boundaries and grain vertices (> 92% density)



M.N. Rahaman, *Sintering of Ceramics*, 2007

Final Stage Sintering



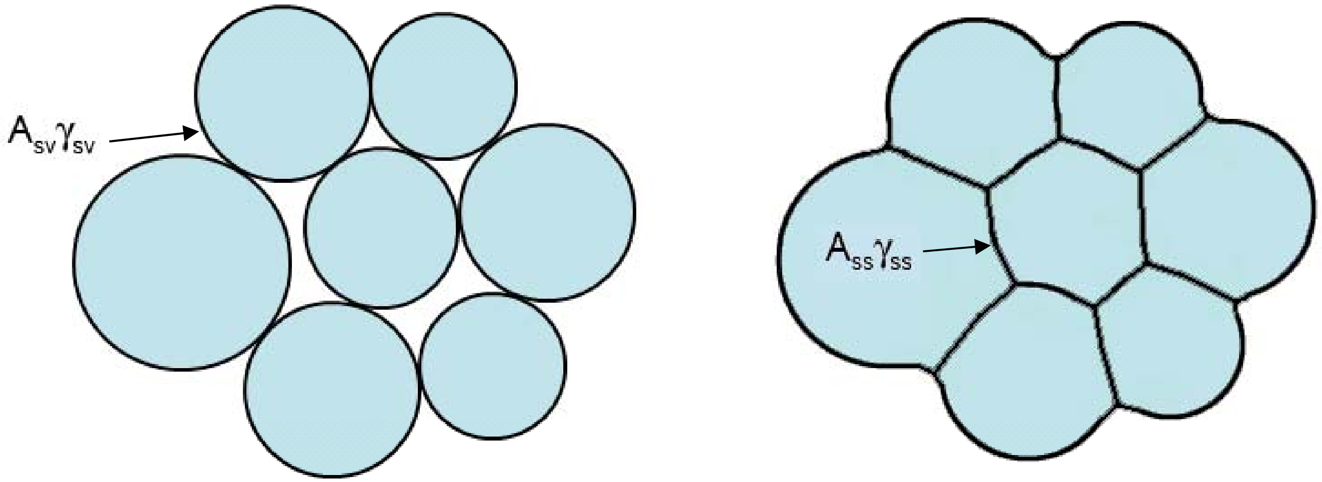
Nd:YAG

A. Stevenson, Ph.D. Thesis, Pennsylvania State University (2010)

Thermodynamics of Sintering

Sintering is the result of a thermodynamic driving force and a transport mechanism

Driving force for sintering is the reduction in surface free energy



$$\text{Driving Force} = A_{sv}\gamma_{sv} - A_{ss}\gamma_{ss}$$

$$\frac{\text{Driving Force}}{\text{volume}} = \frac{6\rho_b}{d\rho_o}\gamma_{sv}$$

ρ_b = bulk density
ρ_o = theoretical Density
d = particle diameter

Smaller powders will have more surface area and thus greater driving force for sintering

Sintering Mechanisms

1. **Solid State Sintering (0 vol% liquid phase)**

   Primary densification mechanisms - grain boundary and bulk diffusion

   Examples:

   Al_2O_3 ZrO_2
   MgO TiO_2
   SiC Ferrites

2. **Liquid Phase Sintering (0-10% vol% liquid phase)**

   Primary densification mechanism – dissolution-precipitation (requires both wetting & solubility of solid phase in liquid)

   Examples:

   $BaTiO_3$ + 1% TiO_2 MgO + 1-3% LiF
   Si_3N_4 + 5% MgO ZrO_2 + CaO/SiO_2 (<1%)
   Al_2O_3 + 5%Talc

3. **Viscous Sintering (>40 vol% liquid phase)**

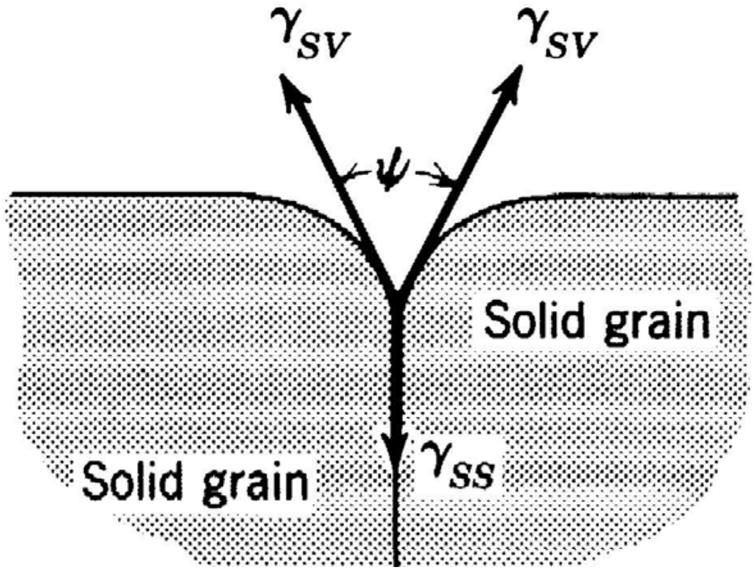
   Primary densification mechanism – viscous flow of liquid phase

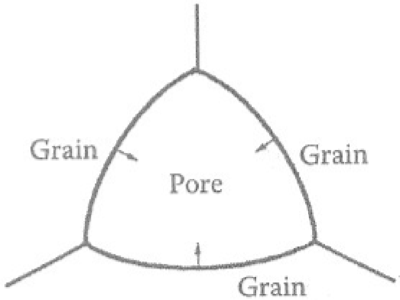
   Glasses with and without ceramic fillers

Geometry & Pore Removal

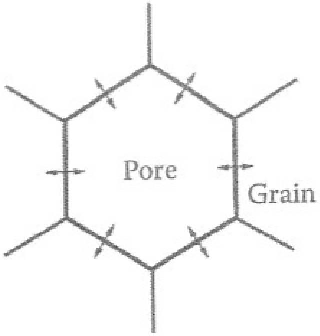
Dihedral Angle: $$\cos\left(\frac{\psi}{2}\right)=\frac{\gamma_{ss}}{2\gamma_{sv}}$$

if $\gamma_{ss} \approx \gamma_{sv}$, dihedral angle ≈ 120°

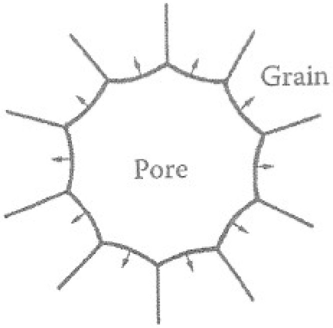




(a) Pore shrinks



(b) Metastable pore



(c) Pore grows

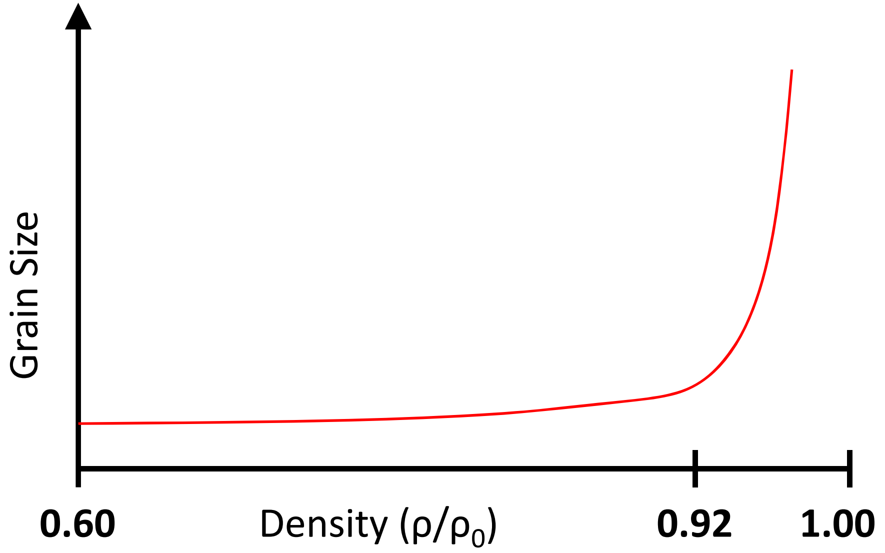
Pore stability is determined by dihedral angle and by the size of the pore relative to the grain size (this diagram assumes 120°)

Densification & Grain Growth

During sintering we observe:

1. The average grain size increases
2. The rate of densification decreases at some density (< 100%)

For well dispersed, well packed particles, we expect a sintering trajectory like this:



2 factors contribute to this shape:

1. Grain growth is restricted until $\rho/\rho_{Theoretical}$ = 0.92 to 0.95 (due to interconnected porosity)
2. The densification rate drops rapidly as grain growth occurs

Reduction in the Densification Rate:

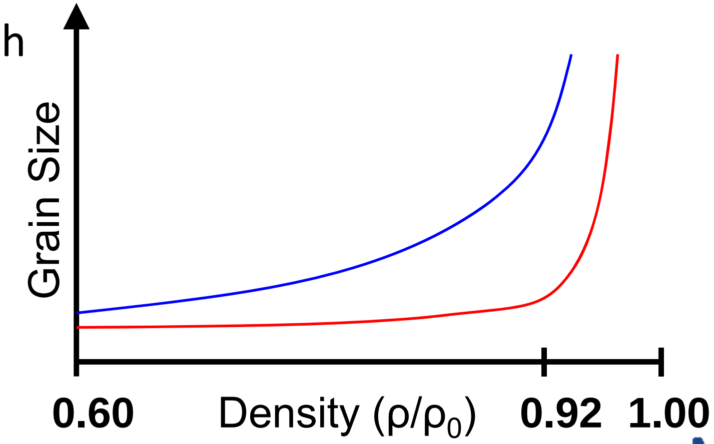
In the initial stage the rate of sintering is constant but decreases with increasing densification – why?

(a) Sintering driving force is reduced by grain growth

(b) Sintering driving force is reduced due to trapped gases in pores
(c) Some closed pores are <u>stable</u> and cannot be removed (change in mechanism)

- (i) too large to begin with (pore geometry)
- (ii) pore coarsening → (i)
- (iii) isolated within grains – no (reasonable) mass transport mechanism

By far the most important factor is grain growth

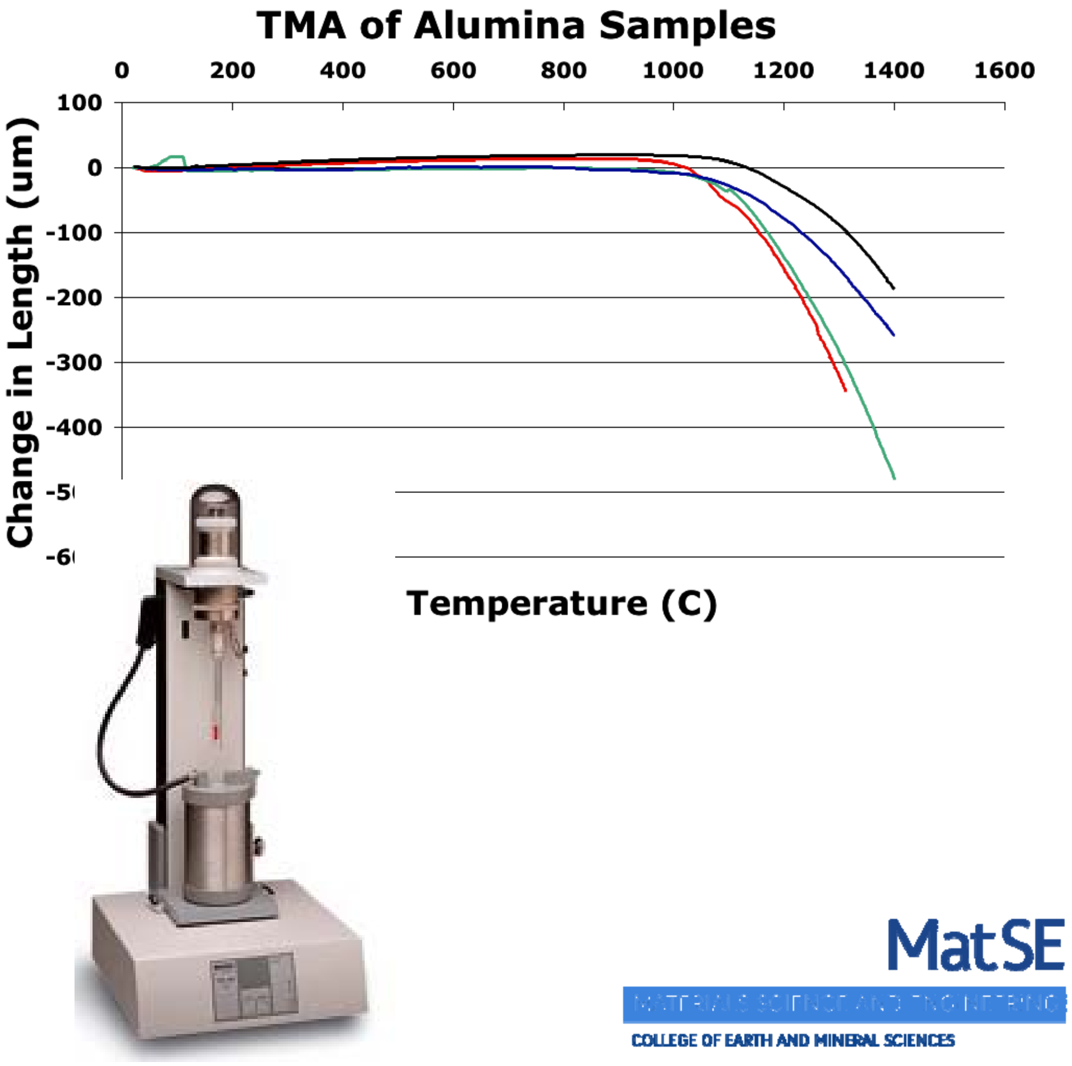


Wide size distribution or poor packing – densification is non-uniform and grain growth occurs in some regions before bulk reaches high density.

Uniform green density, good packing – material becomes dense uniformly, grain growth accelerates uniformly and rapidly.

Determination of Sintering Conditions

- ThermoMechanical Analysis (TMA)
- Measure shrinkage as a function of temperature (and atmosphere)
- Shrinkage occurs as part begins to sinter/densify
  - Particle rearrangement occurs during initial stage
  - Necks form between particles and their centers approach
  - Process causes part to shrink as particles grow together



Sintering Techniques

During sintering, we usually want to maximize density and avoid grain growth:

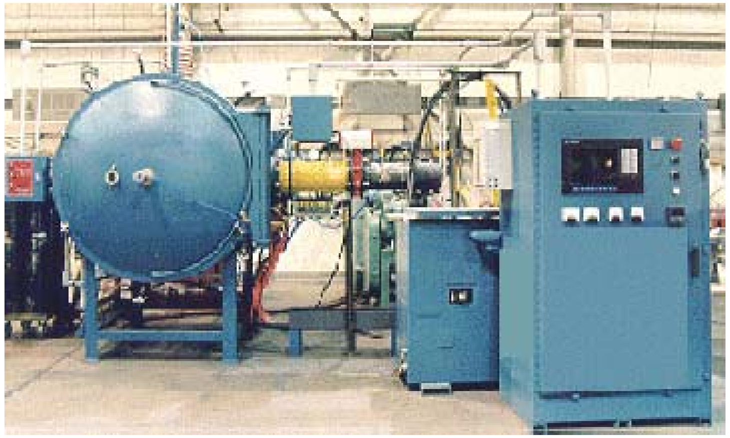
1. To improve mechanical properties (critical flaw will be the largest pore, if no pores, maximum flaw size ≈ grain size)
2. To improve functional properties (electrical properties such as dielectric constant, dielectric breakdown strength, etc)

As previously discussed, grain growth can be controlled by chemical factors, impurities, etc. but in some systems these effects are not sufficient to obtain 100% density.

We can often favor densification over grain growth by:

1. Use of external pressure – increases the sintering pressure but does not increase driving forces for grain growth
2. Rapid heating – in some (many?) systems, densifying sintering mechanisms have a higher activation energy than non-densifying mechanisms. Therefore, densification is favored at higher temperature, coarsening at lower temperatures and rapid heating “avoids” this coarsening regime.

Pressureless Sintering



Vacuum sintering furnace

- Heating
  - Electric
  - Gas
- Atmosphere
  - Air
  - Inert gas
  - Vacuum
  - Reducing gas

Tunnel kiln

The Effect of Pressure

Densification can be greatly enhanced by the use of external pressure:

$\Delta C/C_0 = \Omega / kT\ (2\gamma / r + \sigma_{eff})$ σ_{eff} = local stress at the interface

$$\sigma_{eff.} = \frac{\sigma_{applied}}{\rho_{rel.}}, \quad \rho_{rel.} = \frac{\rho_b}{\rho_o}$$

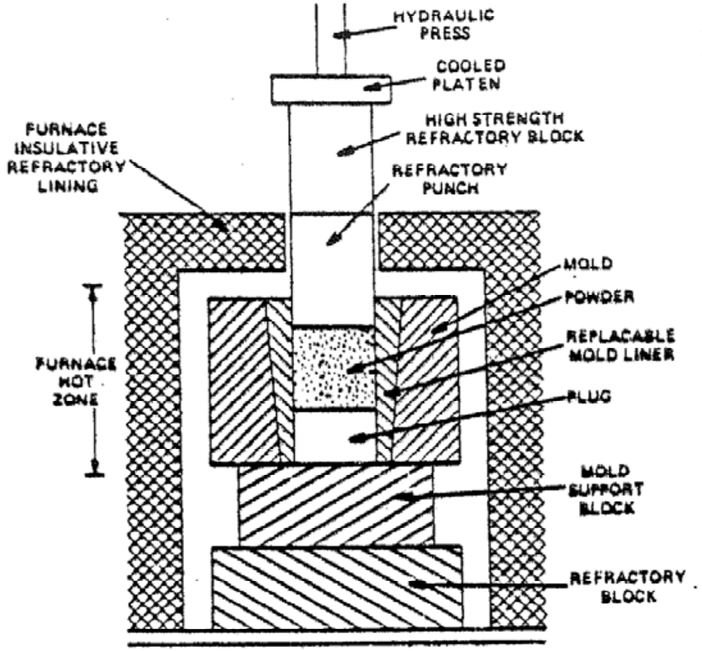
Hot pressing:

- Used for materials that sinter poorly (e.g., SiC, BN, B_4C, composites).
- Typically uses a heated graphite die (reducing atmosphere).
- Strength of graphite limits pressure to ~35 MPa.
- Typically parts require substantial machining to achieve desired dimensions.

Hot Isostatic Pressing (HIP):

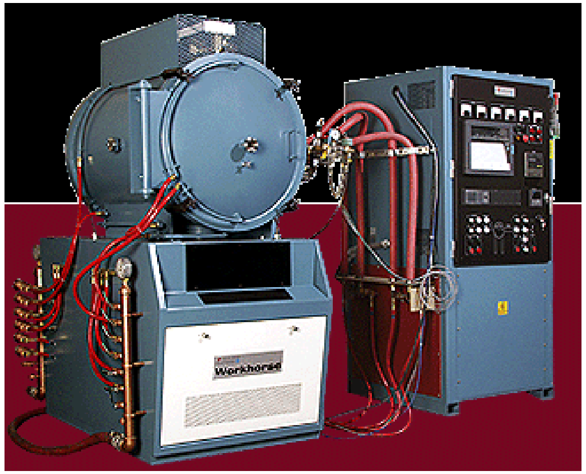
- Uses inert, high pressure gas to deliver pressure (typically N_2 or Argon)
- Samples are first sintered to obtain closed porosity (sinter-HIP) or can be encased in metal or glass envelopes
- Used when 100% density is absolutely required (WC-Co cutting tools, optical ceramics)

Uniaxial Hot Pressing



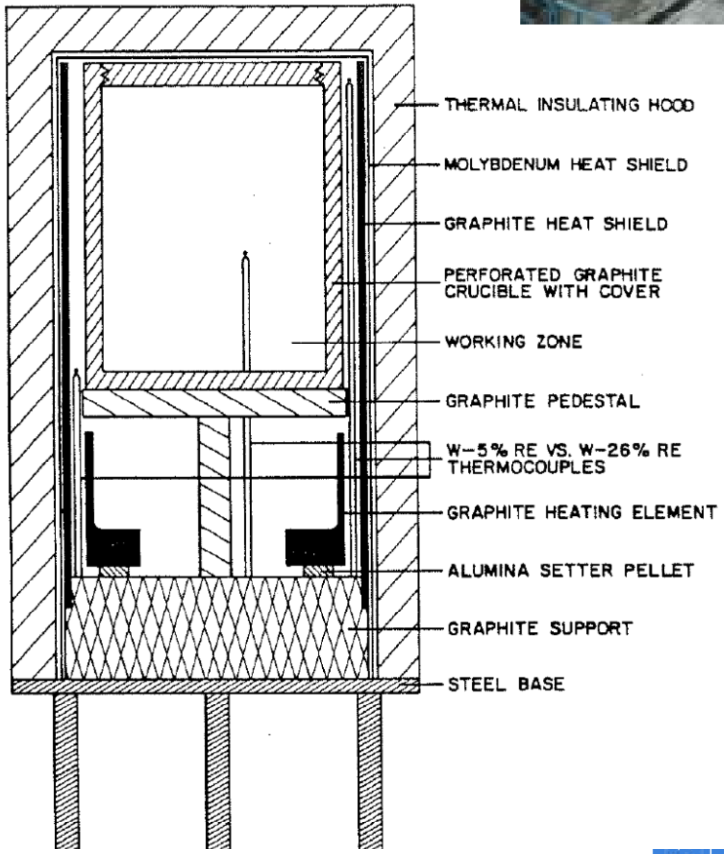
DIE MATERIAL IS CRITICAL.

- MUST WITHSTAND TEMPERATURE, TRANSIENT THERMAL STRESS AND HIGH LOADS.
- MUST BE CHEMICALLY INERT TO MATERIAL BEING HOT PRESSED.
- DIE LININGS OR COATINGS FREQUENTLY USED TO SUPPRESS REACTIVITY.
- GRAPHITE, $A\ell_2 0_3$, SiC FREQUENTLY USED FOR DIE MATERIALS.



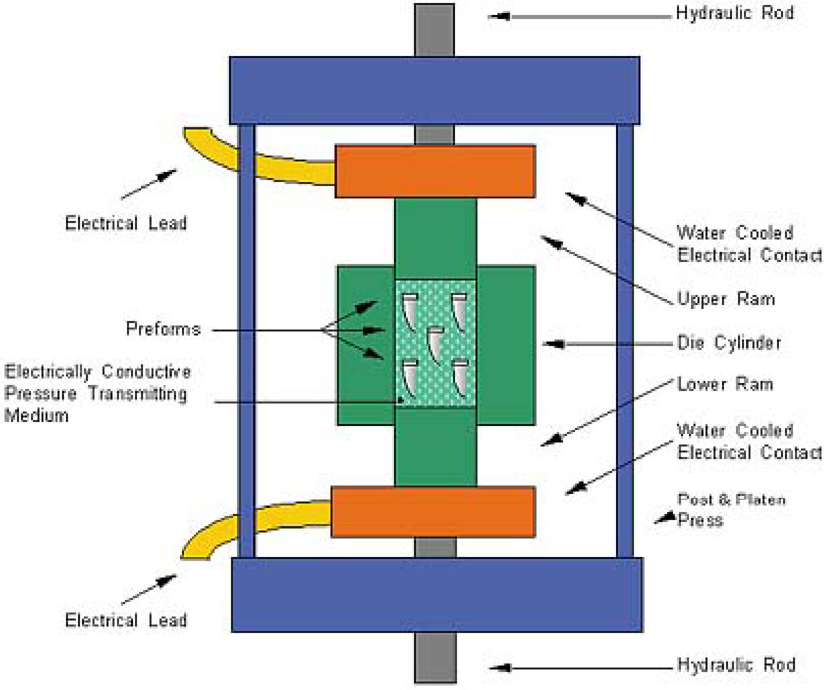
Hot Isostatic Pressing

- External pressure is applied isotropically using gas pressure – maximum ~200 MPa
- Parts must be pre-sintered to obtain closed porosity, or must be encased in glass or metal
- More expensive than HP, conventional sintering but achieves 100% density when needed for high reliability parts
- Large reduction in sintering temperature, limited grain growth
- Used for: WC-Co cutting tools, hip prostheses, ceramics for laser gain media



Spark Plasma Sintering (Field Assisted Sintering Technology)

- SPS or FAST is hot pressing with the addition of an electric field to increase heating rates
- Heating and cooling rates of 100s of degrees per minute
- High driving force for densification with little grain growth
- Uniform heating a challenge with thermally and/or electrically insulating materials (i.e., ceramics)



http://graphites-carbons.superiorgraphite.com/

Processing-Microstructure-Property Relationships

- Changes in composition and processing conditions (e.g., forming, sintering conditions) affect the microstructure and properties of final material
- The following examples from the literature illustrate these relationships

Effect of Sintering Conditions on Microstructure

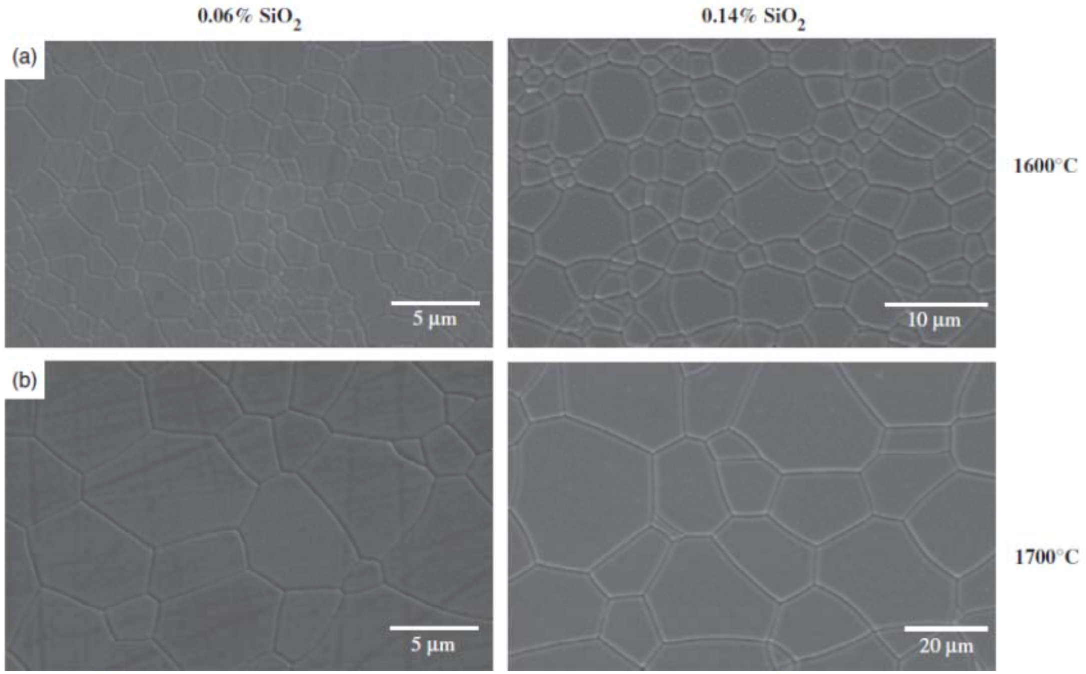


Fig. 2. SEM images of dry-pressed 1 at.% Nd:YAG specimens with 0.06 wt% (left) and 0.14 wt% (right) SiO_2, sintered at (a) 1600°C and (b) 1700°C for 2 h in vacuum and hot isostatic pressed at 1750°C for 2 h in 200 MPa Ar. The magnifications are not all the same so that the grain structure can be clearly seen for each sample.

Effect of sintering conditions on the density and grain size of dry-pressed Nd:YAG

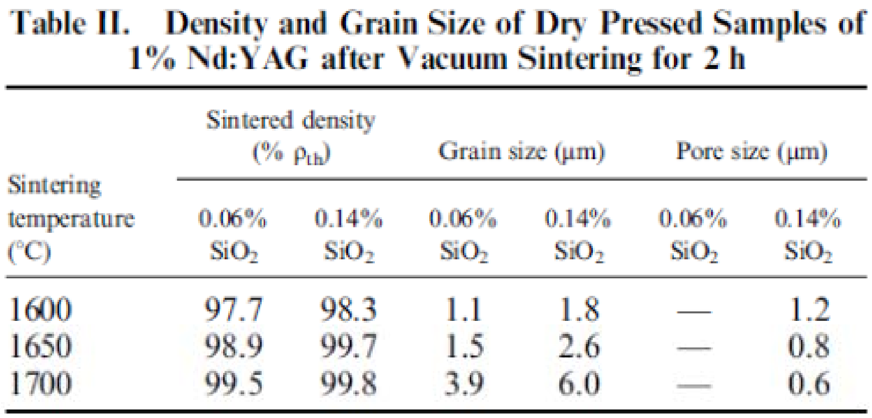


Table II. Density and Grain Size of Dry Pressed Samples of 1% Nd:YAG after Vacuum Sintering for 2 h

	Sintered density (% ρ_{th})		Grain size (µm)		Pore size (µm)	
Sintering temperature (°C)	0.06% SiO_2	0.14% SiO_2	0.06% SiO_2	0.14% SiO_2	0.06% SiO_2	0.14% SiO_2
1600	97.7	98.3	1.1	1.8	—	1.2
1650	98.9	99.7	1.5	2.6	—	0.8
1700	99.5	99.8	3.9	6.0	—	0.6

Lee et al., J. Am. Ceram. Soc., **92** (2009)

Effect of Sintering Conditions on Properties

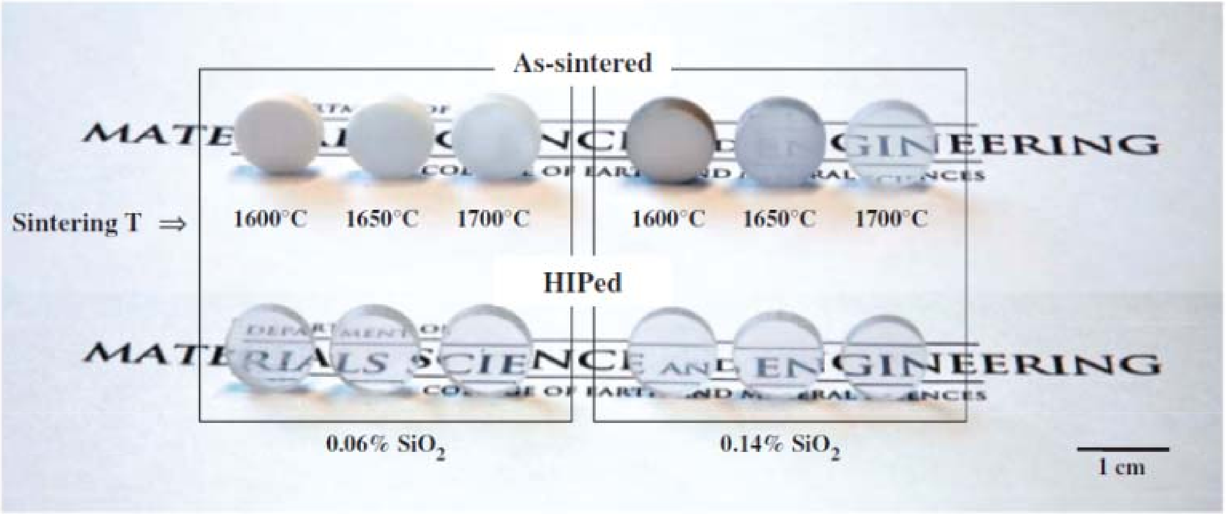


Fig. 3. Dry-pressed 1% Nd:YAG specimens doped with 0.06 and 0.14 wt% SiO_2, sintered for 2 h at the temperatures shown above and subsequently hot isostatic pressed at 1750°C for 2 h in 200 MPa Ar.

Effect of sintering conditions on the optical transmittance of dry-pressed Nd:YAG

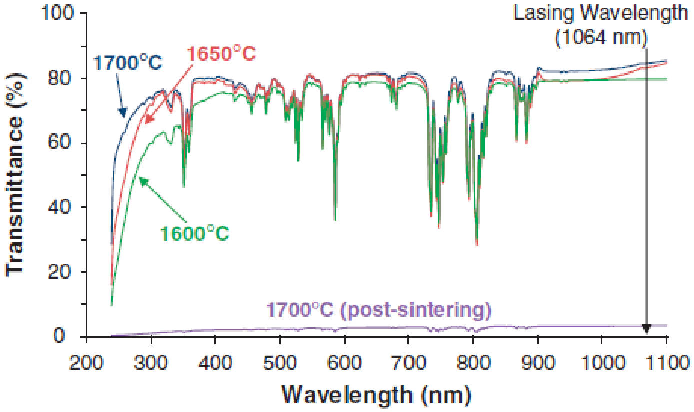


Fig. 5. In-line transmittance of dry-pressed 1 at.% Nd:YAG specimens doped with 0.06% SiO_2, sintered at 1600°, 1650°, and 1700°C for 2 h and hot isostatic pressed at 1750°C for 2 h in 200 MPa Ar. The sample sintered at 1700°C for 2 h before hot isostatic pressing is shown for comparison.

Lee et al., J. Am. Ceram. Soc., **92** (2009)

Effect of Macrostructure on Properties

- Bone scaffolding fabricated using fused deposition modeling
- Effect of scaffold spacing on bone ingrowth

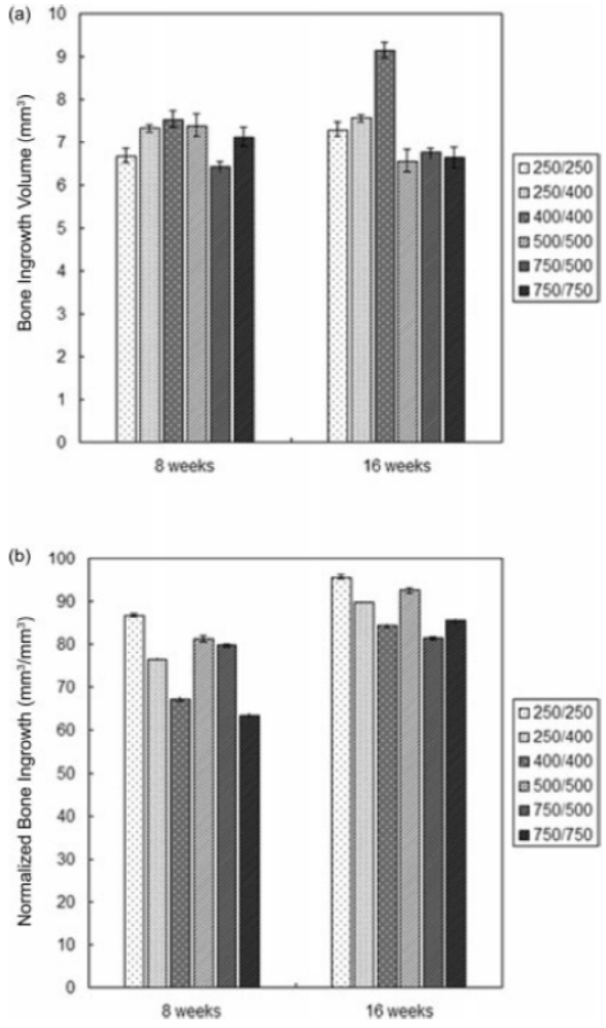


Figure 6. Plots of bone ingrowth into the HA scaffolds with varying quadrant designs: (a) total volume of bone ingrowth and (b) normalized volumetric bone ingrowth.

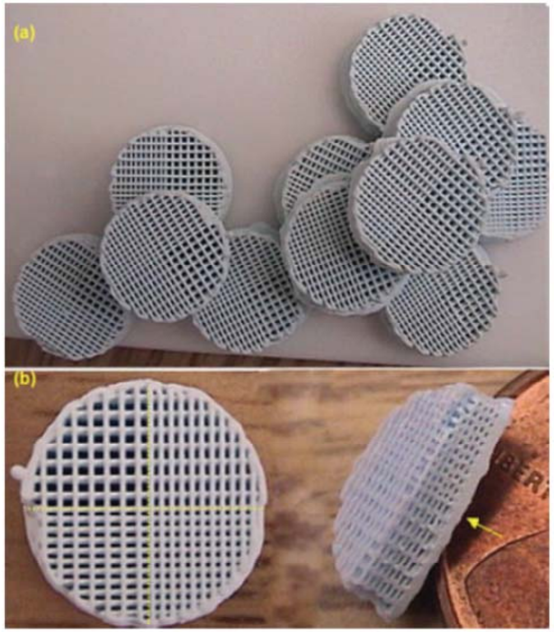


Figure 1. Optical micrographs of (a) HA scaffolds patterned with the DW250 quadrant design and (b) top and cross-sectional views of a representative DW250 scaffold illustrating the four distinct periodic arrays and their solid capping layer, respectively.

Simon et al., J. Biomed. Mater. Res. Pt. A (2007)

Effect of Composition on Microstructure and Properties

- Textured PMN-PT ceramic
- Undoped and 2% Mn-doped
- Effect of dopant on microstructure and piezoelectric properties

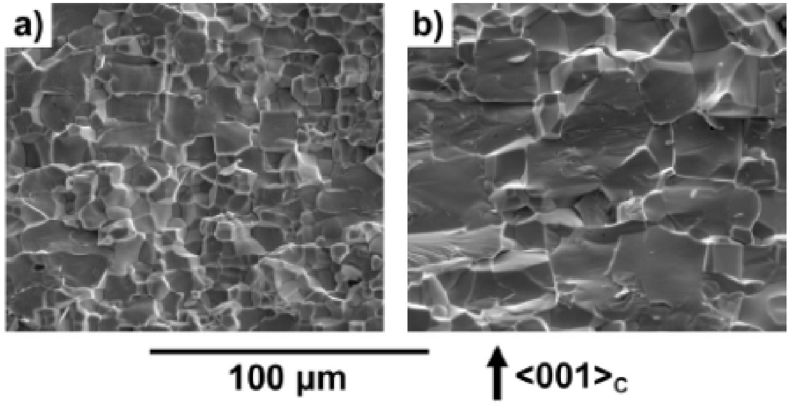


FIG. 1. Fracture surfaces of (a) undoped and (b) 2 at% Mn-doped $<001>_C$ textured PMN-PT ceramics. Samples were sintered at 1150 °C for 1 h in O_2 (PbO deficient atmosphere), and were annealed at 1150 °C for 10 h (excess PbO atmosphere).

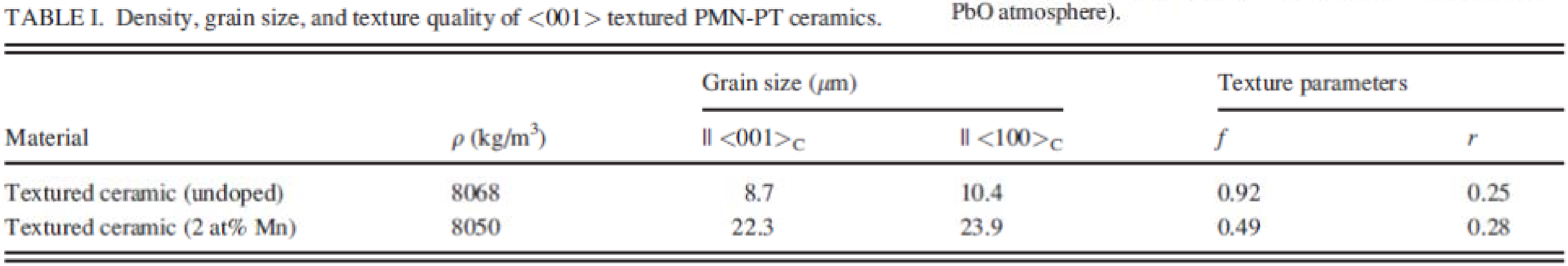


TABLE I. Density, grain size, and texture quality of <001> textured PMN-PT ceramics.

		Grain size (μm)		Texture parameters	
Material	ρ (kg/m^3)	∥ $<001>_C$	∥ $<100>_C$	f	r
Textured ceramic (undoped)	8068	8.7	10.4	0.92	0.25
Textured ceramic (2 at% Mn)	8050	22.3	23.9	0.49	0.28

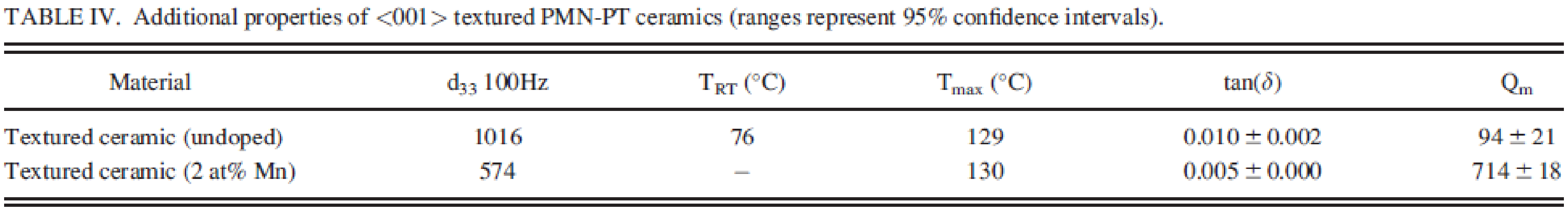


TABLE IV. Additional properties of <001> textured PMN-PT ceramics (ranges represent 95% confidence intervals).

Material	d_{33} 100Hz	T_{RT} (°C)	T_{max} (°C)	tan(δ)	Q_m
Textured ceramic (undoped)	1016	76	129	0.010 ± 0.002	94 ± 21
Textured ceramic (2 at% Mn)	574	–	130	0.005 ± 0.000	714 ± 18

Poterala et al., J. Appl. Phys., **110** (2011)

Effect of Microstructure on Properties

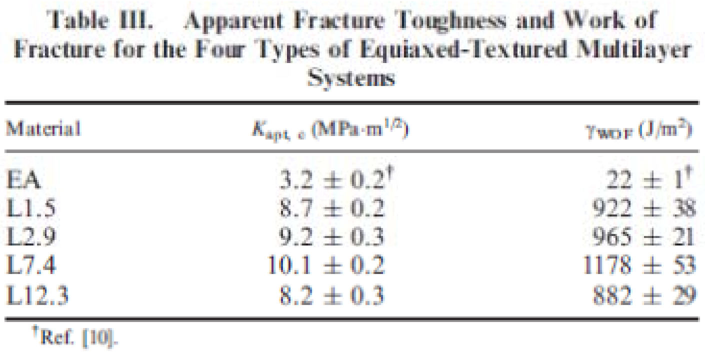


Table III. Apparent Fracture Toughness and Work of Fracture for the Four Types of Equiaxed-Textured Multilayer Systems

Material	$K_{apt,c}$ (MPa·m$^{1/2}$)	γ_{WOF} (J/m^2)
EA	$3.2 \pm 0.2^{\dagger}$	$22 \pm 1^{\dagger}$
L1.5	8.7 ± 0.2	922 ± 38
L2.9	9.2 ± 0.3	965 ± 21
L7.4	10.1 ± 0.2	1178 ± 53
L12.3	8.2 ± 0.3	882 ± 29

†Ref. [10].

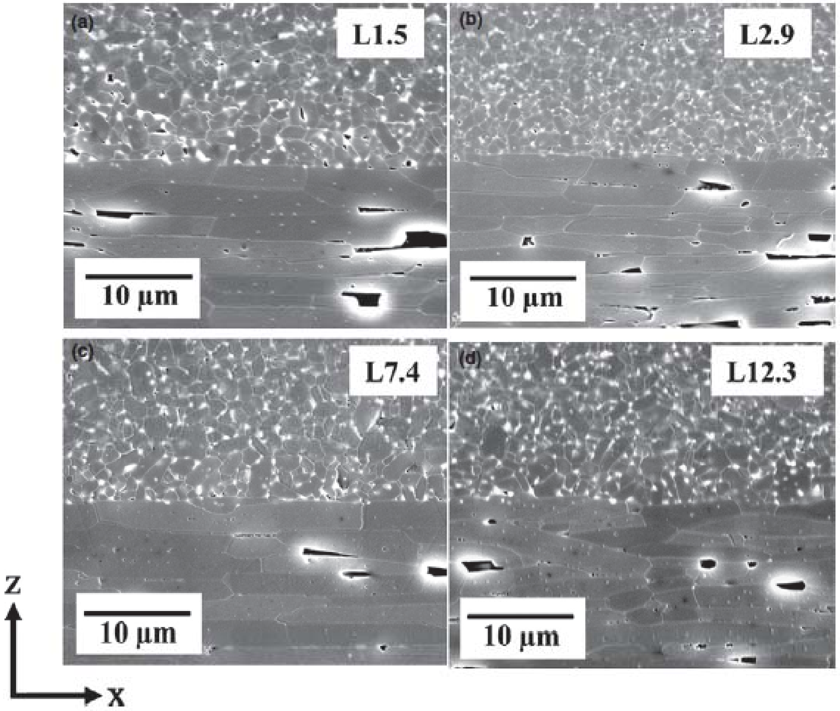


Fig. 1. SEM images of the microstructures and interfaces between the EA and TA layers for the (a) L1.5, (b) L2.9, (c) L7.4, and (d) L12.3 composites.

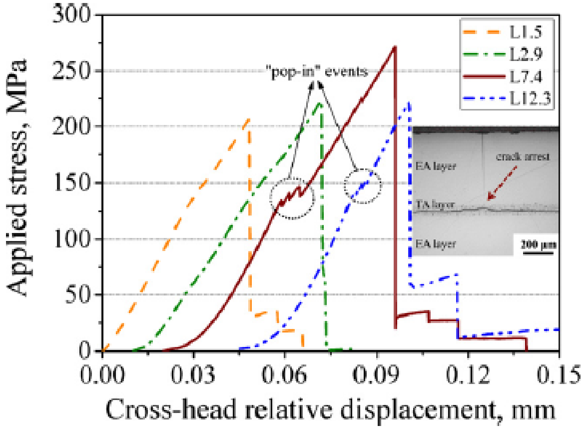


Fig. 4. Typical load–displacement curves of the L1.5, L2.9, L7.4, and L12.3 multilayer composites. Inset: cross section of laminate L7.4 during indentation-strength test, showing crack arrest of the 50*N* indentation at the TA layer.

- Equiaxed Al_2O_3 (EA)– textured Al_2O_3 (TA) composites
- Effect of EA:TA ratio on strength and work of fracture

Chang et al., J. Am. Ceram. Soc., **97** (2014)

Effect of Microstructure on Properties

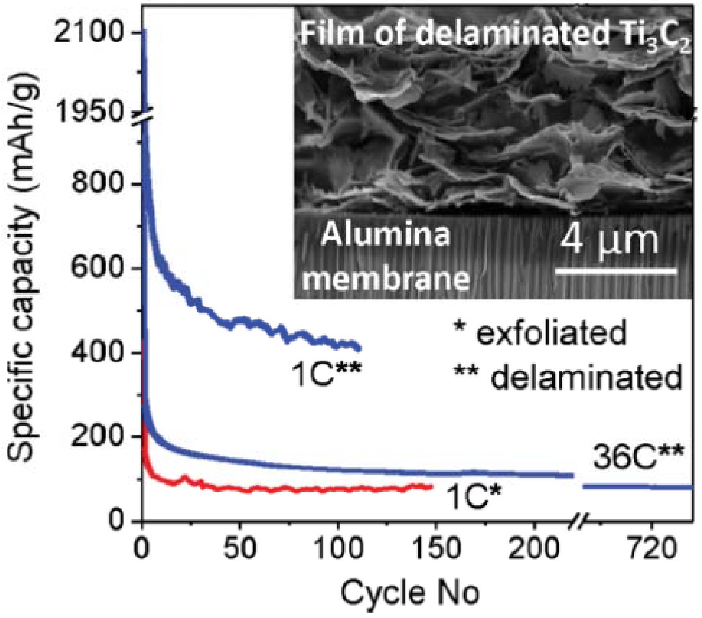
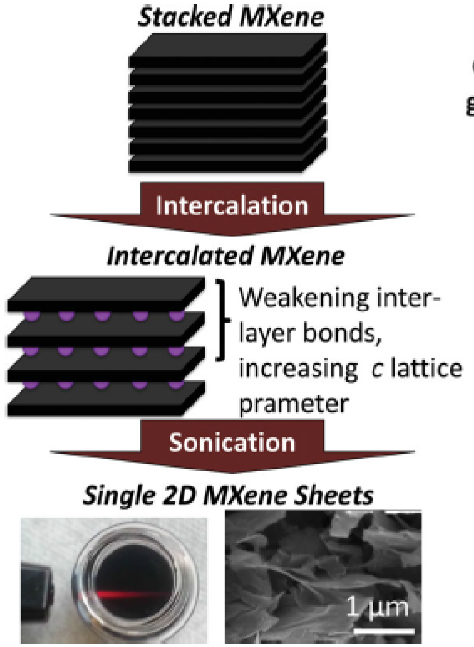


Figure 9. Comparison of the performance of multilayer Ti$_3$C$_2$T$_x$ powder film electrode (exfoliated MXene) and Ti$_3$C$_2$T$_x$ paper electrode prepared from delaminated few-layer MXene as anode materials in Li-ion batteries. Inset shows cross-sectional SEM image of an additive-free MXene paper on a porous anodic alumina membrane. Reproduced with permission.[26] Copyright 2013, Macmillan Publishers Ltd.



Chemical exfoliation of A-group element (Al) yielded stacked MXene

Intercalation between the layers of MXene

Weak sonication breaks inter-layer bonds and delaminates the layers

- MAX phases separated using different techniques yield different capacitance values

Naguib et al., Adv. Mater., **26** (2014)

Effect of Processing Conditions on Microstructure

- Alumina samples fabricated using selective laser melting
- Effect of layer thickness and laser energy density of part microstructure and density, respectively

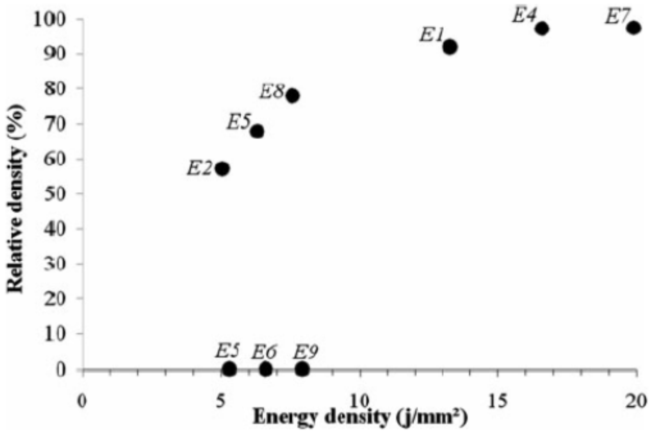


FIG. 10. Change of parts relative density as a function of laser energy density.

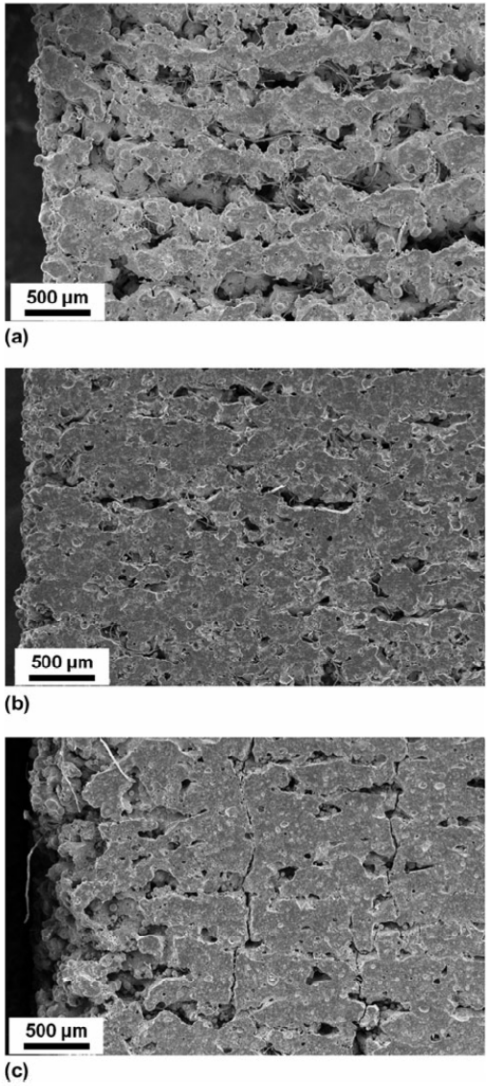


FIG. 12. Influence of layer thickness upon SLM microstructures (a) 100 µm slice, (b) 50-µm slice, and (c) 50 µm slice with postthermal treatment at 1550 °C/2 h.

Juste, J. Mater. Res., **29** (2014)

Summary

- Ceramic materials have unique properties because of their bonding and crystal structures
- Understanding the effects of processing variables on microstructure and properties and careful processing utilizing this understanding is necessary to take advantage of these properties
- Tailoring of the microstructure and properties of ceramics can also be achieved using these relationships