Ceramic Processing
7 Sintering

Introduction

- **Sintering is the heat treatment process of ceramic green body that leads to densification and bonding of ceramic body**
- **Major factors impacting sintering**
  - Compositions
  - Starting powder characteristics and packing
  - Processing
    - Heat schedule – always required
    - Atmosphere – very critical in some cases
      - For non-oxide ceramics (e.g., carbides, borides, nitrides)
      - For oxides: piezoeletric ceramics, ferrites
    - External pressure (constrains)
    - Others processing factors, e.g., Electrical/magnetic field/Microwave, Current
- **Major types of sintering**
  - Conventional **pressureless** sintering
  - **Pressure sintering** – higher cost, used when high density must be guaranteed
  - **Electrically assisted sintering**
    - e.g., microwave sintering, SPS, flash sintering (FS)

Rahaman (2003), p. 328

Conventional Pressureless Sintering – Furnace Heating Elements

❑ **Heating elements**

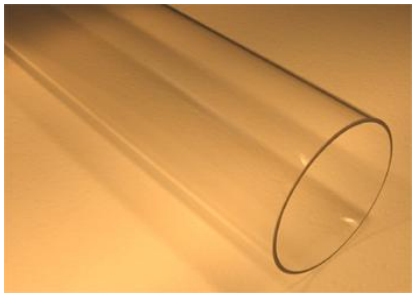
Element material	Max Temp (°C)	Atmosphere
Nichrome (80wt%Ni-20wt%Cr)	1200	Oxidizing, inert, reducing
SiC	1500	Oxidizing
$MoSi_2$	1750	Oxidizing
$LaCrO_3$	1750	Oxidizing
Mo, W, Ta	2000	Vacuum, inert, reducing
Graphite	2800	Inert, vacuum, and reducing

Conventional Pressureless Sintering – Lab Furnace Configuration

❑Conventional air box furnace/muffle furnace

❑Tube furnace w/ atmosphere control

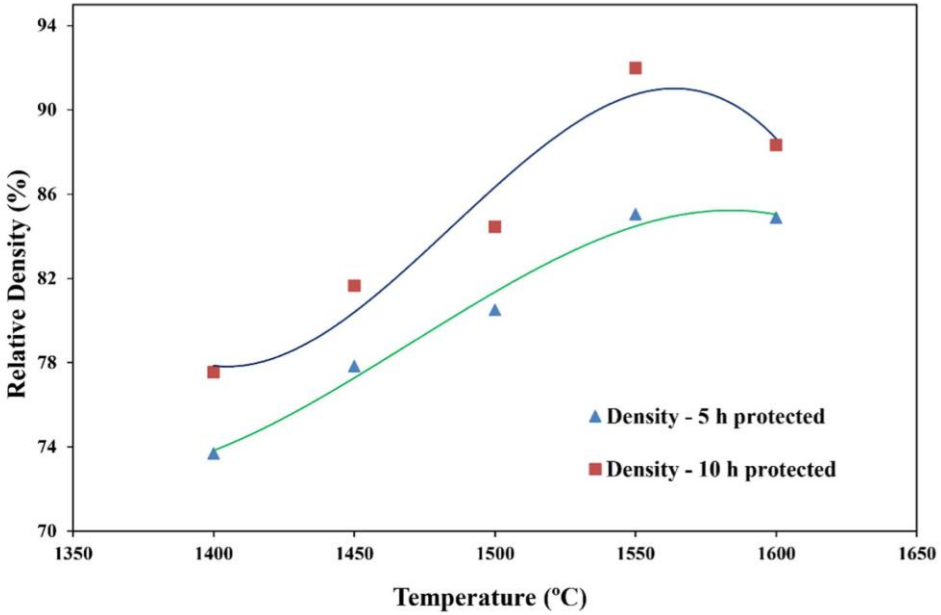
- Stainless steel tube: up to ~1100 °C
- Quartz tube: up to ~1200 °C
- Mullite tube: up to ~1450 °C
- Alumina (Al_2O_3) tube: up to ~1750 °C
- Yttria stabilized zirconia (YSZ) tube
- Graphite tube: up to ~2600 °C in inert/ vacuum



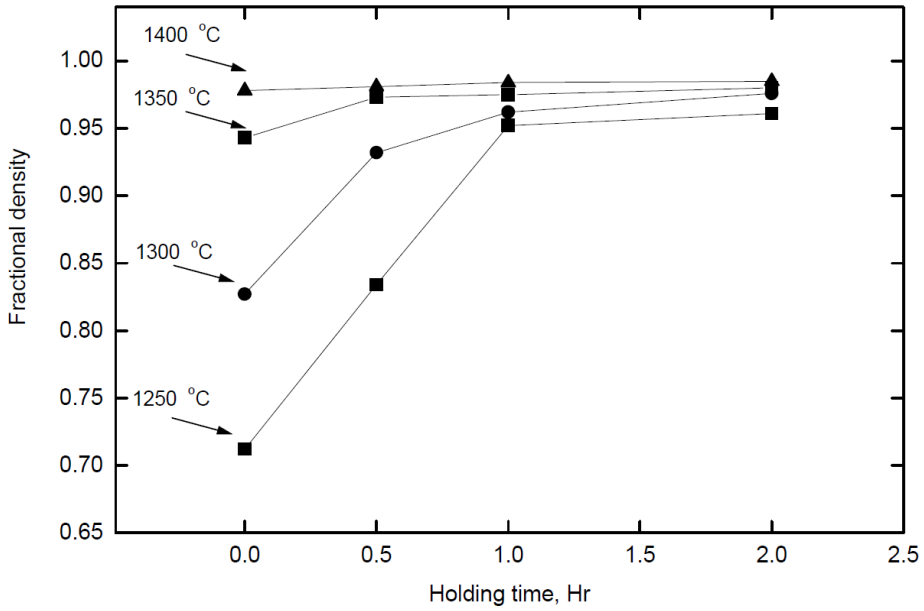
www.mtixtl.com https://www.mcqueenlabs.com/furnace

Monitoring of Sintering – Direct Dimension/Relative Density Measurement

- Simple with no special equipment, but time consuming if complete sintering kinetics behavior to be obtained



A. VahidMohammadi and Z Cheng, J Electrochem Soc, 2015 vol. 162, F803



M. Mazaheri, Proceedings of 10th European Ceram Soc Conference, (2007)

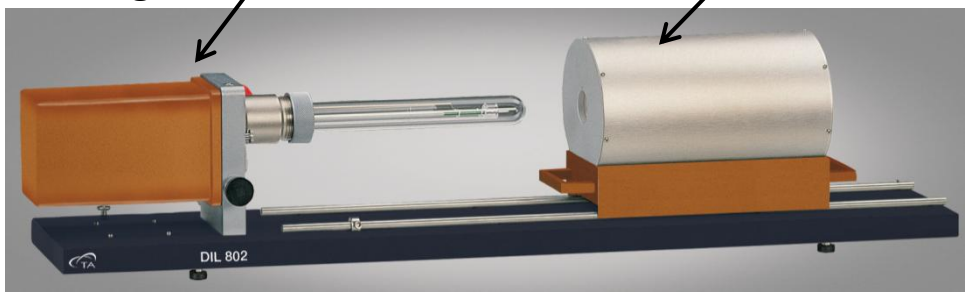
Monitoring of Sintering - Dilatometry

- **Continuous measurement of sample dimension with temperature/time**

Dilatometer

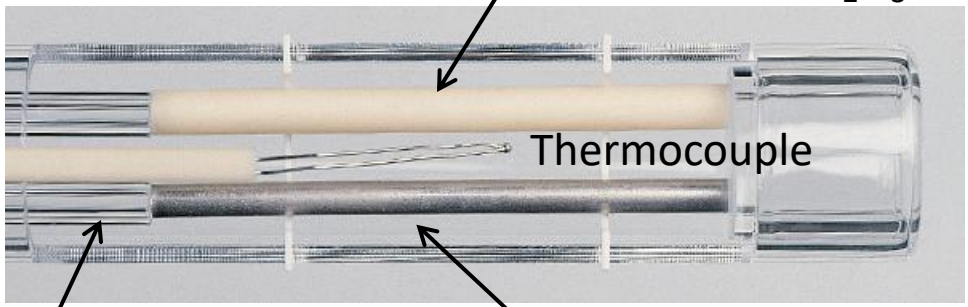
Loading/measurement unit

Furnace



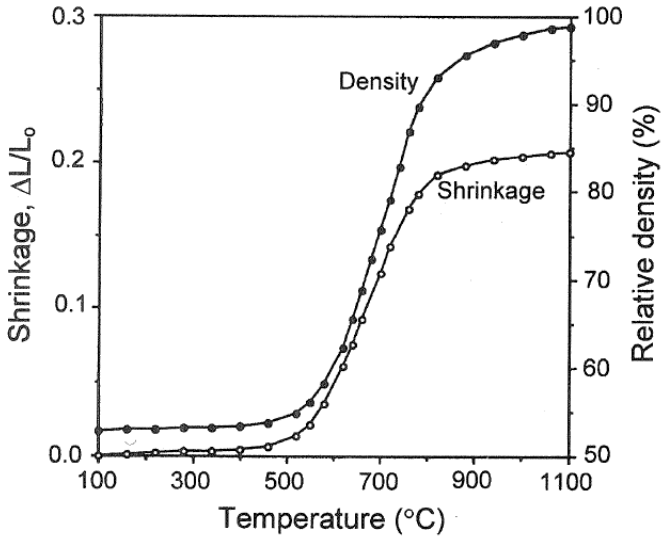
Sample loading section

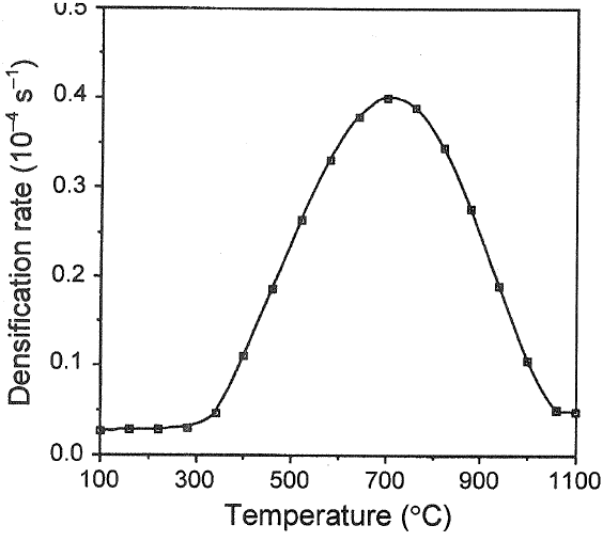
Reference sample (e.g., sintered Al_2O_3)



Pictures credit of TA Instrument,
http://thermophysical.tainstruments.com/instruments/dilatometers/horizontal-dilatometers/dil-802-differential/

Dilatometry for ZnO sintering at 5 °C/min





Rahaman (2003), p. 784

Sintering Temperature-Time Schedules

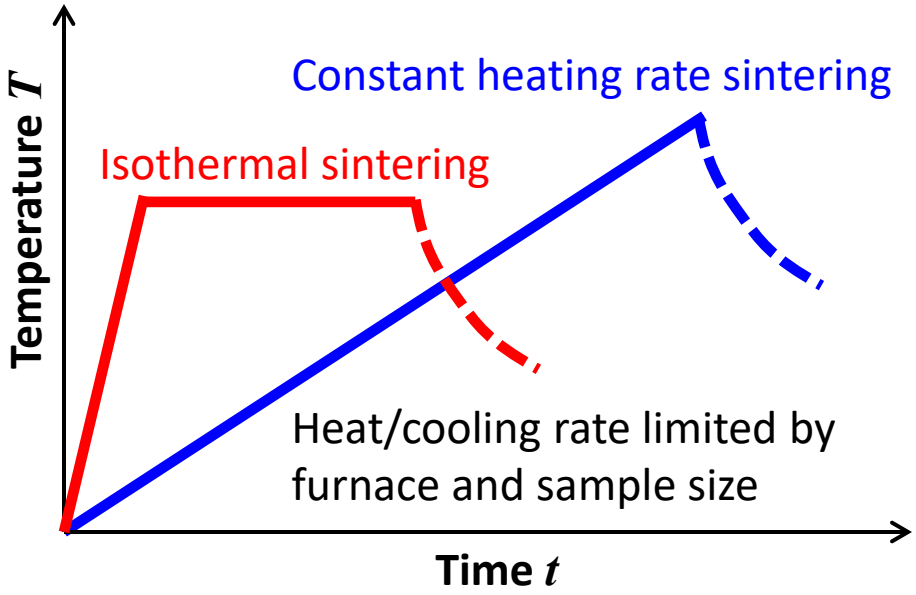
❑Isothermal sintering

Ramp to a fixed temperature and hold isothermally

- Most common
- NOT real isothermal due to finite heating rate possible (typically up to 100 °C/min) – significant sintering always occur during heating up stage

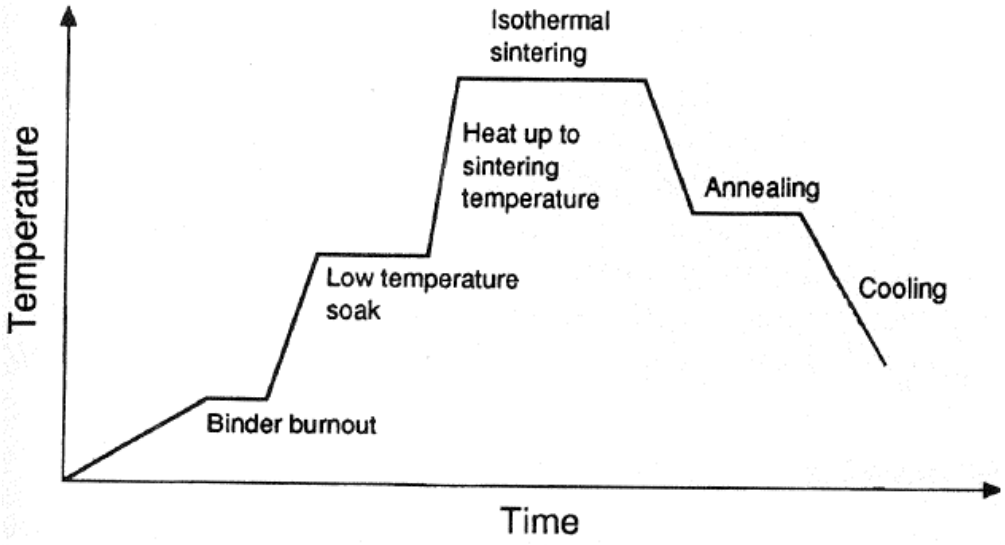
❑Constant heat rate sintering

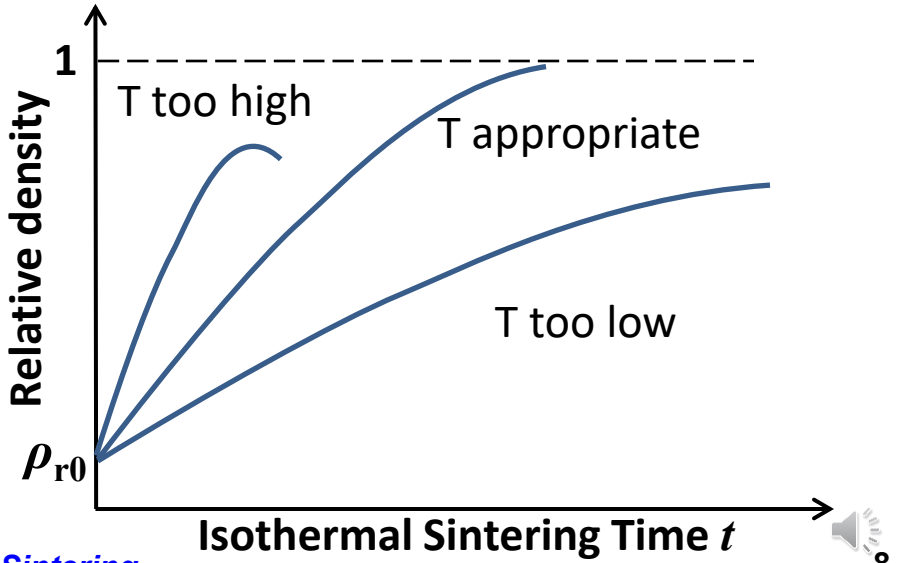
Constant ramp rate to a fixed temperature



Multi-stage Isothermal Heating Schedule for Sintering

- **Binder burnout**
  - Removal of volatile materials (e.g., organics)
  - Often < 2 C/min w/ brief hold at 400-500 °C
- **Low temperature soaking**
  - Optional for reaction/homogenization
  - Below onset of sintering temperature
- **Heating up to sintering temperature**
  - Faster heating often leads to better densification
  - Heating rate limited by furnace capability and thermal expansion
- **Isothermal sintering**
  - Too low temperature - not sufficient sintering
  - Too high temperature - coarsening before full densification and abnormal grain growth
- **Annealing**
  - Optional for stress relief or precipitation of second phase
- **Cooling**
  - Can be fast if sample size is small
  - Need to manage cooling rate for thermal stress and/or precipitation

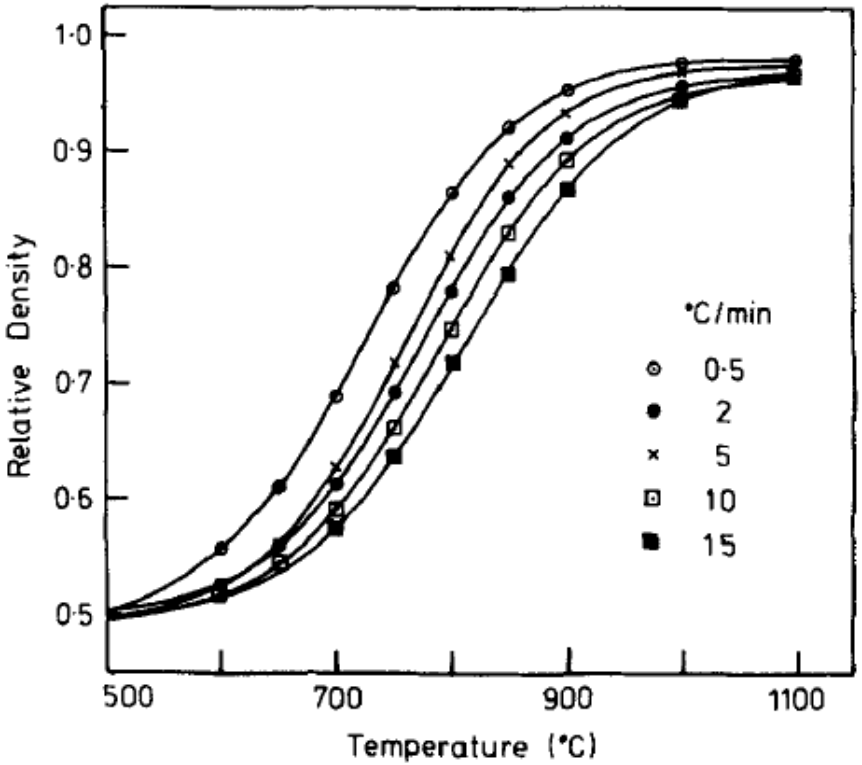


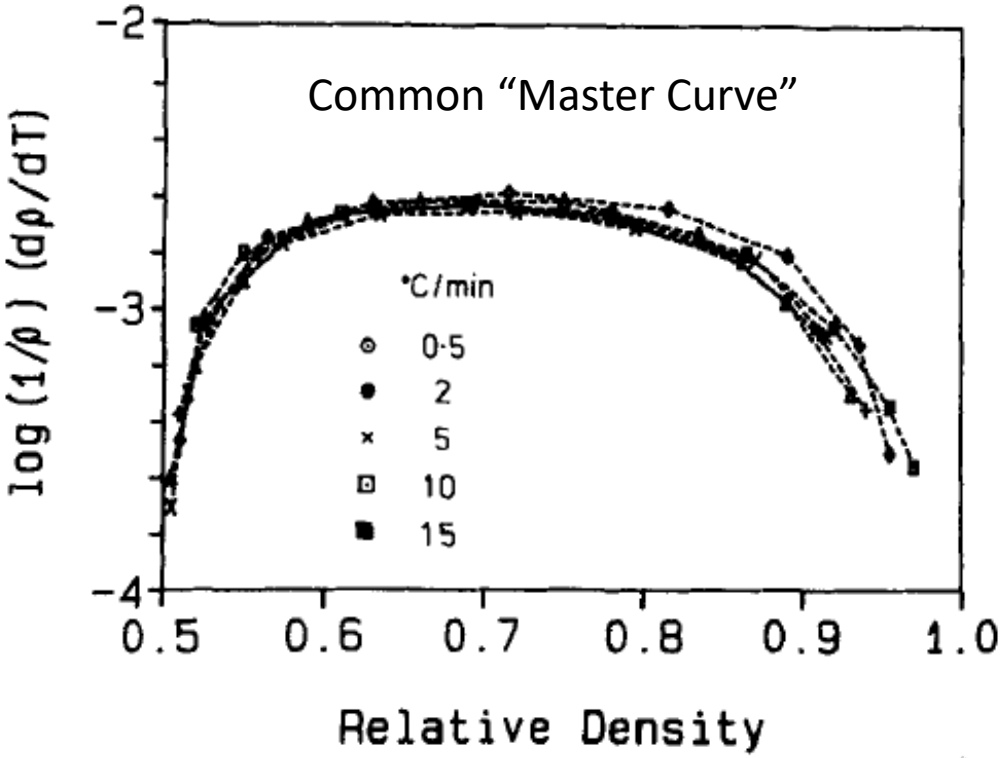


Sintering at Constant Heating Rate (1)

- Lower heating rate often leads to greater densification at the same temperature
- Temperature derivative of densification strain independent of heating rate and maximizing/plateauing in relative density range of ~0.6-0.8

Constant heating rate sintering at 500-1100 °C from 50% dense green body of ~0.1 μm ZnO



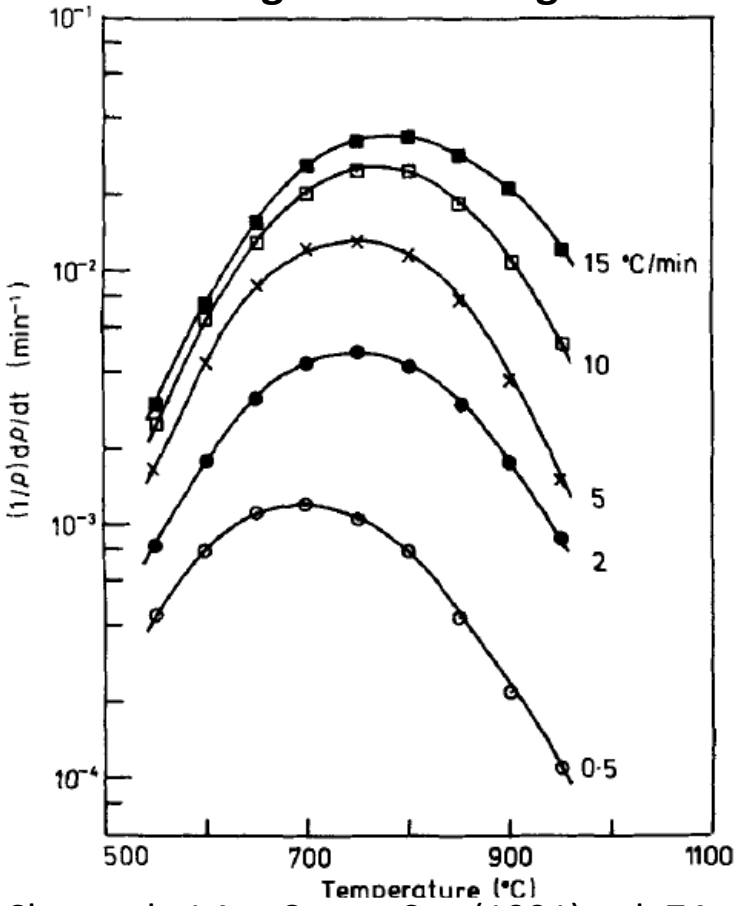


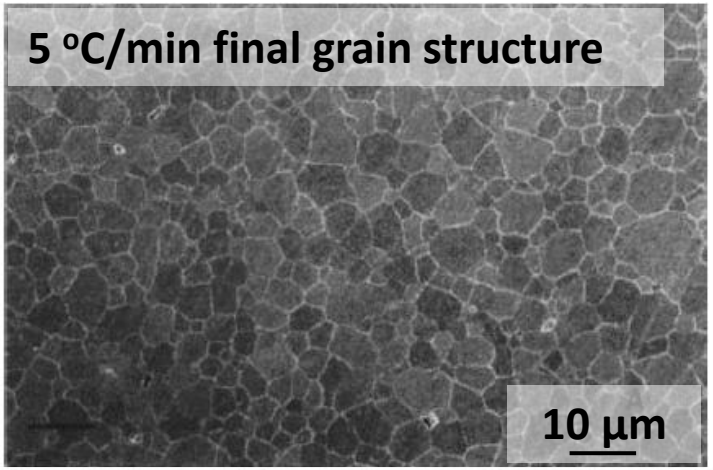
M. Y. Chu et al., J Am Ceram Soc (1991) vol. 74, p. 1217

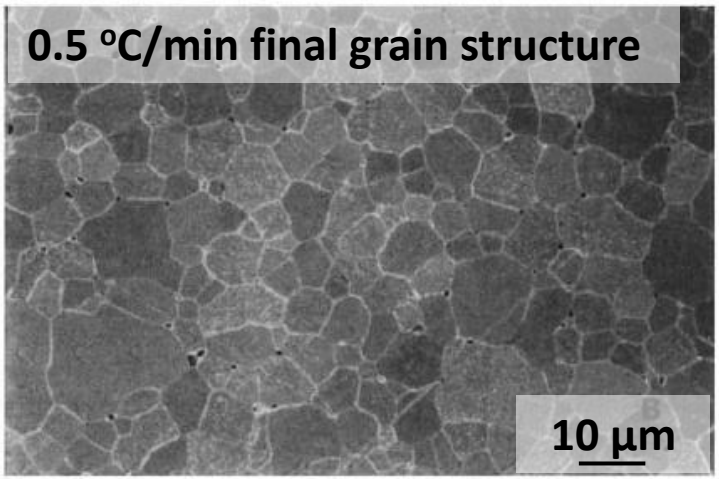
Sintering at Constant Heating Rate (2)

- At same T, volumetric strain rate increases with increasing heating rate
- Faster heating rate enables finer microstructure

Constant heating rate sintering at 500-1100 °C from 50% dense green body of ~0.1 µm ZnO







M. Y. Chu et al., J Am Ceram Soc (1991) vol. 74, p. 1217

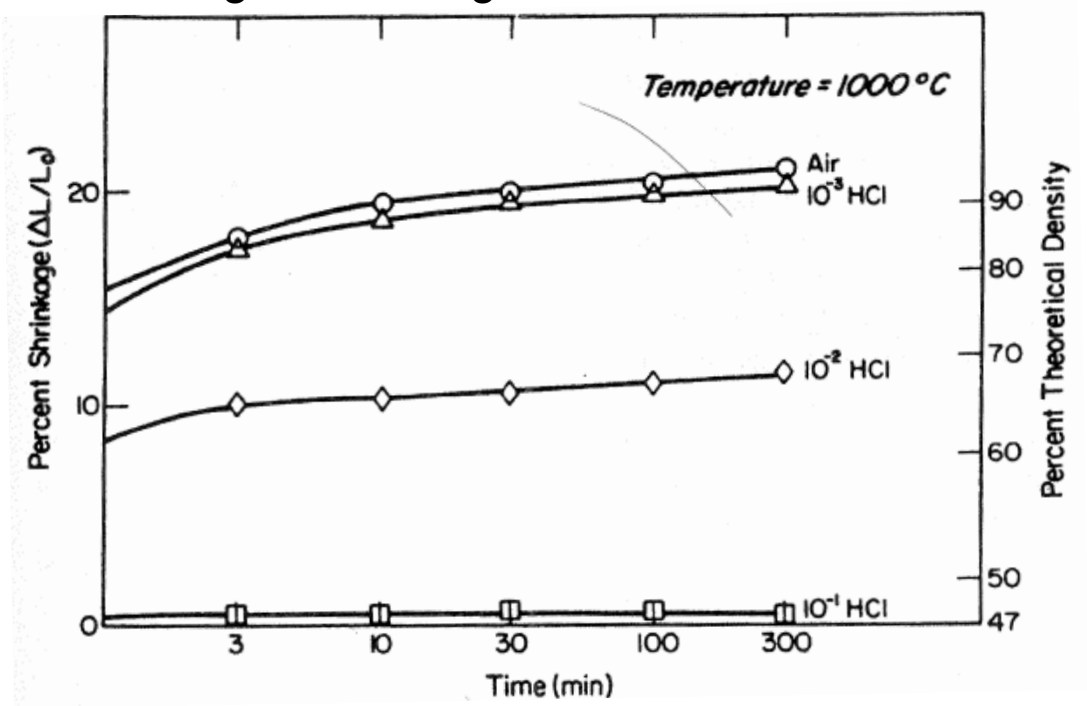
Impacts of Atmosphere on Sintering (1)

- **Atmosphere leading to enhanced vapor transport inhibits sintering**

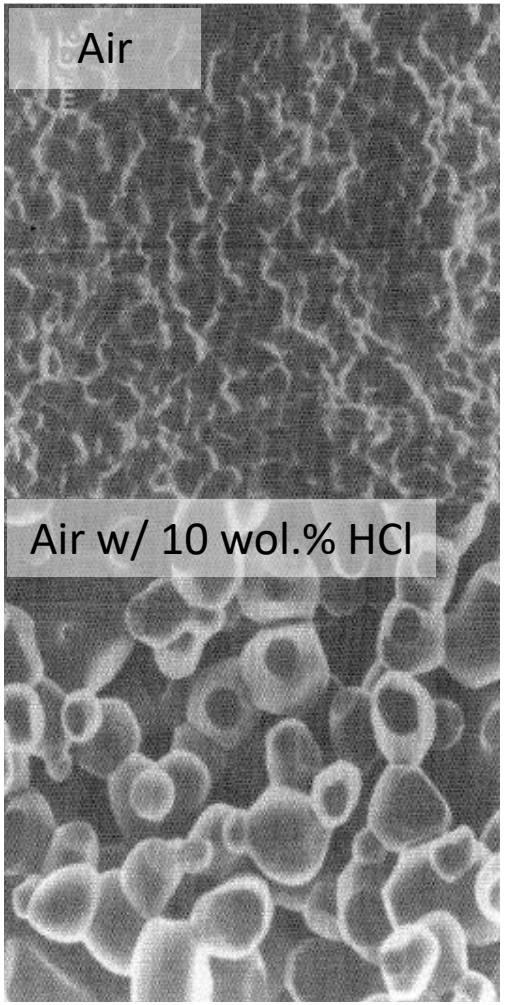
Example: Fe_2O_3 sintering in air vs. Argon w/ 0.1 vol.%
1 vol.%, 10 vol.% of HCl

$$Fe_2O_3 + HCl = Fe_2Cl_6\ (g) + 3H_2O\ (g)$$

- Addition of HCl enhances vapor transport, causing coarsening and reduces densification



D W Readey., Ceram Trans (1990) vol. 7, p. 86

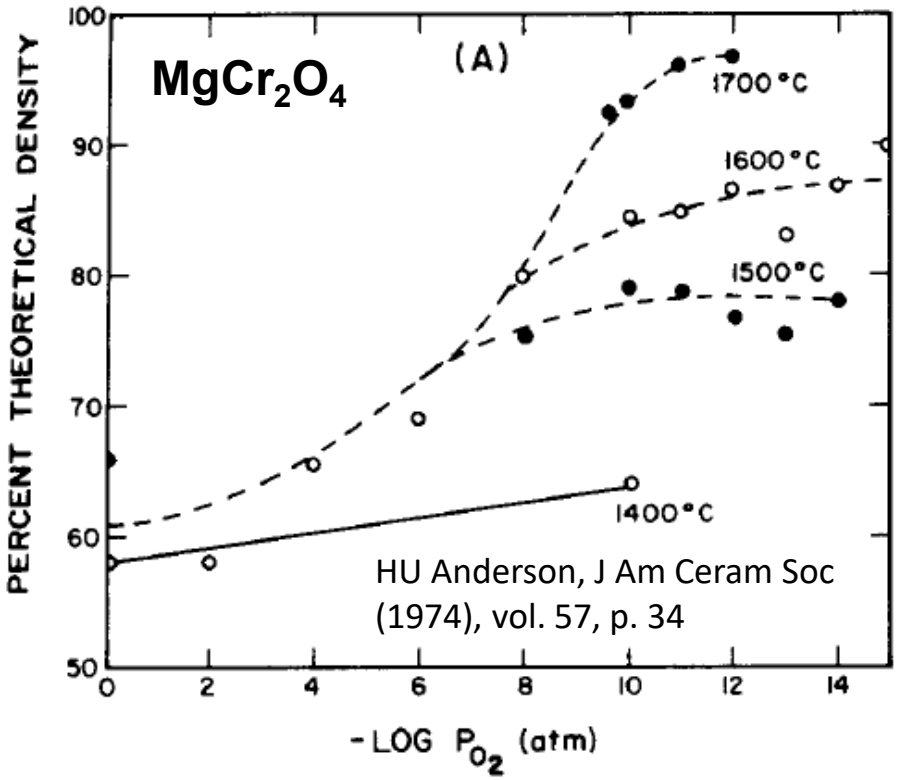


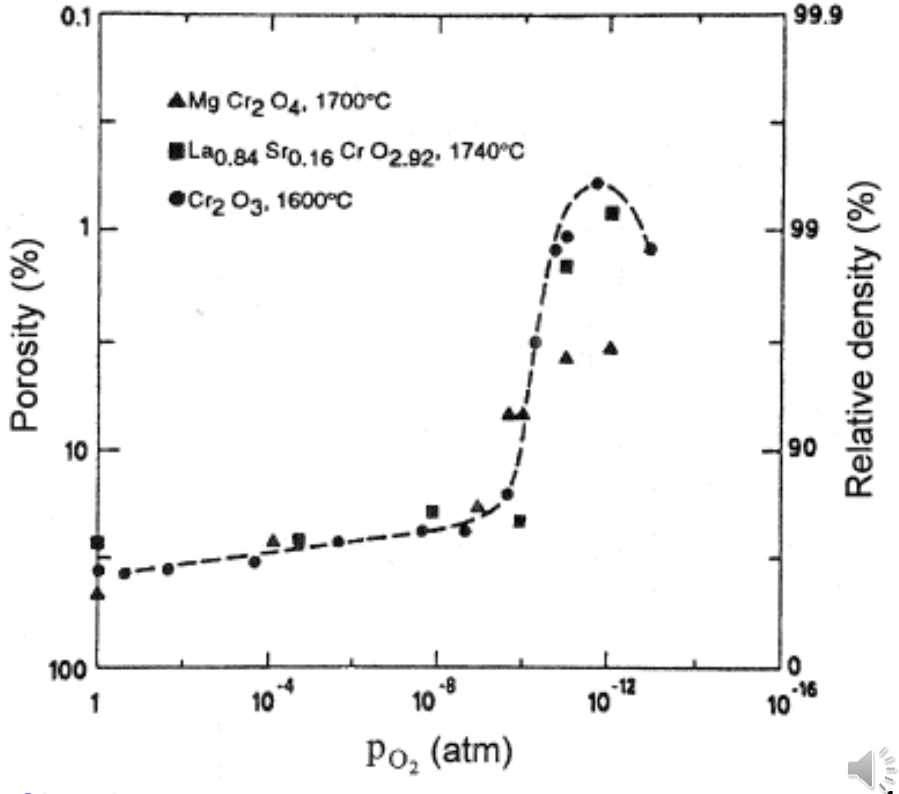
Impacts of Atmosphere on Sintering (2)

- **pO_2 can impact oxidation state/species volatility and resulting densification**

  Example: sintering of oxides containing Cr at 3+ state

  - Very little densification when $pO_2 >> 10^{-12}$ (due to more volatile CrO_2 and CrO_3)
  - Densification gets much better when $pO_2 << 10^{-12}$

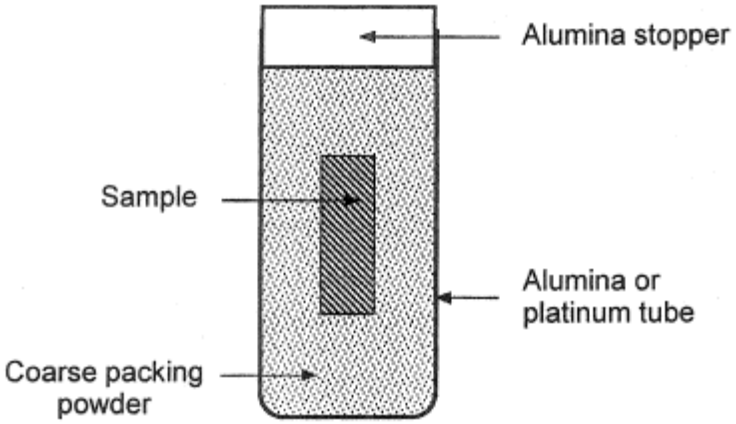




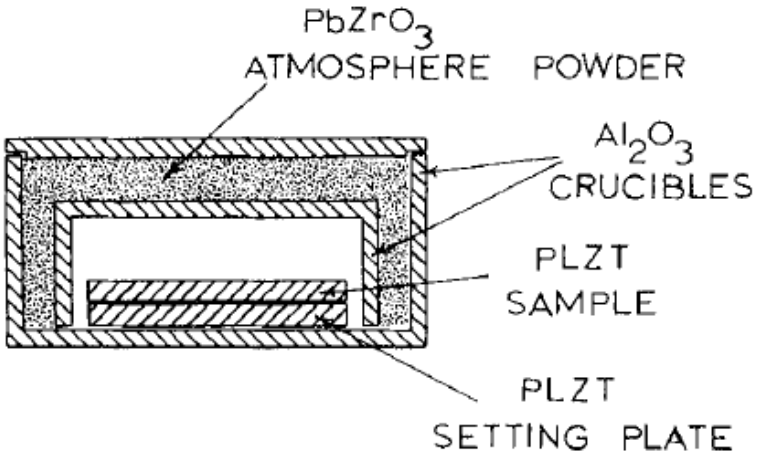
Impacts of Atmosphere on Sintering (3)

- **Volatilization/Decomposition at high temperature inhibits densification**
- **Examples**
  - β-alumina or $(Na_2O)_{1+x}\bullet 11Al_2O_3$: loss of Na_2O
  - Pb-based electroceramics, e.g., $PbZrO_3$: loss of PbO
  - Ba-based proton conducting ceramics, e.g., $Ba(Ce_{0.8}Y_{0.2})O_3$: loss of BaO
  - Si_3N_4: decomposition $Si_3N_4 = 3Si\ (g) + 2N_2\ (g)$
- **Solution: "protected" sintering**

  Contain volatile species/enrich atmosphere and avoid sample contact with container



Rahaman (2003), p. 800-815



G Snow, J Am Ceram Soc (1973) vol. 56, p. 479

Impacts of Atmosphere on Sintering (4)

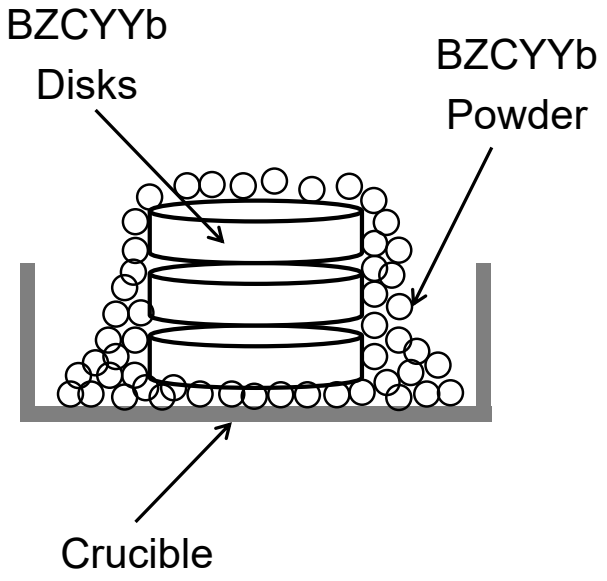
❑ "Protected" sintering

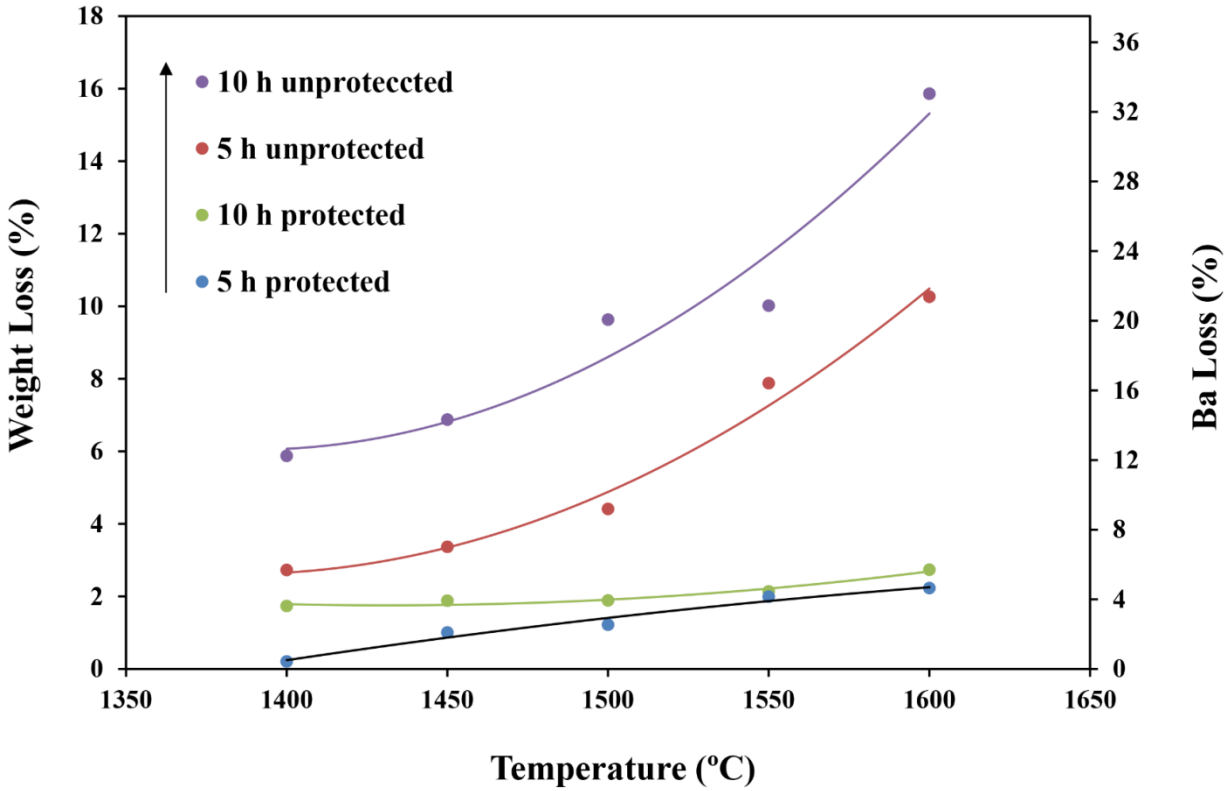
Example of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_3$ (BZCYYb)

- Reaction with Al_2O_3 crucibles: forming $BaAl_2O_4$
- Evaporation of BaO

} "Protection" to mitigate reactions/BaO evaporation

"Protected" Condition

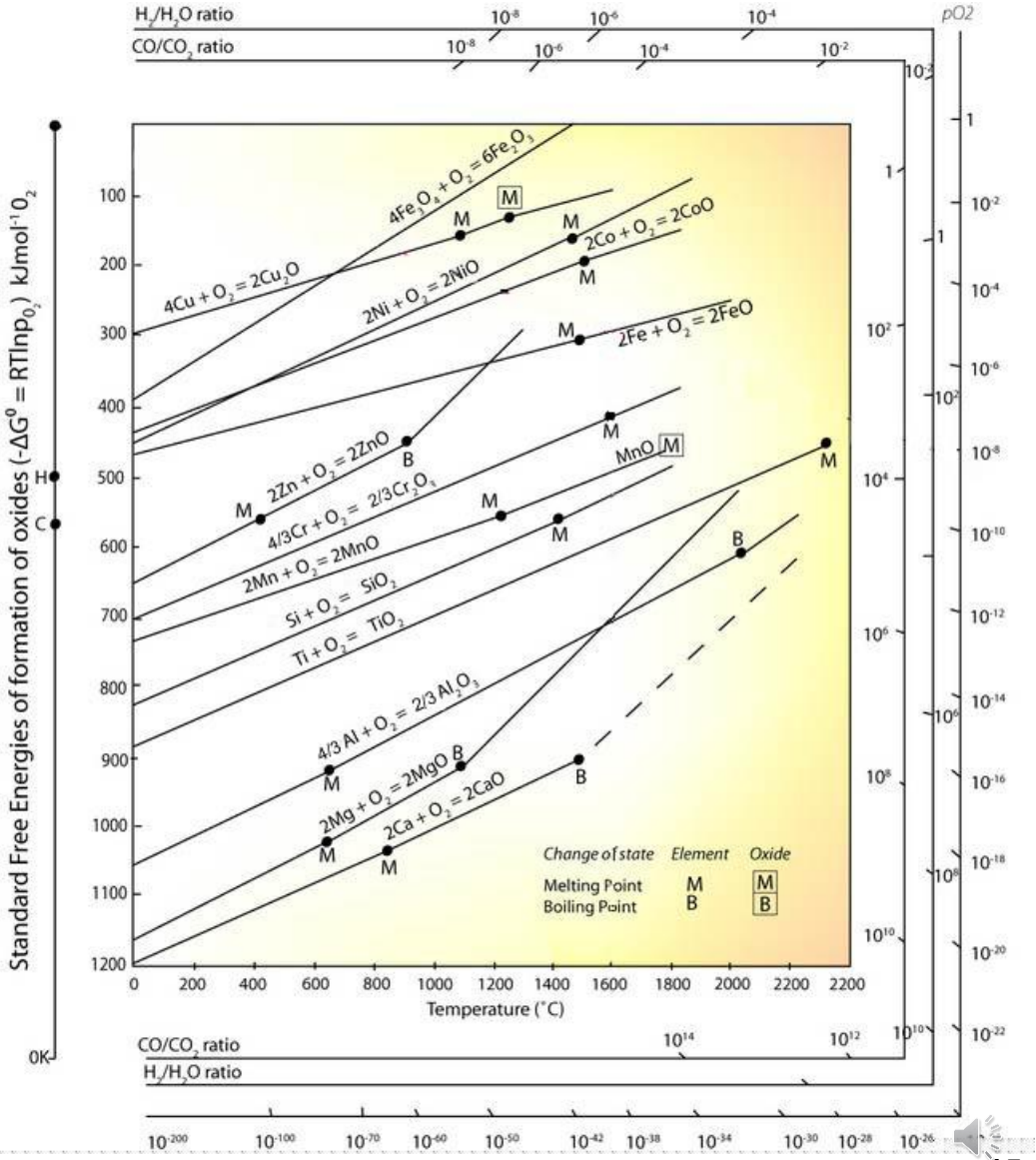




A VahidMohammadi and Z Cheng, J. Electrochem Soc, (2015), vol. 162, p. F803

Control of Atmosphere in Sintering

- **Vacuum: different vacuum pump and related setup**
- **Process gas**
  - Inert gas: Ar, He, N_2 (<~1200 °C) UHP grade still contains ~5 ppm of O_2/H_2O
  - N_2 gas: for nitride
  - Oxidizing gas: air, O_2
  - Reducing gas: H_2, CO
  - Special gas and gas mixture: accuracy to ~1% range
- **pO_2 control**
  - O_2-inert gas mixture: for 100%-0.01% (100 ppm) range
  - H_2/H_2O or CO/CO_2 mixture for lower pO_2
  - **BE CAREFUL with SAFETY**



Additional Sintering Practices

❑Pressure Sintering

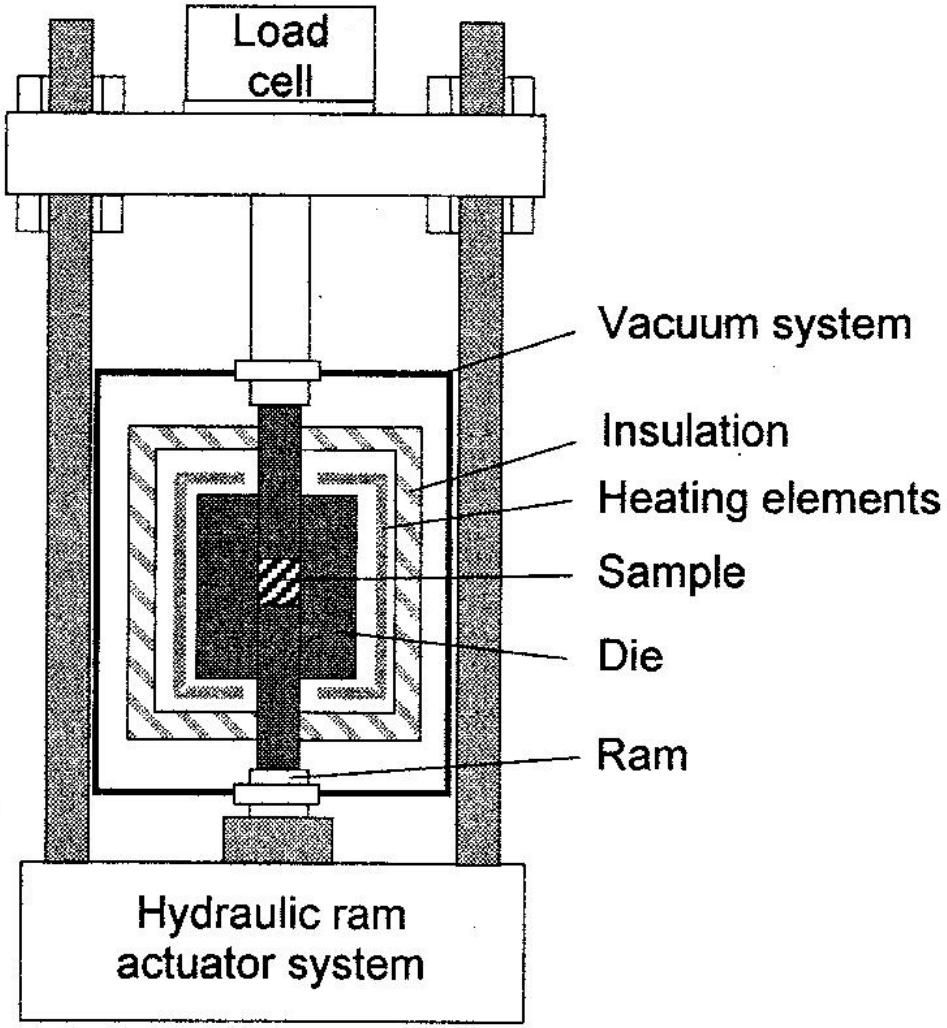
- Hot pressing (HP)
- Hot isostatic pressing (HIP)
- Sinter forging

❑Electrically-assisted sintering

- Microwave sintering
- Plasma sintering/Spark plasma sintering (SPS)
- Flash sintering (FS)

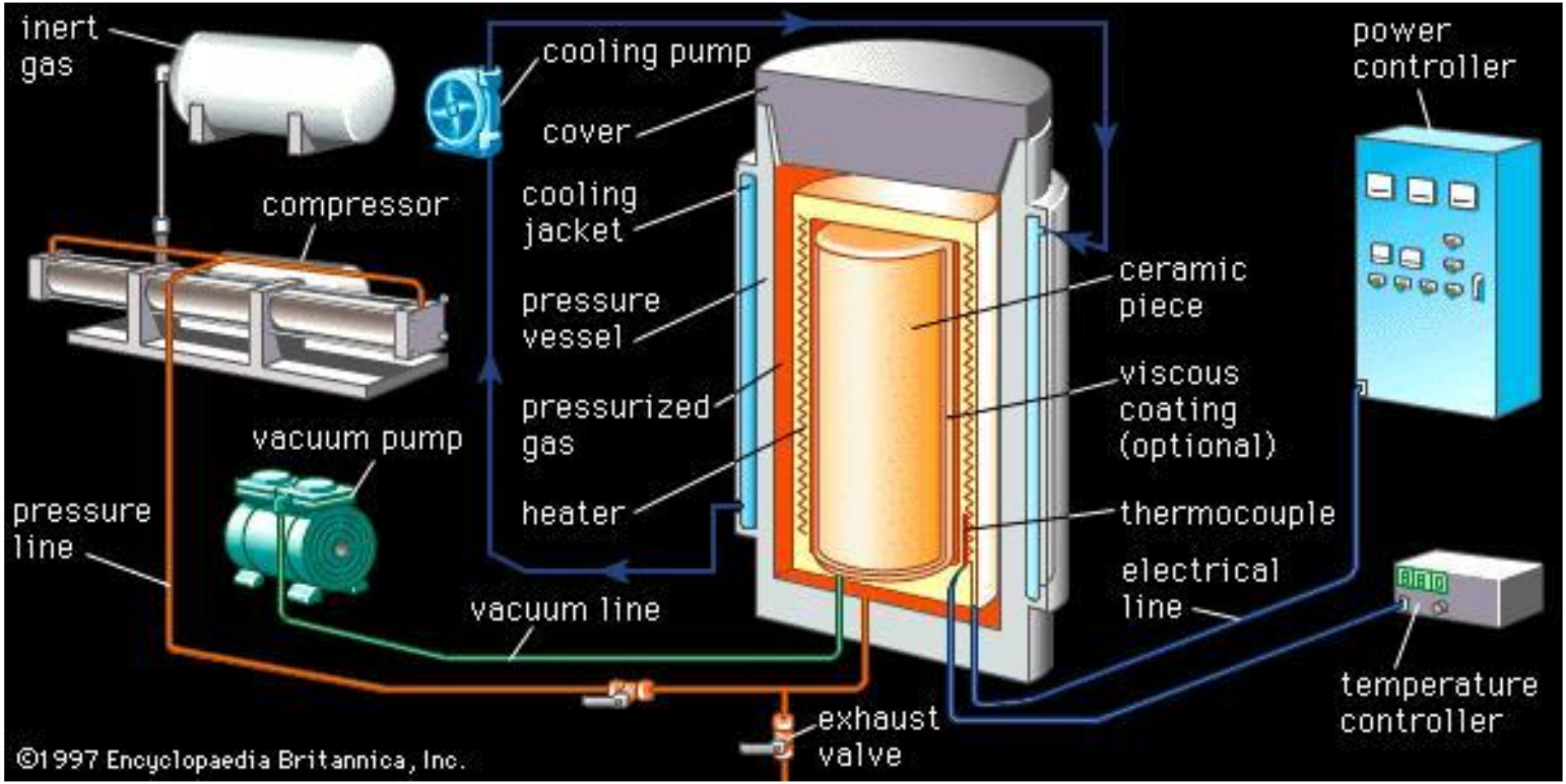
Hot Pressing (HP)

- **Application of steady uniaxial compression using a die during sintering**
  - Enhanced densification
  - Complicated setup and higher cost
  - Anisotropy possible
- **Die materials**
  - Mostly graphite: up to ~40 MPa in air up to 1200 ^{o}C
  - Other dies/atmosphere possible for higher temperature and/or higher pressure
- **Process variables**
  - Pressure
  - Isothermal temperature/time



Hot Isostatic Pressing

- Application of pressure while heating



http://www.britannica.com/technology/hot-isostatic-pressing

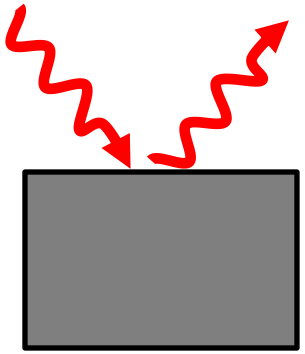
Microwave Sintering (1)

❑Feature/difference from conventional sintering

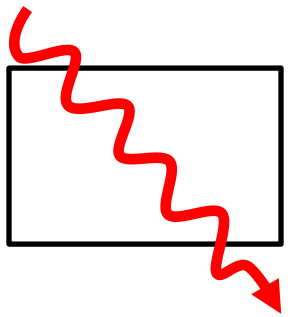
Use electromagnetic wave with frequency 0.3-300 GHz or wavelength of 1 -1000 mm, about sample dimension

- Heat generated internally
- Much faster heating rate: up to 1000 ^{o}C/min

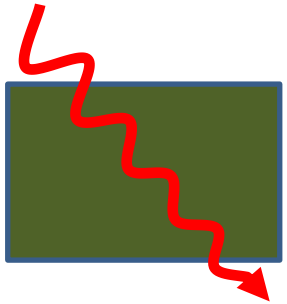
❑Materials interactions with microwave



Opaque - Conductor
Metals and other highly conducting materials



Transparent -
Low loss insulator
MgO, SiO_2, Al_2O_3



Absorber -
Lossy insulator
e.g., SiC, Cr_2O_3

(Rahaman (2003), p. 818-828)

Microwave Sintering (2)

- **Power generation by microwave heating** $W = \pi E_0^2 f \varepsilon_0 \varepsilon_r' \tan\delta$

  E_0 Electrical field amplitude

  f Frequency of microwave

  ε_0 Vacuum permittivity

  ε_r' Relative dielectric constant (real part)

  $\tan\delta$ Loss tangent for dielectrics

- **Skin depth**

  Distance into materials where electrical field amplitude falls to 1/e of its surface value

$$D_s = \frac{c}{\sqrt{2}\pi f \left(\varepsilon_r'\right)^{1/2} \tan\delta}$$

  c Light speed

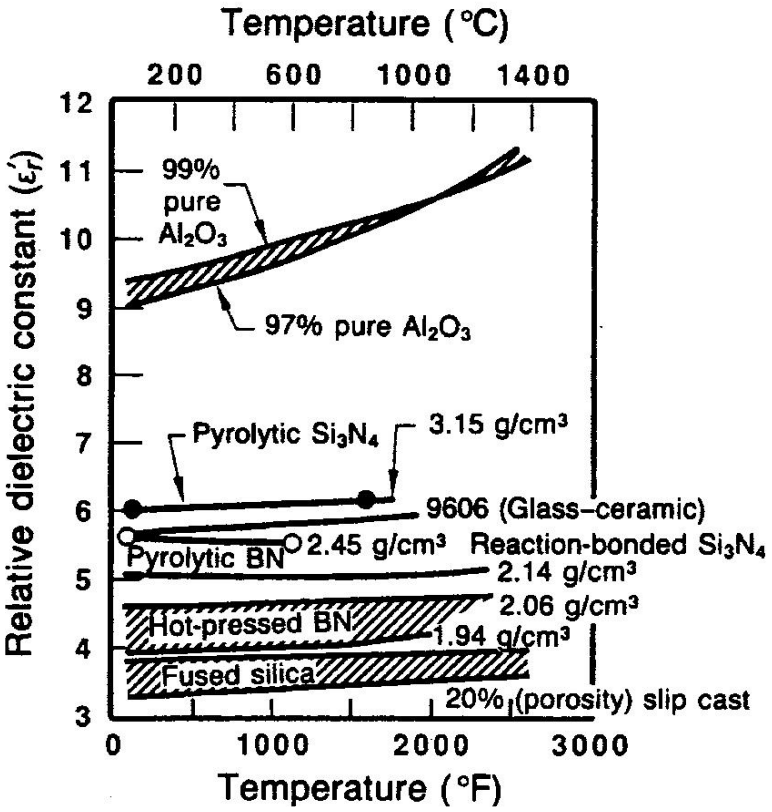
  For microwave in metals, D_s ~ 1 μm; in Al_2O_3, D_s ~ 1 m.

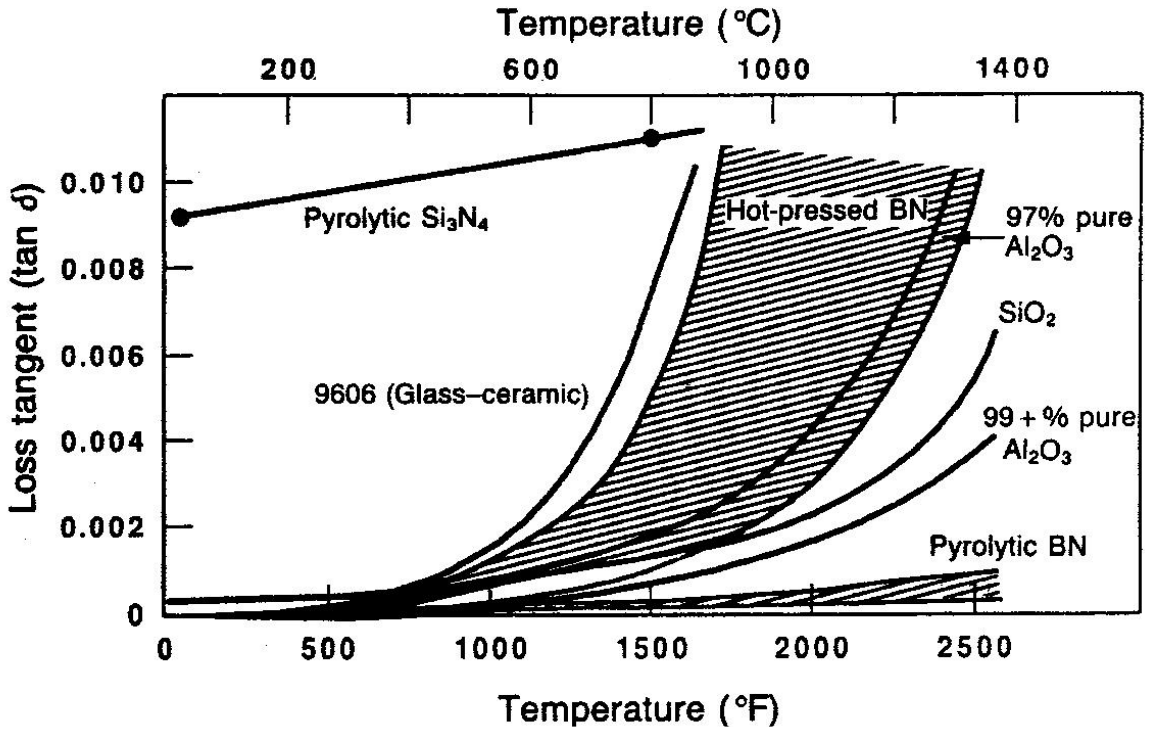
- **As f is fixed (2.45 GHz in most cases), factors determining microwave heating/penetration are primarily ε_0 and $\tan\delta$, especially loss factor**

Microwave Sintering (3)

- **Relative dielectric constant and loss tangent change with temperature**
- **More significant for loss tangent**

  Preheat sample to intermediate temperature before applying microwave

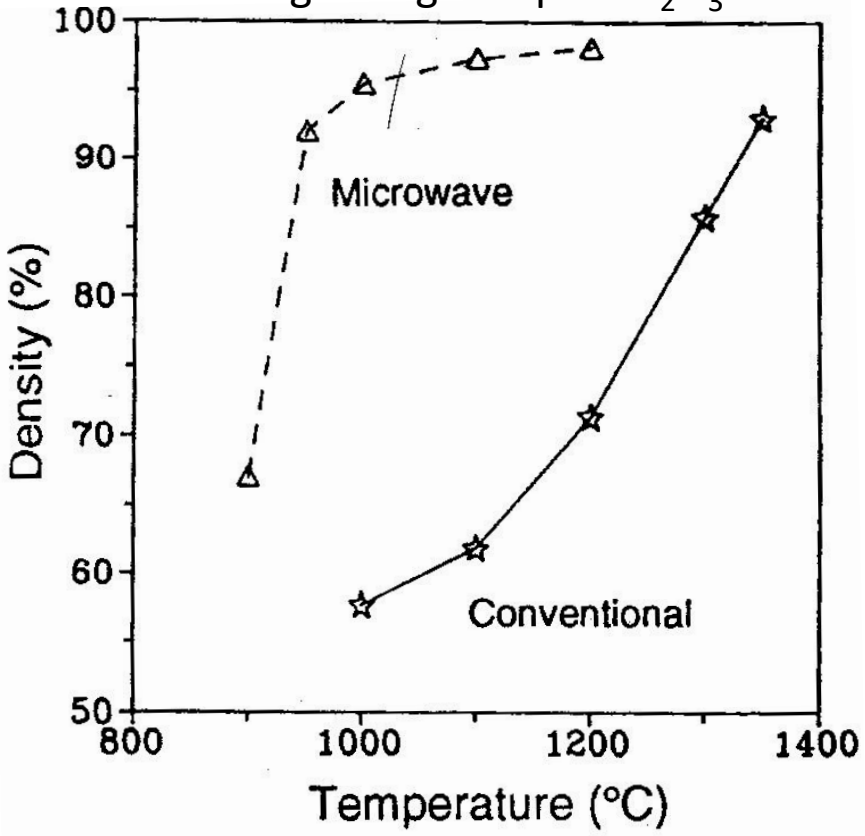




Microwave Sintering (4)

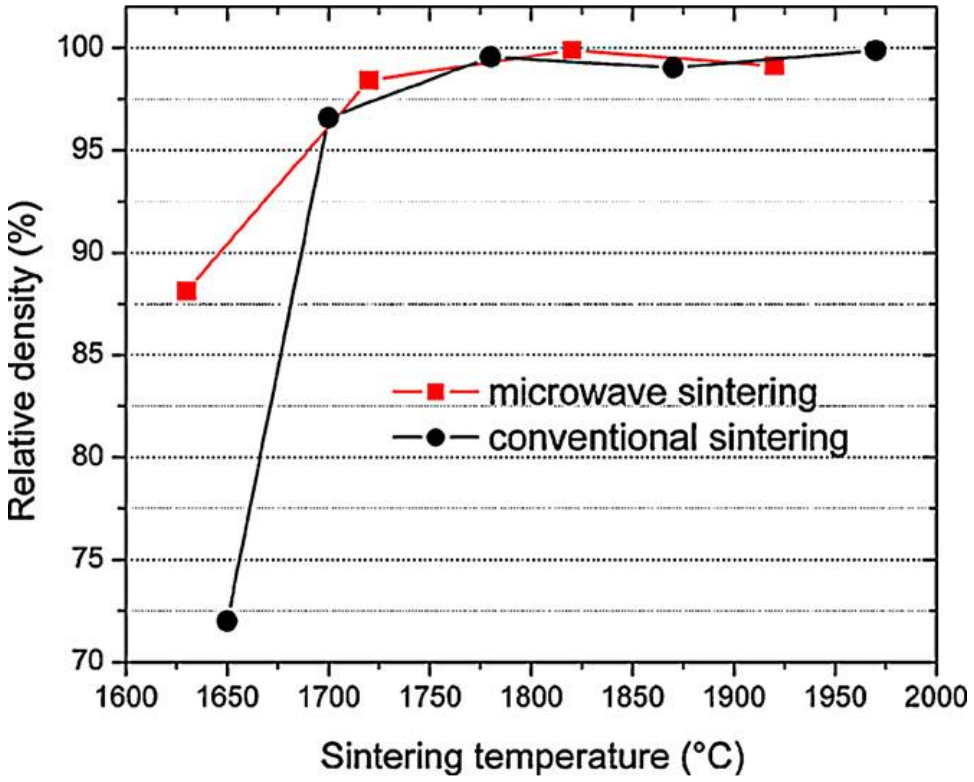
- **Microwave sintering offers enhanced densification (via faster heating rate) in some situations**

Sintering of MgO-doped Al_2O_3



Jannet abd Kimrey, Mater Soc Symp Proc, 1991, vol. 189, 215

Sintering of ZrB_2-4%B_4C composite



S Zhu et al. Composites, (2008), vol. 39, p.449

Issues/Challenges with Microwave Sintering

- **Temperature measurement difficult**

  Interaction of microwave with conventional thermal couple make temperature measurement relying on optical methods

- **Still suffers from very rapid grain growth at the end of sintering when relative density reaches above ~92 %**

- **Limited frequency choice**

  e.g., 0.915, **2.45**, 5.85, 20.2-21.2, 28, 60, 140 GHz) due to FCC regulation

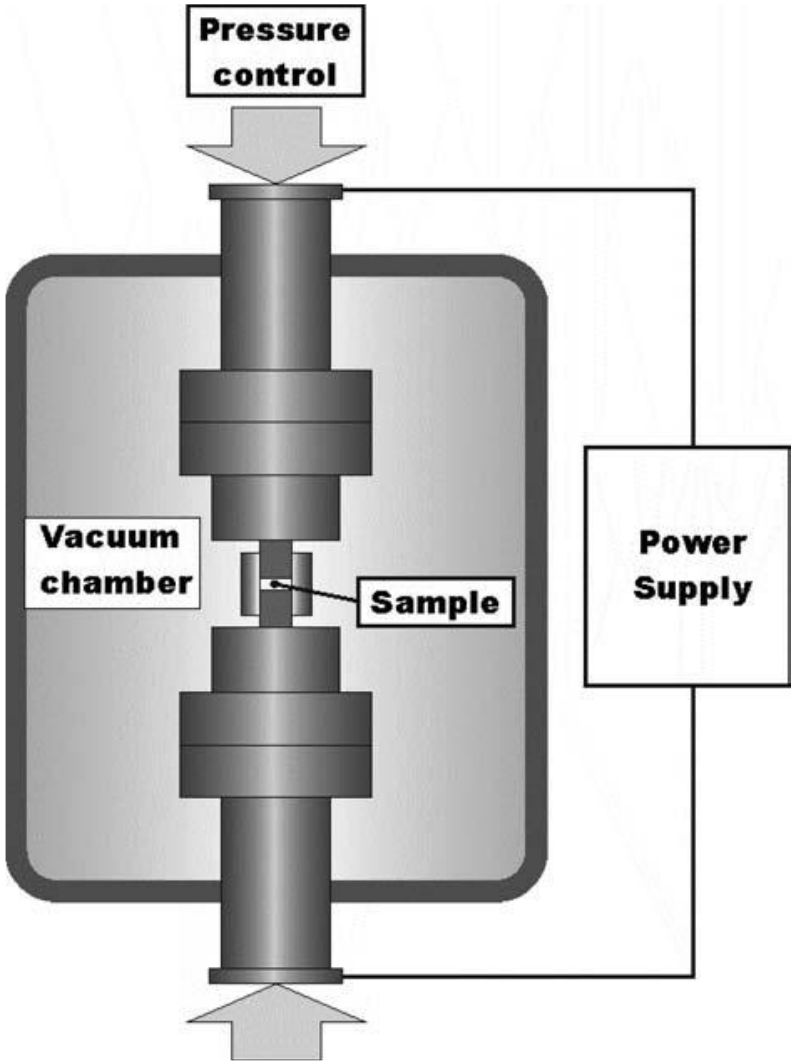
- **Non-homogeneous and often uncontrollable heating, especially for complex shaped sample or large samples**

- **Other**
  - Lacking of fundamental understanding of the sintering mechanism
    e.g., debates about claims of reduced activation energy for diffusion
  - Claim of energy saving also questionable for industrial sintering when heat source could be chemical fuel instead of electricity

- **"microwave processing has yet to see wide spread application in the ceramic industry" (**Katz, 1992, Annu Rev Mater Sci, 1992, 22, 153**)**

Spark Plasma Sintering (SPS)

- **Applying pressure while at the same time applying (pulsed) current flow through the sample (Often in graphite die) in vacuum, which provides the heating effect**
- **Advantages**
  - Fast heating: even higher than 600 ^{o}C/min
  - Preservation of fine (submicron) microstructures
- **Disadvantages**
  - Complicated setup and limited sample shape
  - Not very clear mechanism sometimes



Z A Munir et al. J Mater Sci (2006), vol. 41, p.763

Flash Sintering (1)

- **Direct current passing through sample for sintering without application of pressure**
- **Features**

  Current directly go through sample
- **Advantages**
  - Extremely fast heating and sintering process:
    within a few seconds in some cases
  - Preservation of fine (submicron) microstructures
- **Disadvantages**
  - Not very clear mechanism
  - Limited sample choice and sample geometry/dimesion

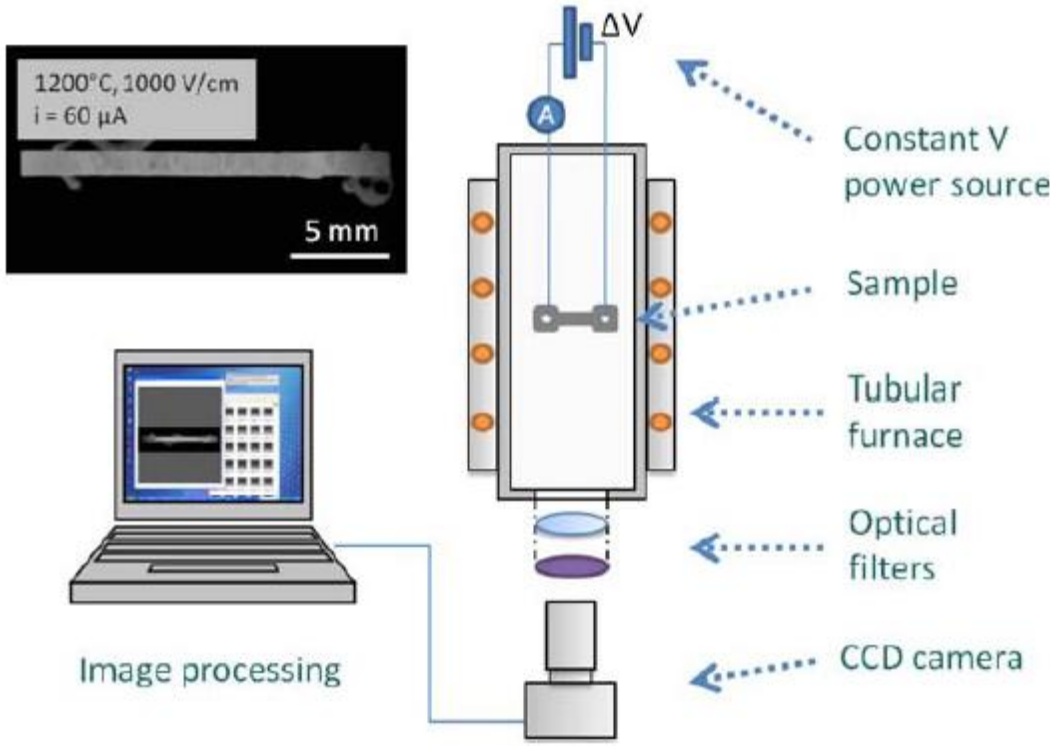


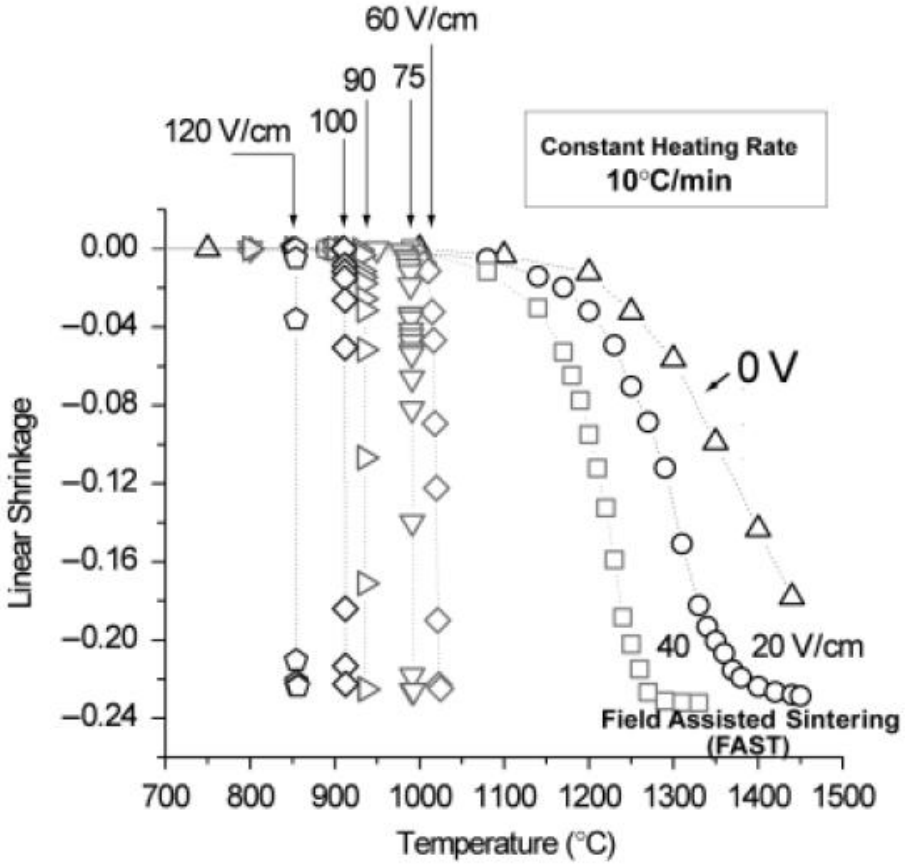
Fig. 1. Field-assisted sintering apparatus.

M Cologna et al., J Europ Ceram Soc (2011), vol. 31, p.2827

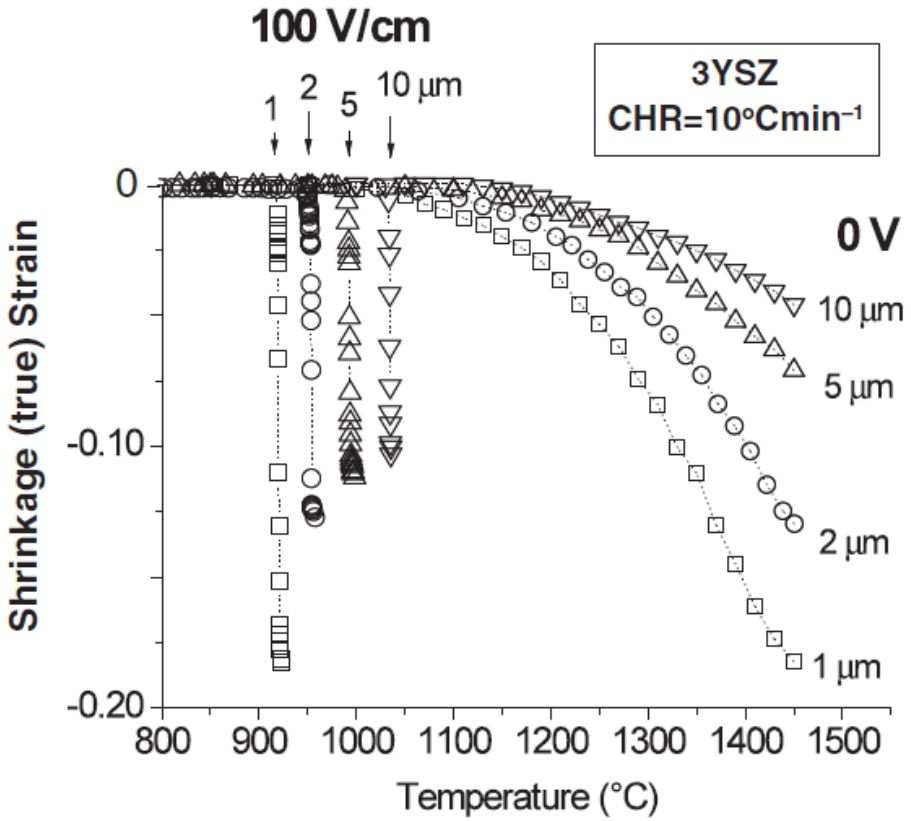
Flash Sintering (2)

- **Extremely fast sintering**

https://www.youtube.com/watch?v=HvOfoyhu2aE

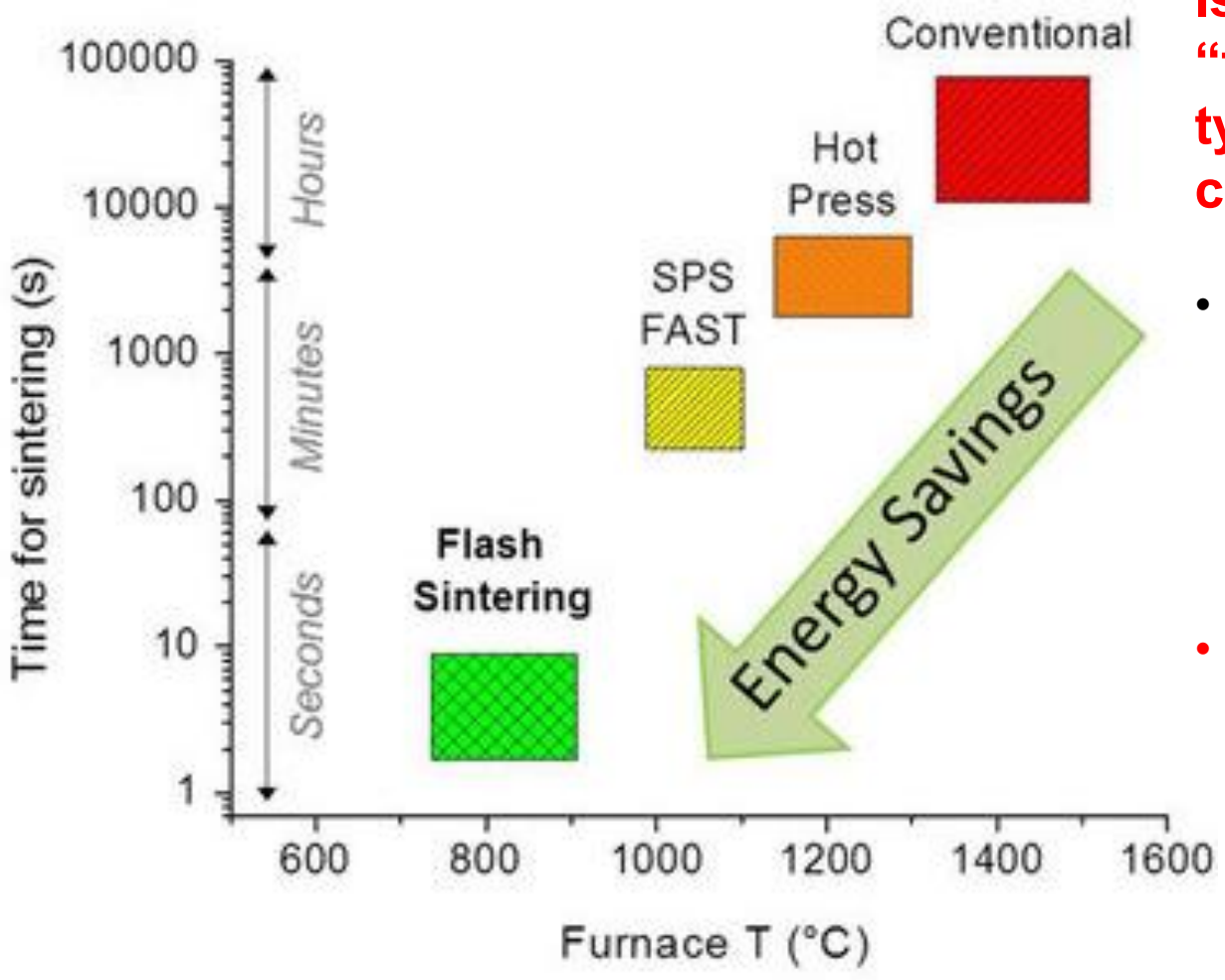


M Cologna et al., J Am Ceram Soc (2010), vol. 93, p.3556



J Francis et al., J Europ Ceram Soc (2012), vol. 32, p.3129

Electrical Field Assisted Sintering (EFAS)



Credit: Marco Cologna & Rishi Raj, Univ. of Colorado
http://www.fastceramics.com/innovative-research.html

Is flash sintering merely a "thermal runaway" (i.e., a type of failure/lack of control)?

- R. I Todd, et al., "Electrical characteristics of flash sintering: thermal runaway of Joule heating," J Europ Ceram Soc (2015), vol. 35, p. 1865
- J Park and I-Wei Chen, "In Situ Thermometry Measuring Temperature Flashes Exceeding 1,700°C in 8 mol% Y_2O_3-Stablized Zirconia Under Constant-Voltage Heating" J Am Ceram Sco (2013), vol. 96, p. 697

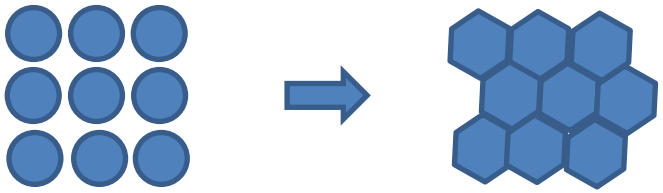
Classification and Microstructural Evolution in Sintering

❑Classification

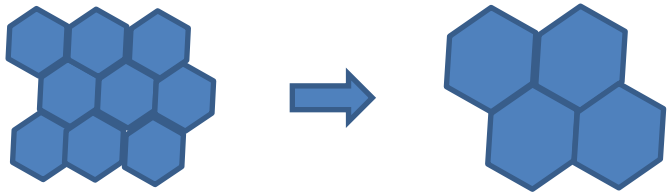
- Solid state sintering
- Liquid phase sintering

❑Microstructural evolution processes that happen in sintering

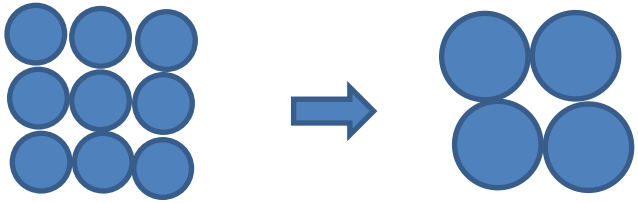
- **Densification**
  - Bonding of particles with elimination of pores



- **Grain growth**
  - Bonded particles grow in size



- **Coarsening**
  - Growth of particles without much elimination of pores



- Most sintering involve all three processes

Small Driving Force for Coarsening

❑Coarsening: Driving force come from reduction in surface energy

Assuming initial particles are cubes with size of a = 0.5 μm and surface energy γ_{sv} = 1 J/m^2,

For unit volume of 1 cm^3 of "net" powder material, total surface energy for all particles is

$$E_{sur} = \left(\frac{0.01}{a}\right)^3 \cdot 6a^2 \cdot \gamma_{sv} = \frac{1 \times 10^{-6} m^3 \times 6 \times 1 J/m^2}{0.5 \times 10^{-6} m} = 12J$$

If the particles are coarsened to size a = 10 μm, total surface energy for all particles is:

$$E_{sur}{}' = \left(\frac{0.01}{a}\right)^3 \cdot 6a^2 \cdot \gamma_{sv} = \frac{1 \times 10^{-6} m^3 \times 6 \times 1 J/m^2}{10 \times 10^{-6} m} = 0.6J$$

The driving force for such "pure coarsening" for 1 cm^3 (~0.1 mol) of material is:

$$E_{sur}{}' - E_{sur} = 0.6 - 12 = -11.4J$$

M W Barsoum (2003), Fundamentals of Ceramics, p. 305-306

Even Smaller Driving Force for Densification

- **Pure sintering without coarsening: Driving force come from small difference in surface energy versus grain boundary energy**

Assuming initial particles are cubes with size of a = 0.5 μm and surface energy γ_{sv} = 1 J/m^2,

For unit volume of 1 cm^3 of "net" powder material, total surface/interface related energy for all particles is

$$E_{sur} = \left(\frac{0.01}{a}\right)^3 \cdot 6a^2 \cdot \gamma_{sv} = \frac{1 \times 10^{-6} m^3 \times 6 \times 1 J/m^2}{0.5 \times 10^{-6} m} = 12J$$

If all the particles are sintered together without porosity and assuming no grain growth and grain boundary energy of γ_{gb} = 1.28 J/m^2, total grain boundary energy is:

$$E_{gb} \approx 3 \cdot \left(\frac{0.01m}{a}\right) \cdot (0.01m)^2 \cdot \gamma_{gb} = 3 \times \frac{10^{-6} m^3}{0.5 \times 10^{-6} m} \times 1.28 J/m^2 = 7.68J$$

The driving force for such "pure densification" for 1 cm^3 (~0.1 mol) of material is only:

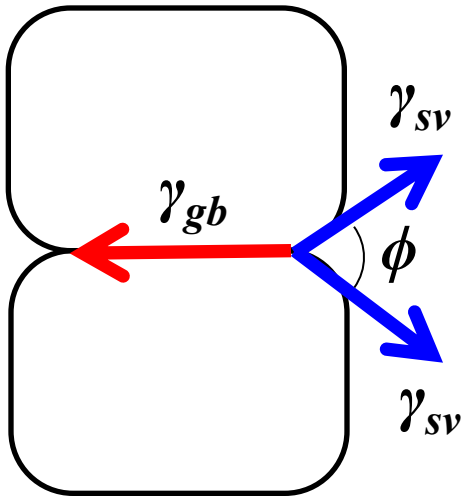
$$E_{gb} - E_{sur} = 7.68 - 12 = -4.32J$$

M W Barsoum (2003), Fundamentals of Ceramics, p. 305-306

Necessary Condition for Densification

- **For polycrystalline material, under equilibrium condition, grain boundary energy and surface energy satisfy**

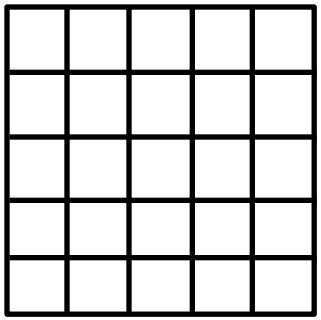
$$\gamma_{gb} = 2\gamma_{sv} Cos\frac{\phi}{2}$$



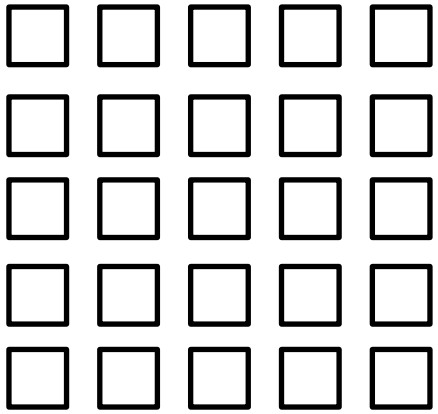
- **Necessary condition for densification**

$$\gamma_{gb} < 2\gamma_{sv}$$

Otherwise, grain boundary energy will be so high that the system will exist as individual, separated grains

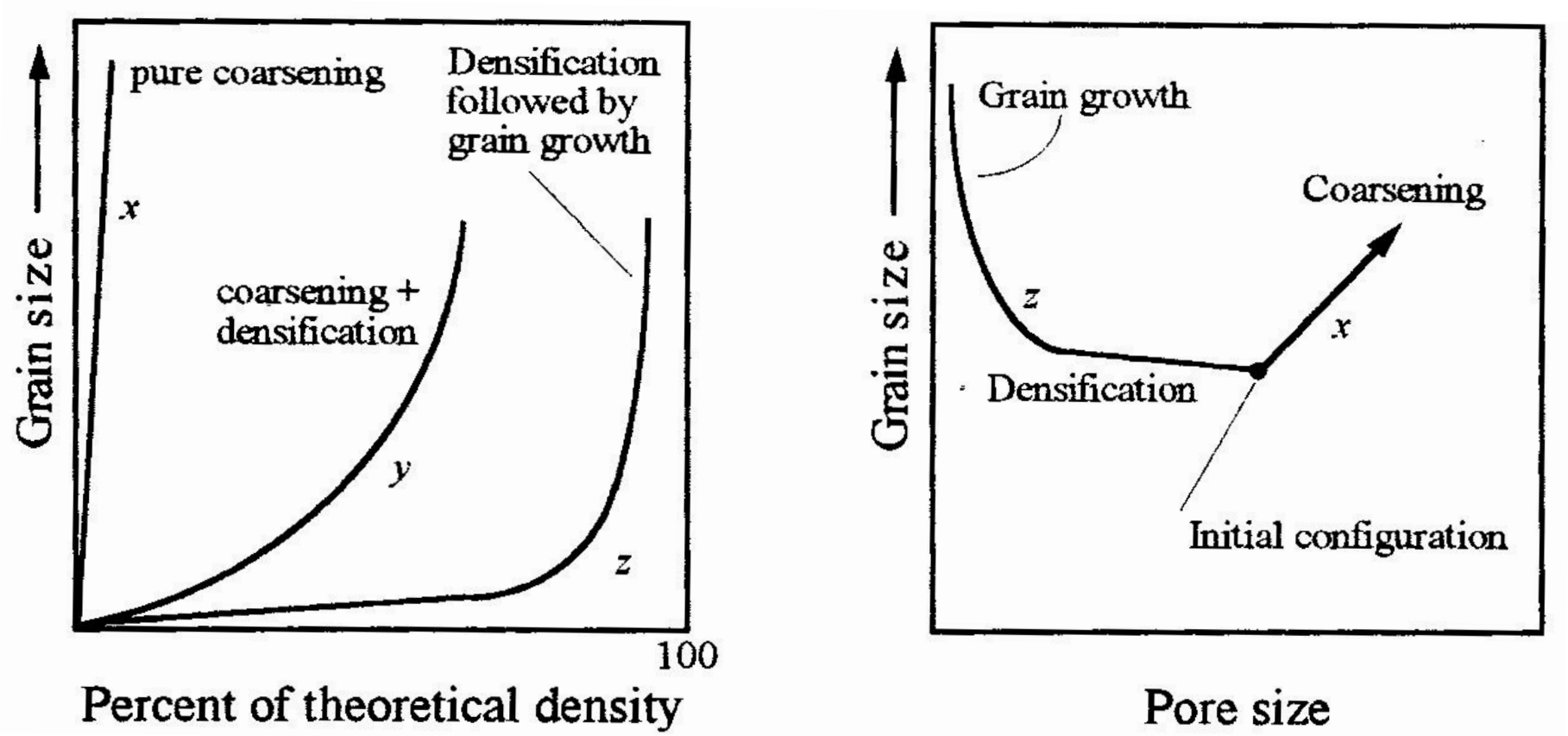


$\Sigma\gamma_{gb}$ vs. $\Sigma\gamma_{sv}$



Grain Size and Pore Size Evolution in Sintering

- **Both grain size and pore size will grow as relative density increase**
  - Ideal situation: densification followed by small extent of grain growth, which occur at the very end of sintering



M W Barsoum (2003), Fundamentals of Ceramics, p. 307

Mechanism for Mass Transport in Sintering (1)

❑Vapor pressure over curved (solid/liquid) surface

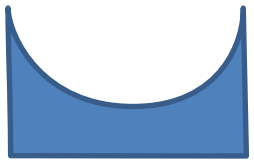
- Kelvin equation

$$\ln \frac{P}{P_0} = \frac{2\gamma_{SV} V_m}{RTr}$$

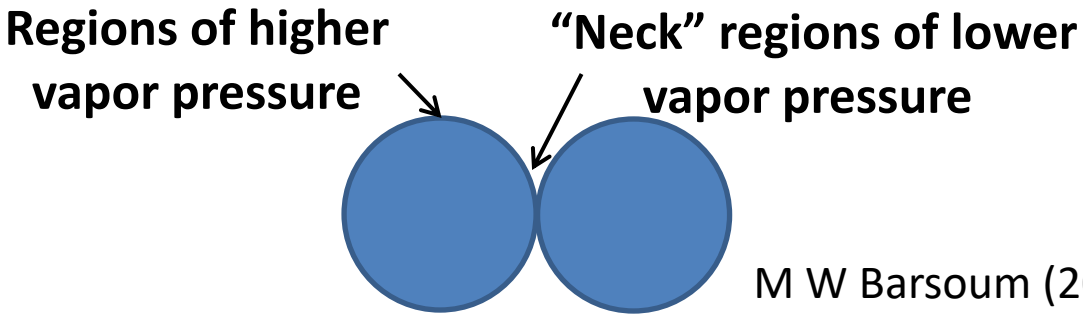
$r > 0$
$P > P_0$

$r \to \infty$
$P = P_0$

$r < 0$
$P < P_0$



- Vapor pressure over particles with smaller diameter is higher than that over larger particles than over "neck" regions → constituting underlying driving force behind materials transport mechanism in sintering



M W Barsoum (2003), Fundamentals of Ceramics, p. 309-315

Mechanism for Mass Transport in Sintering (2)

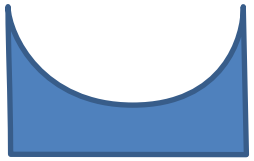
❑ **Vacancy concentration beneath curved (solid/liquid) surface**

$$\ln\frac{C_v}{C_{v0}} = -\frac{2\gamma_{SV}V_m}{RTr}$$

$r > 0$
$C_v < C_{v0}$

$r \to \infty$
$C_v = C_{v0}$

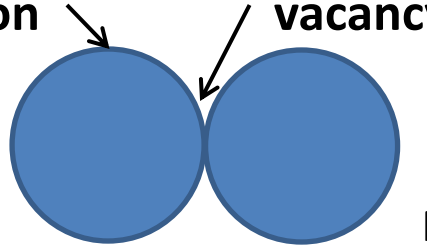
$r < 0$
$C_v > C_{v0}$



- Naturally, vacancy concentration in regions with smaller diameter is lower than that over larger particles than over "neck" regions, which also constitutes underlying driving force behind materials transport mechanism in sintering

Regions of lower vacancy concentration

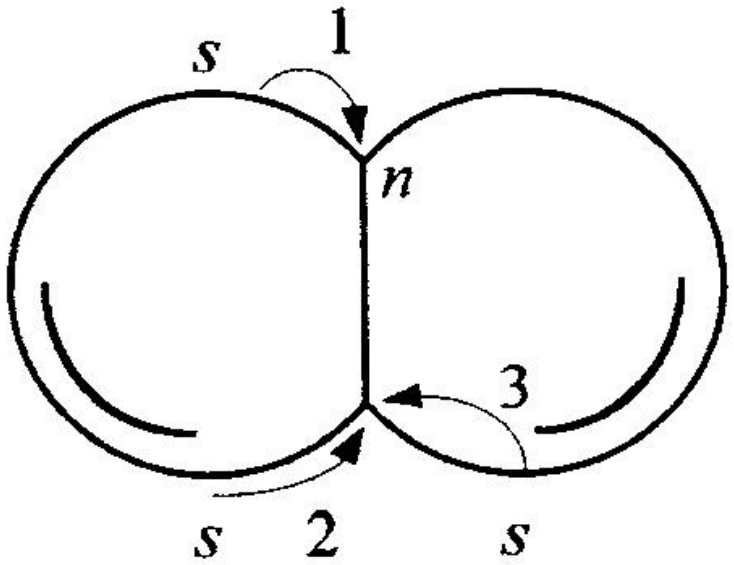
"Neck" regions of higher vacancy concentration



M W Barsoum (2003), Fundamentals of Ceramics, p. 309-315

Mass Transport Mechanisms Leading to Densification vs. Coarsening

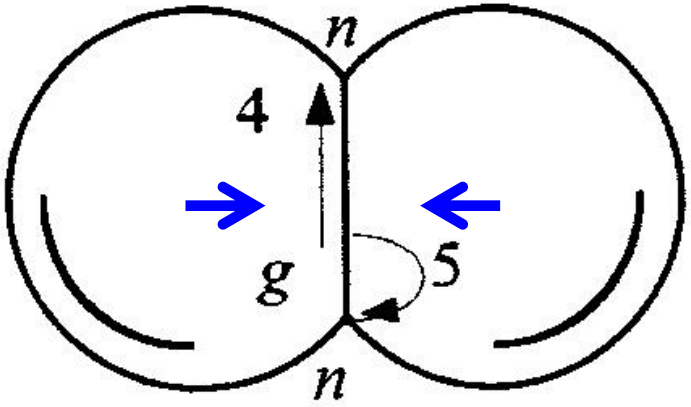
Mechanisms leading to COARSENING



1. Evaporation-condensation from surface to "neck"
2. Surface diffusion to "neck"
3. Lattice diffusion from surface to "neck"

M W Barsoum (2003), Fundamentals of Ceramics, p. 309-315

Mechanisms leading to DENSIFICATION



4. Grain boundary (GB) diffusion from GB center to "neck"
5. Lattice diffusion from GB center to "neck"
6. Plastic/viscous (for glass) flow to "neck"

Kinetics of Sintering

❑Central questions

- How does ceramic body densify in sintering process and how does microstructure evolute?
- What determines whether particle compact will densify or coarsen?

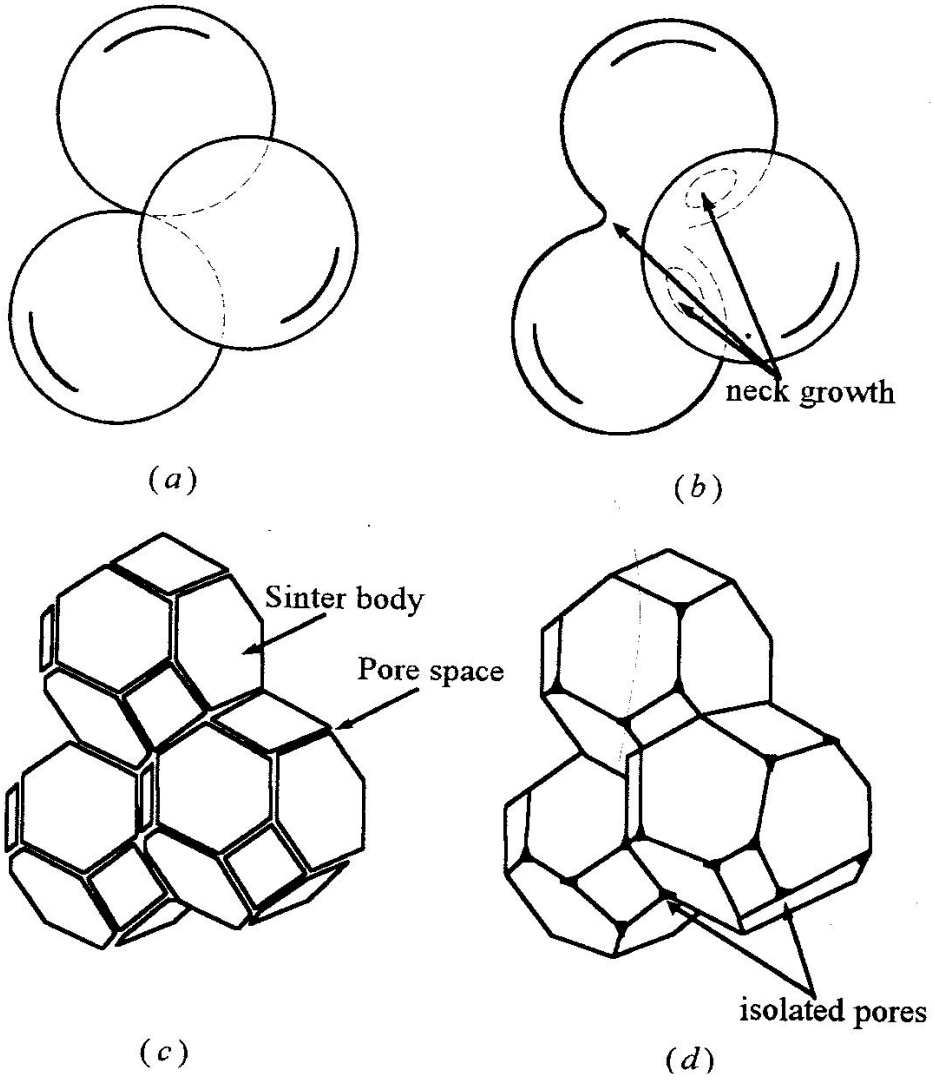
❑Practical considerations

- Many models developed over the years to account for sintering kinetics
- Complication arises from many different variables/factors in real systems
  - Powder size, shape, distribution
  - Bulk/surface chemistry
  - Powder packing
  - Additives
  - Heating/cooling schedule (temperature, time)
  - Other: pressure, atmosphere
- All models developed are highly simplified in terms of geometry/mass transport flow, which deviate from real system – they have "limited validity" and serve the purpose of help "**appreciating the general trends … and identifying the critical parameters than …predictive capabilities**"

M W Barsoum (2003), Fundamentals of Ceramics, p. 315

Stages in Solid-State Sintering

- **Initial stage**
  - "Inter-particle contact area increases by neck growth from 0 to ~0.2, and the relative density increases from about 60 to 65 percent"
- **Intermediate stage**
  - "characterized by continuous pore channels that are coincident with three-grain edges…the relative density increases from 65 to about 90 percent"
- **Final stage**
  - "when pore phase is eventually pinched off and is characterized by the absence of a continuous pore channel…increase in pore and grain boundary mobilities," which lead to significant coarsening or grain growth



M W Barsoum (2003), Fundamentals of Ceramics, p. 315-318

Kinetics for Initial Stage Sintering

- **Kinetics generally satisfy**

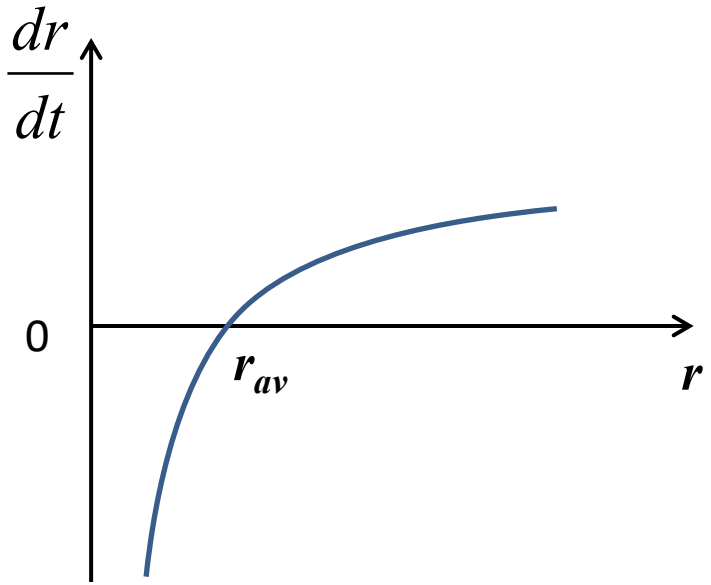
$$\left(\frac{\Delta L}{L_0}\right)^{m/2} = -\frac{H}{2^m r_0^2} t$$

Mechanism	*m*	*n*	*H*
Surface diffusion	7	4	$\frac{56 V_m D_s \delta_s \gamma_{sv}}{RT}$
Lattice diffusion from surface	4	3	$\frac{20 V_m D_l \gamma_{sv}}{RT}$
Vapor transport	3	2	$\frac{3 \rho_0 \gamma_{sv}}{(2\pi m k T)^{1/2} RT}$
Grain boundary diffusion	6	4	$\frac{96 V_m D_{gb} \delta_{gb} \gamma_{sv}}{RT}$
Lattice diffusion from grain boundary	5	3	$\frac{80 \pi V_m D_l \gamma_{sv}}{RT}$
Viscous flow	2	1	$\frac{3 \gamma_{sv}}{2\eta}$

Rahaman (2003), p. 486-494

Coarsening

- **Particles smaller than average tend to disappear while particles larger than average will grow**



$$\frac{dr}{dt} = \frac{2\gamma_{sv} V_m P_0 K_r}{RT}\left(\frac{1}{r_{av}} - \frac{1}{r}\right)$$

K_r Coarsening rate constant

Coarsening over time satisfy

$$r_{av}^2 - r_{av,0}^2 = \frac{2\gamma_{sv} V_m P_0 K_r}{RT} t$$

Coarsening kinetics increases with higher γ_{sv} and P_0

M W Barsoum (2003), Fundamentals of Ceramics, p. 327-334

Grain Growth Kinetics

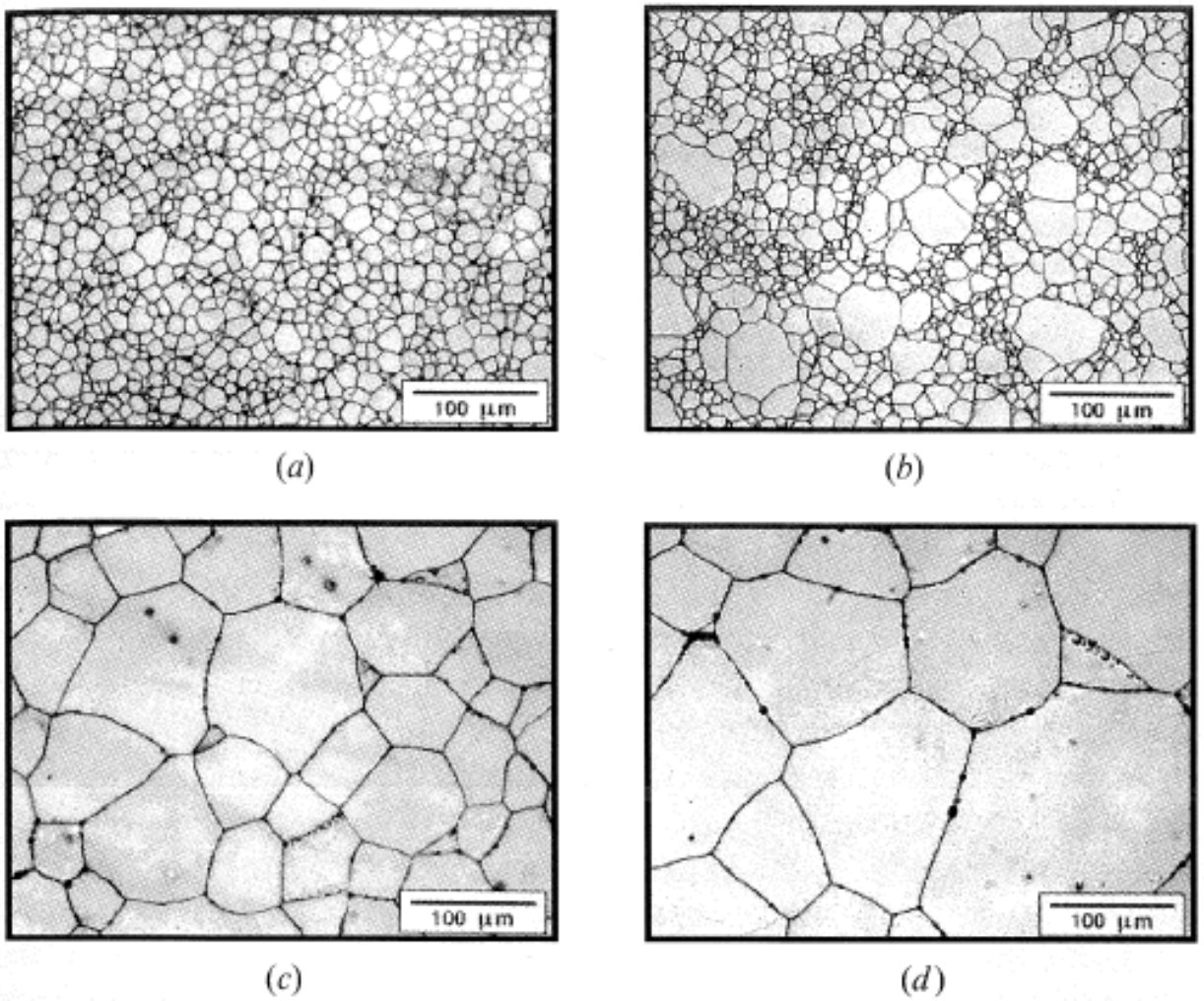
- **For grain growth,**

  If grain boundary is ideal, i.e., free of pores, inclusions, and solutes,

$$d_{av}^2 - d_{av,0}^2 = \frac{4M\gamma_{gb}\Omega_{MX}}{\beta} t$$

  Actual situation complicated due to dragging by solutes, 2nd phase inclusion, and pores

$$d_{av}^m - d_{av,0}^m = kt$$



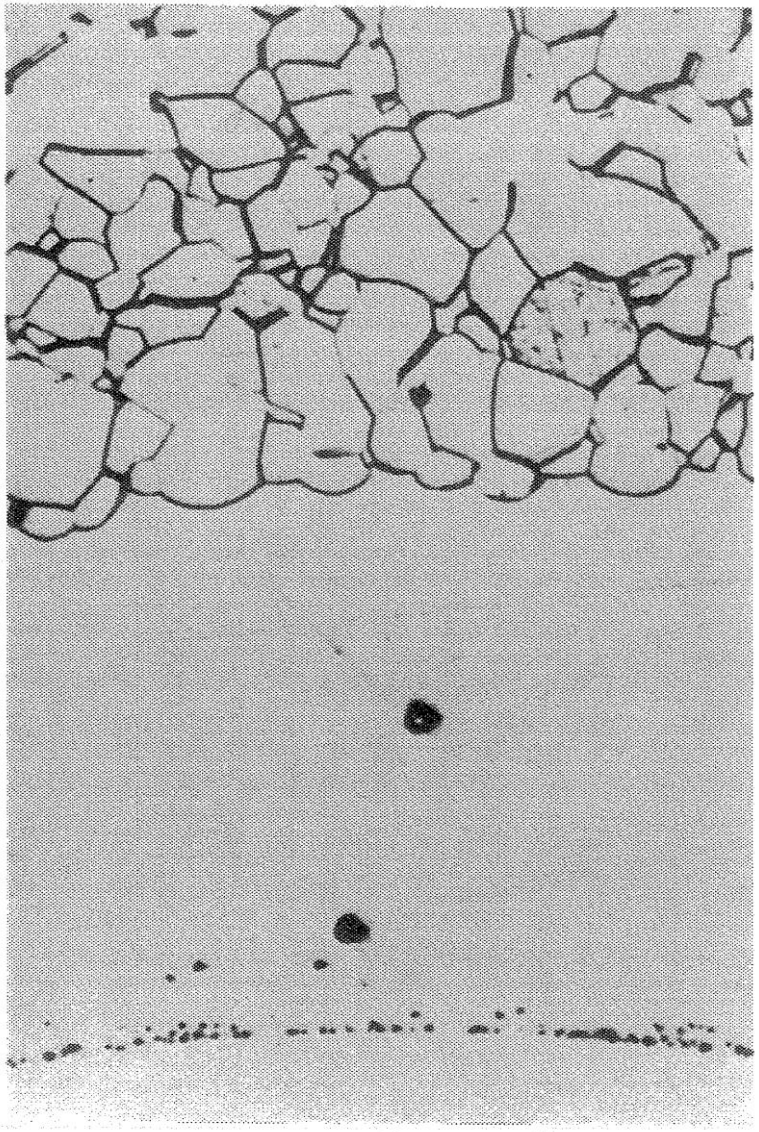
M W Barsoum (2003), Fundamentals of Ceramics, p. 327-334; image by H. E. Kim J. Am Ceram Soc (1990) 73, p. 496

Abnormal Grain Growth

- **Sometimes, some grains grow excessively to much larger size comparing with other grains, which is called abnormal grain growth**

  Example: large Al_2O_3 grow in fine Al_2O_3

  - Need to avoid abnormal grain growth
  - Origins not exactly clear - hypothesized to relate to anomaly in grain boundary mobility and/or interface anisotropy
  - Empirical ways to control abnormal grain growth
    - Introduce proper dopant to slow grain boundary movement, e.g., MgO doping of Al_2O_3
    - Suppress liquid phase



Rahaman (2003), p. 567-573

Image by R. L. Coble, from Rahaman (2003), p. 578

Summary of Qualitative Factors influencing Solid-State Sintering

- **Particle size**
  - Smaller particle size give larger driving force, but has greater tendency for agglomeration and loose or uniform packing.
- **Particle size distribution**
  - Narrower size distribution help limit abnormal grain growth
- **Temperature**
  - Higher temperature increases diffusion, especially bulk diffusion which accelerate sintering
- **Green density**
  - Normally higher green density leads to better sintering
- **Uniformity of green body microstructure**
  - More uniform green body is critical
- **Atmosphere**
  - Higher vapor pressure inhibits densification
- **Impurities**

Liquid Phase Sintering

- **"a majority of ceramic products are fabricated via this route" (Barsoum, 2003, p. 337)**
- **Advantages**
  - Faster
  - Uniform densification
- **Liquid phase sintering mechanism**
  - Particle re-arrangement

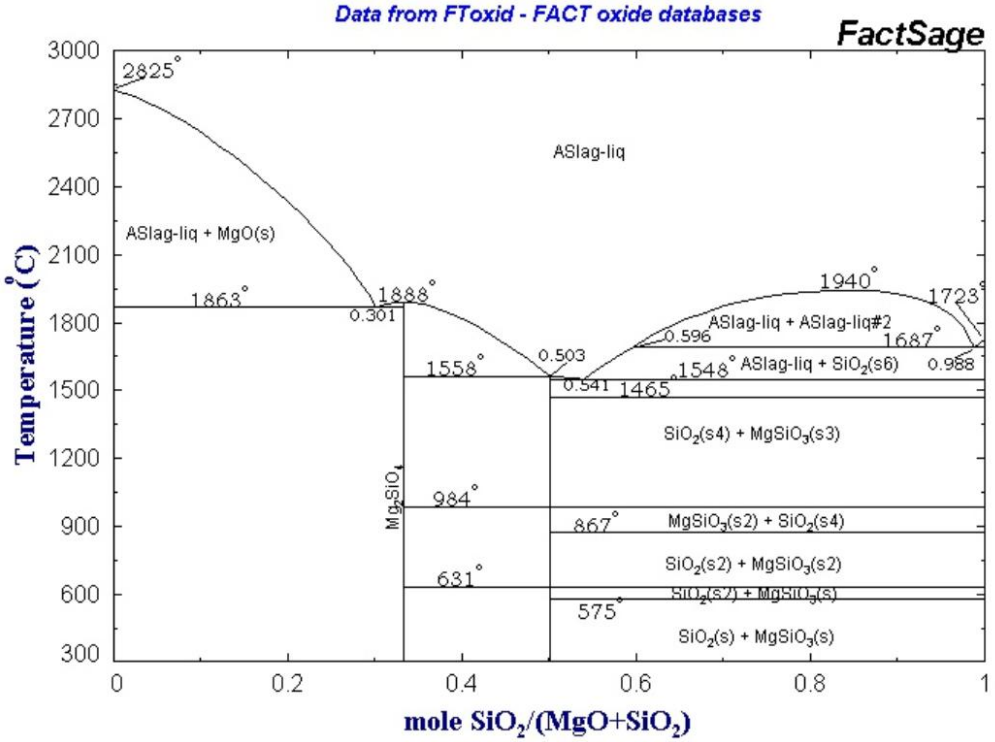
  Fastest
  - Solution-reprecipitation

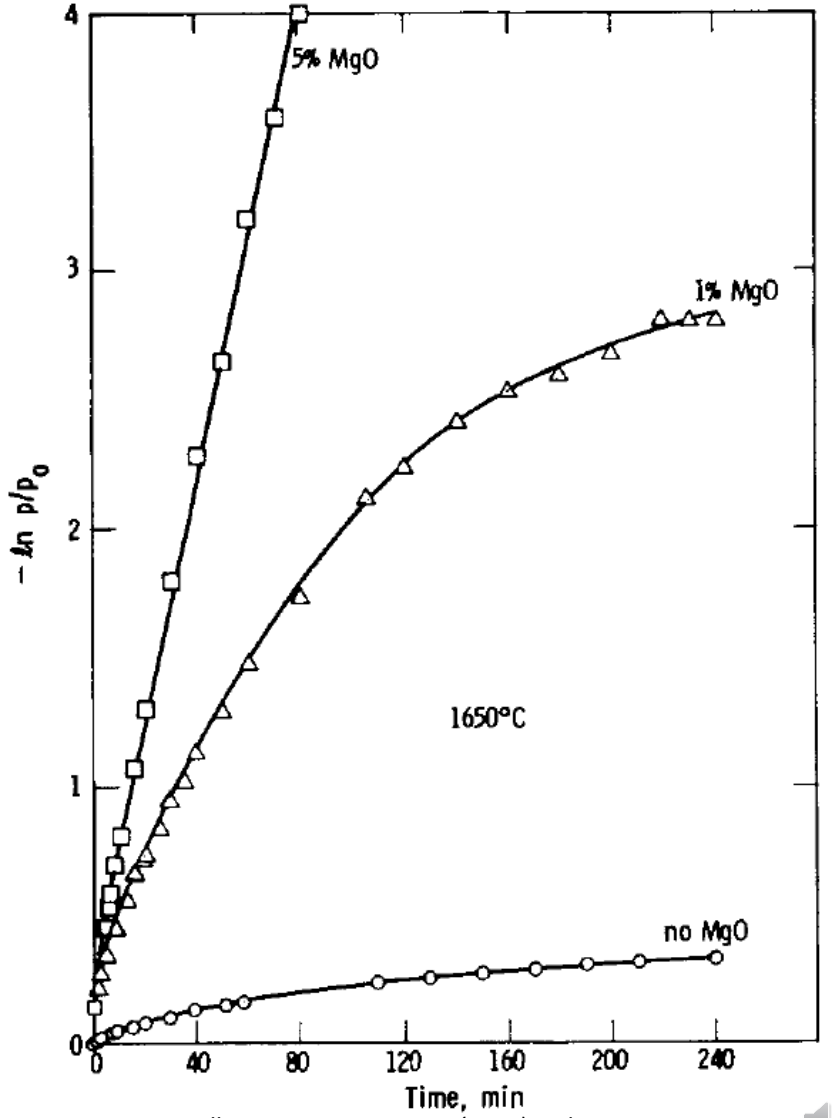
  Higher pressure/chemical potentials lead to higher solubility of particles, which diffuse through liquid phase and re-precipitate in regions with lower pressure/chemical potential
  - Solid state sintering

Example of Liquid Phase Sintering of Si_3N_4 with Addition of MgO

❑Observations

- Si_3N_4 by itself does not show densification in hot pressing at 1650 °C with 27 MPa
- Addition of MgO significantly improves densification for 1650 °C hot pressing



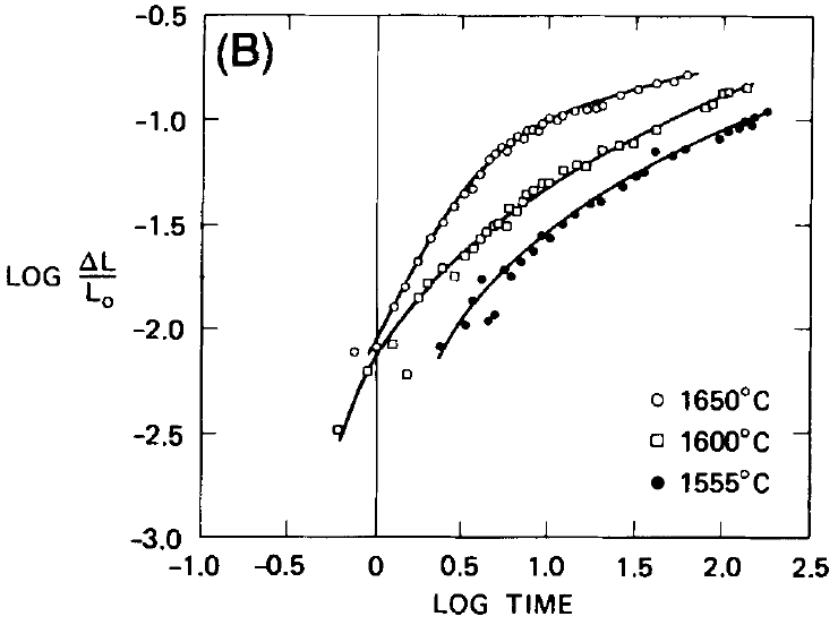


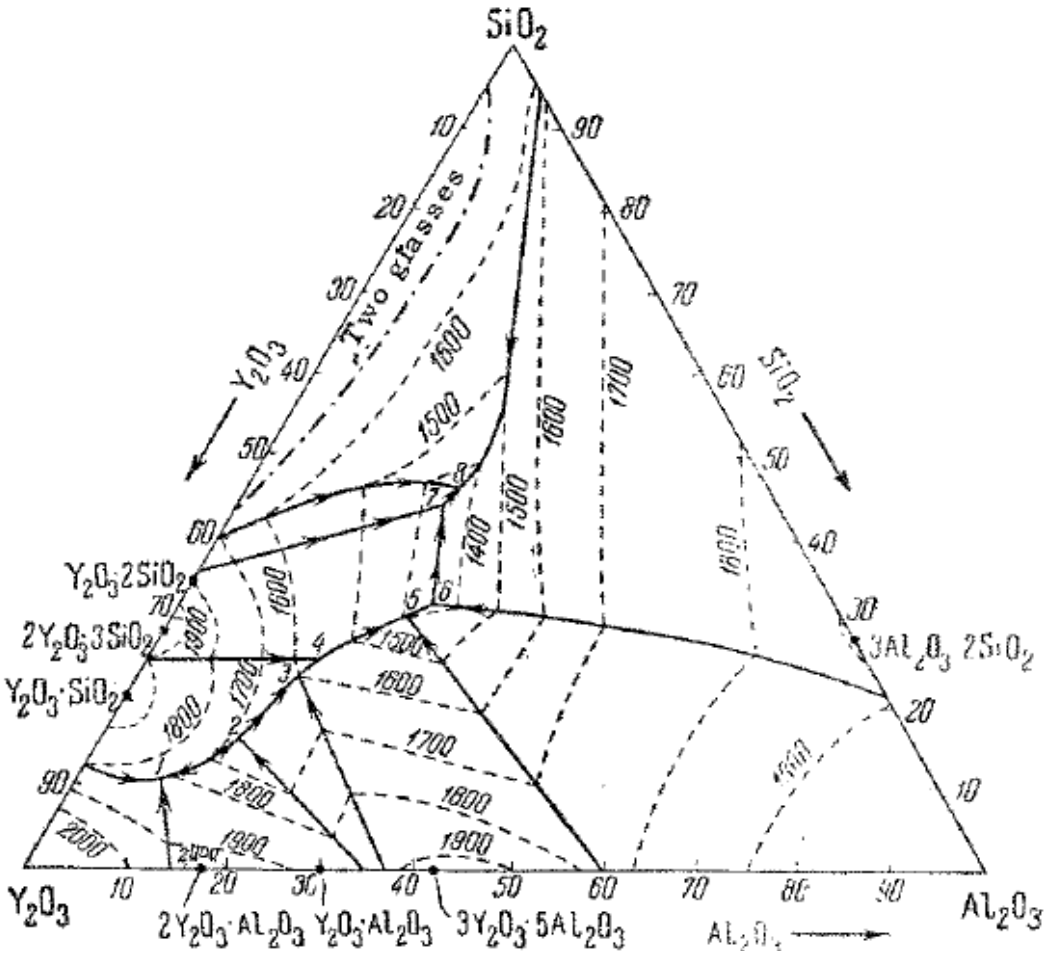
G R Terwilliger, J. Am Ceram Soc (1974), vol. 57, 25
C. Greskovich, J. Am Ceram Soc (1976), vol. 59, 336

Example of Liquid Phase Sintering of Si_3N_4 with Addition of Al_2O_3-Y_2O_3

❑Observations

- NO densification up to 1820 °C for pressureless sintering
- Pressureless sintering at 1500-1750 °C with addition 8 wt.% of (50 wt.% Al_2O_3-50 wt.%Y_2O_3) (69 mol.% Al_2O_3-31 mol.% Y_2O_3 leads to significant densification





C. Greskovich, J. Am Ceram Soc (1976), vol. 59, 336

A. Bondar Bulletin of the Academy of Sciences of the USSR, Division of chemical science, 13 [7] 1231-1232 (1964).

Example of Liquid Phase Sintering of SiC with Addition of Al_2O_3-Y_2O_3 (1)

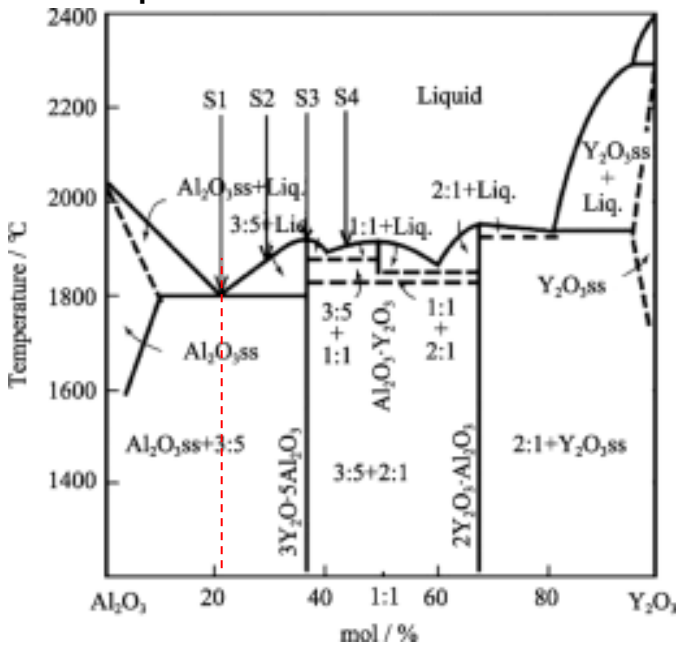
❑Observations

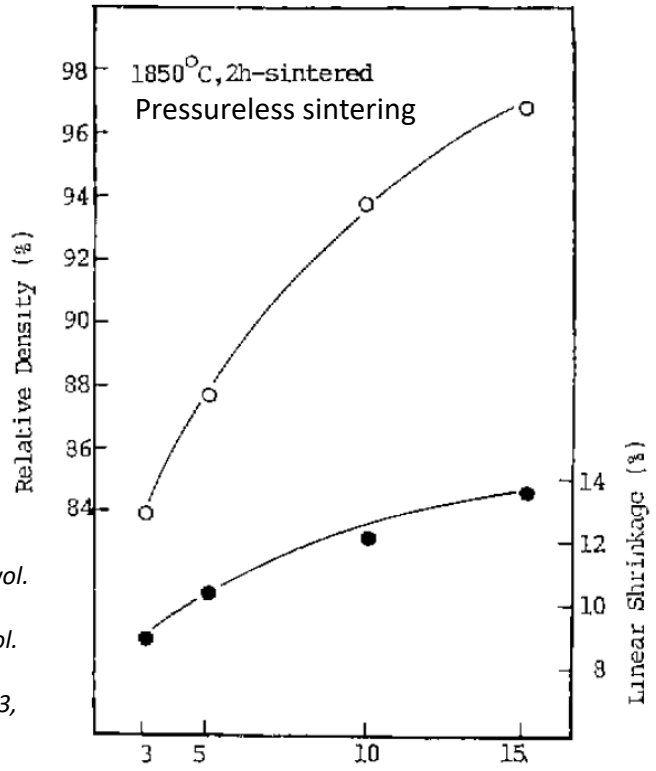
- NO densification up to 1900 °C without proper sintering aid
- Pressureless sintering at 1850 °C or hot pressing at 1800 °C with 60 wt.% Al_2O_3-40 wt.%Y_2O_3 (77 mol.% Al_2O_3-23 mol.% Y_2O_3) improve densification dramatically

Table I. Densities of Doped β-SiC Compacts Fired for 1 h in Flowing Ar

Composition (wt%)	D_0/D_t* (%)	D_{1500}†/D_t (%)	D_{1700}/D_t (%)	D_{1900}/D_t (%)
SiC+0.8 C	59.2	59.2	59.2	59.2
SiC+0.6 B	57.3	57.3	58.6	60.7
SiC+0.8 C+0.6 B	58.6	59.8	65.7	72.3

*D_0 = initial green density, D_t = theoretical density (3.21 g/cm³); †D_{1500} = density after sintering at 1500°C.





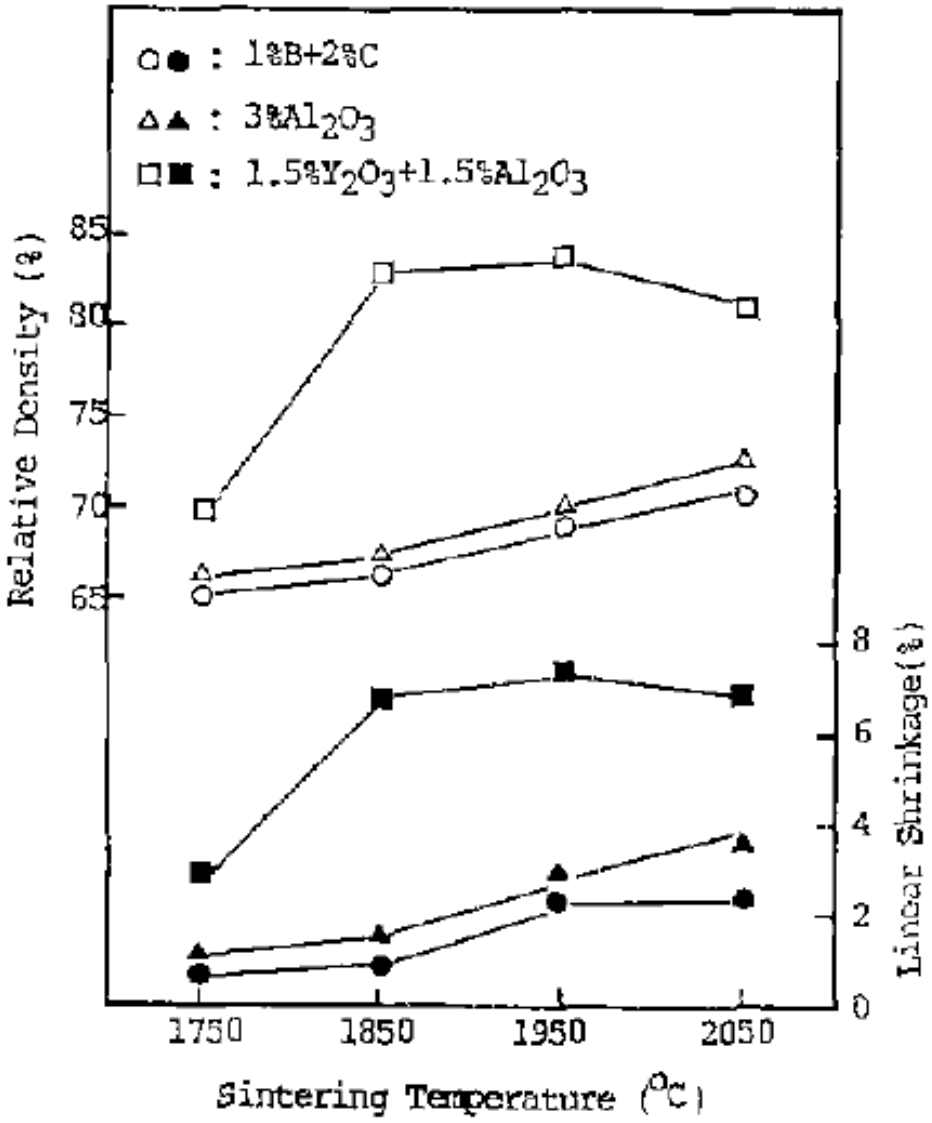
C. Greskovich, J. Am Ceram Soc (1976), vol. 59, 336
D. H. Kim, J Korean Ceram Soc (1989), vol. 26, 228
D. H. Kim, J Am Ceram Soc (1990), vol. 73, 1431

Example of Liquid Phase Sintering of SiC with Addition of Al_2O_3-Y_2O_3 (2)

- Liquid phase sintering aid more effective than other sintering aid (e.g., carbon or pure Al_2O_3) in improving density
- No deterioration of room temperature mechanical properties

Vol.% of Al_2O_3-Y_2O_3	Relative density (%)	KIC (MPa•m$^{1/2}$)	Deflection angle (deg)
0	97	2.5±0.2	2
4	96	3.6±0.2	11
8	99	3.7±0.1	15
12	98	4.0±0.3	16
16	97	4.2±0.2	21

D. H. Kim, J Korean Ceram Soc (1989), vol. 26, 228
D. H. Kim, J Am Ceram Soc (1990), vol. 73, 1431

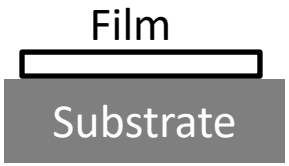


Considerations on Liquid Phase Sintering

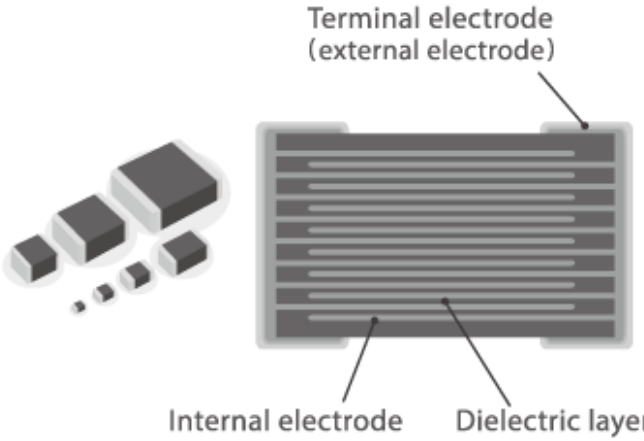
- **Form liquid during heating**
  - Low melting point liquid or forming eutectic
- **Amount of liquids**
  - For technical ceramics
    - Often less than a few vol.%
  - For traditional ceramics (e.g., clay-based including porcelains)
    - Can be high of 25-30 vol.%, and such ceramics are referred to as vitrified, and the sintering process is referred to as **vitrification**
- **Not all liquids work equally**
  - Example: for sintering of Si_3N_4, "addition of CaO, Y_2O_3, Fe_2O_3, Al_2O_3, SrO, SnO, and Na_2O were tried at 5 wt.% level; none resulted in more than 90% densification" *G R Terwilliger, J. Am Ceram Soc (1974), vol. 57, 25*
  - Liquid has to have reasonable solubility of solid
  - Liquid has to wet solid
  - Liquid should not promote unwanted reactions/evaporation
- **Useful when presence of remaining glassy phase does not impact performance – usually for ambient temperature applications**

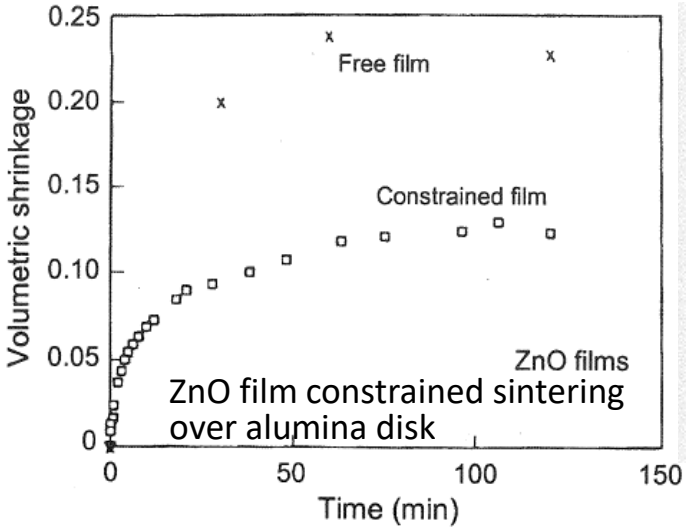
Constrained Sintering

- **Constrained sintering is needed when sintering thin/thick film over substrates**
- **Considerations**
  - Reduced shrinkage under the same condition
  - Defects (e.g., cracks/delamination) may develop between film and substrate
  - Reducing film thickness may mitigate defects
    - <~50 μm for particle film (thinner if fast sintering)
    - <1 μm for sol-gel derived film

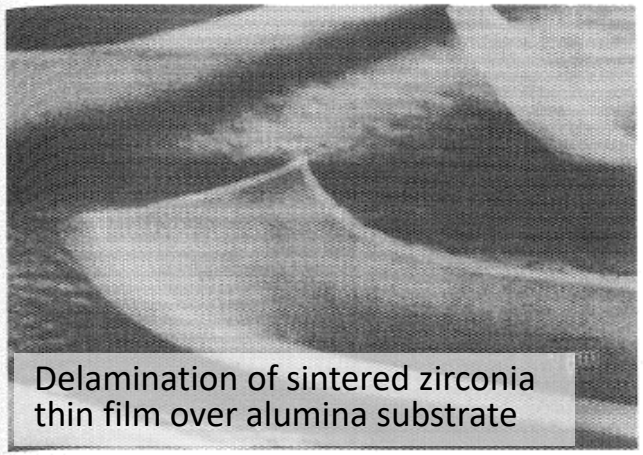


Solid oxide fuel cell (left)
multilayer capacitor (down)



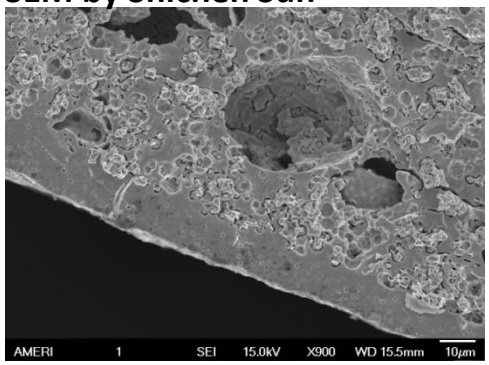


ZnO film constrained sintering over alumina disk



Delamination of sintered zirconia thin film over alumina substrate

NiO-YSZ/YSZ bilayer co-sintered SEM by Shichen Sun



http://www.global.tdk.com/techmag/electronics_primer/vol2.htm

T J Garino, J Am Ceram Soc (1990), vol. 73, 251

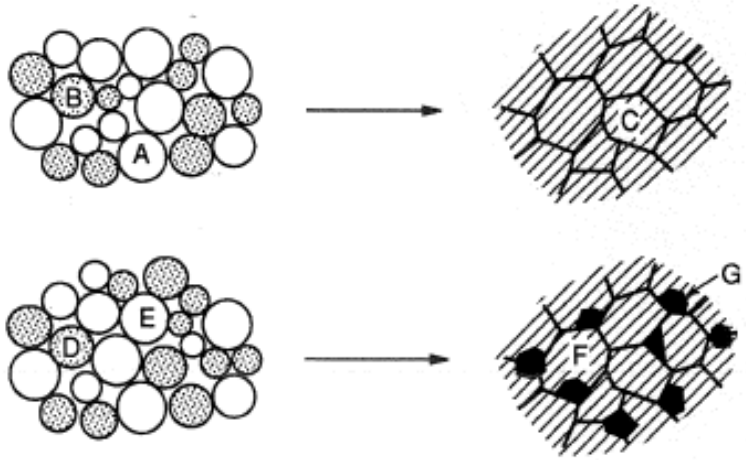
Rahaman (2003), p. 725-733

Reaction (or Reactive) Sintering (1)

- **Process in which chemical reaction between starting materials and densification of product occur in a one heat treatment**
- **Examples**
  - Single phase product:

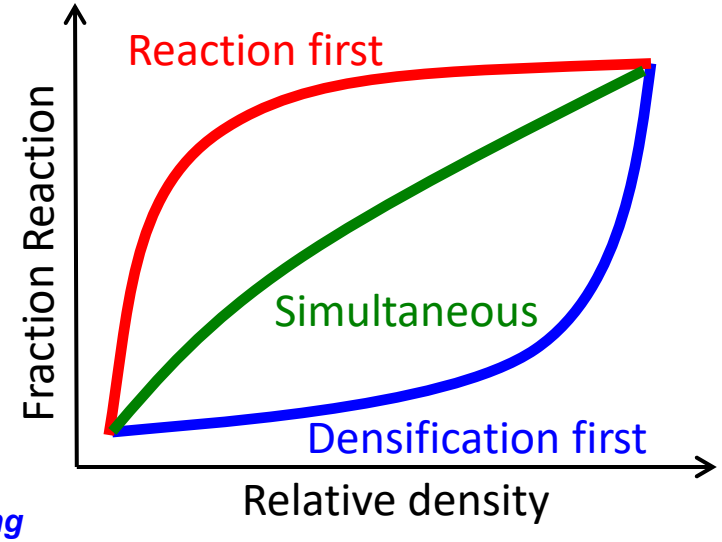
  $ZnO + Fe_2O_3 = ZnFe_2O_4$
  - Composite product

  $3Al_2O_3 + 2\,(ZrO_2 \cdot SiO_2) = 3Al_2O_3 \cdot SiO_2 + 2ZrO_2$



- **Advantages**
  - Simplified processing for certain systems
- **Disadvantages**

  "finds little use in the production of single phase solids" (Rahama (2003), p. 756)
  - Difficulty in controlling microstructure
  - Possibility for inhomogeneity
- **Sequences of reaction vs. densification**

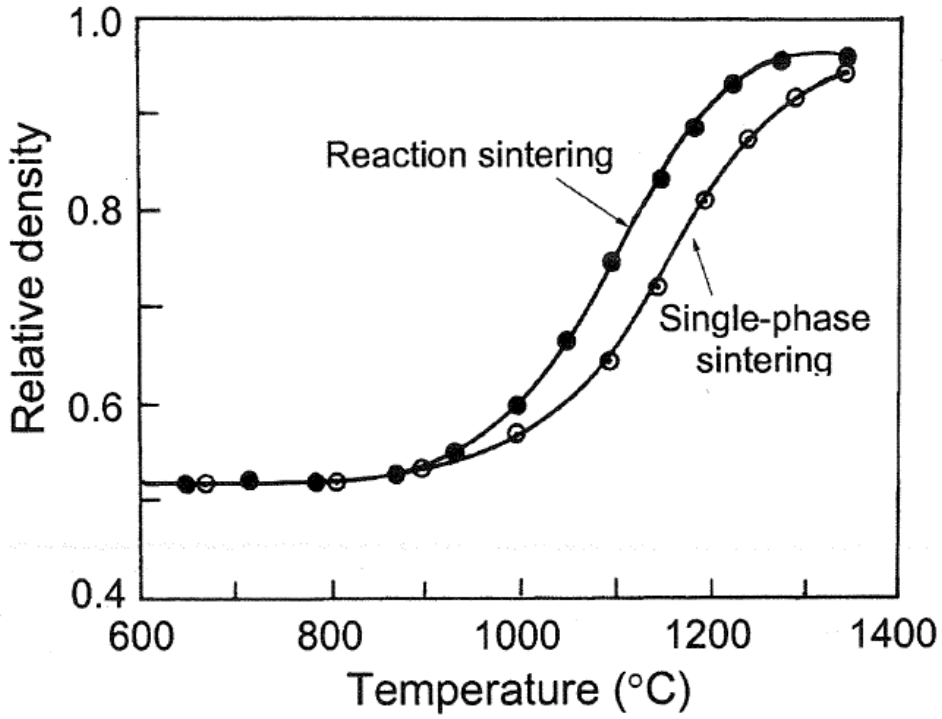


Rahaman (2003), p. 754-763

Reaction (or Reactive) Sintering (2)

- Reaction sintering can help densification in some cases (e.g., $ZnFe_2O_4$), but inhibits sintering for some others (e.g., $ZnAl_2O_4$)

$ZnFe_2O_4$



$ZnAl_2O_4$