Sintering methods

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Introduction of sintering: sintering basic

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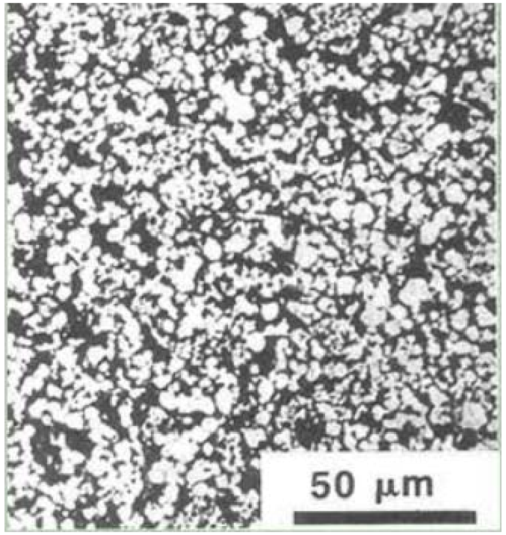
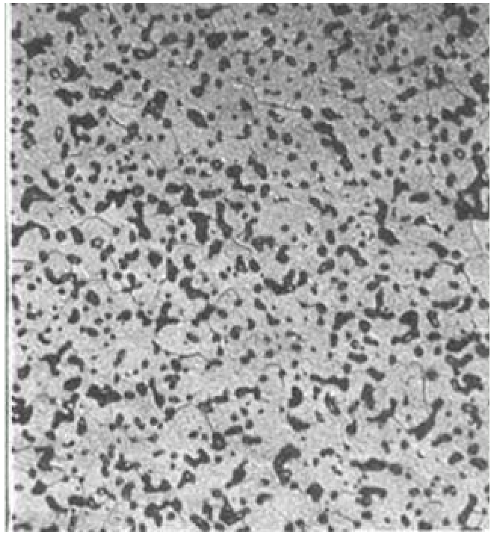
➢ What is sintering?

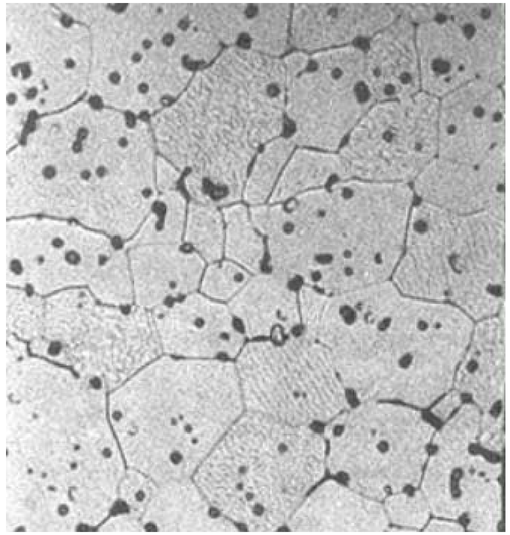
Heat treatment process in which a powder or porous material, already formed into the desired shape, is converted to a useful solid



Initial



Intermediate

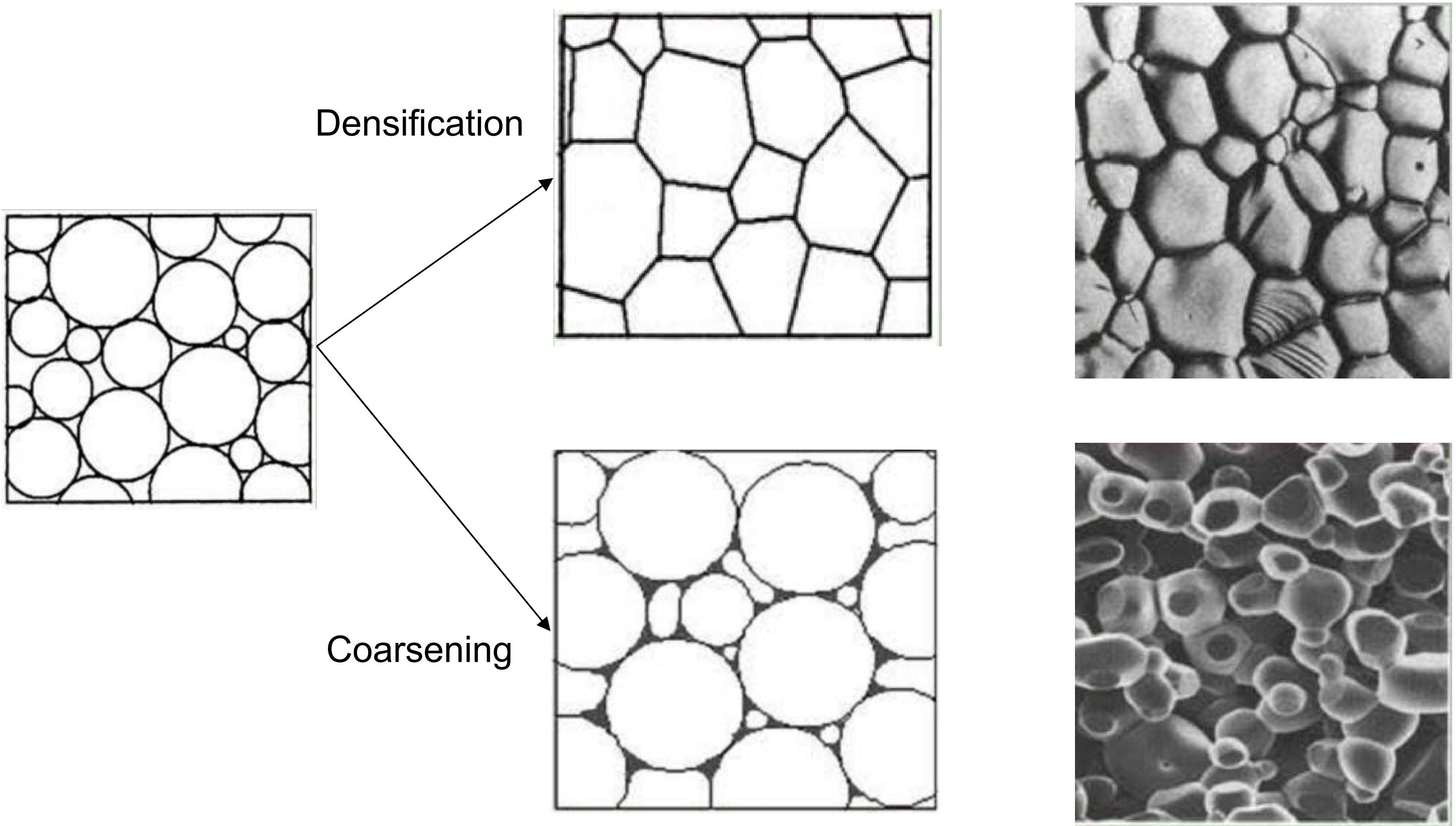


Final

Introduction of sintering: sintering basic

➢ What is sintering?

Competition between densification and coarsening (grain growth)



Introduction of sintering: sintering basic

- Goals of sintering

  Produce materials with the required target microstructures
  -> Commonly high density and controlled (fine) grain size

  Fabrication costs important in industrial production:

  -> Reproducibility; minimize flaws; dimensional and composition control; production efficiency

  -> Use of additives or special techniques to modify sintering cycle for improved productivity and lower sintering temperatures

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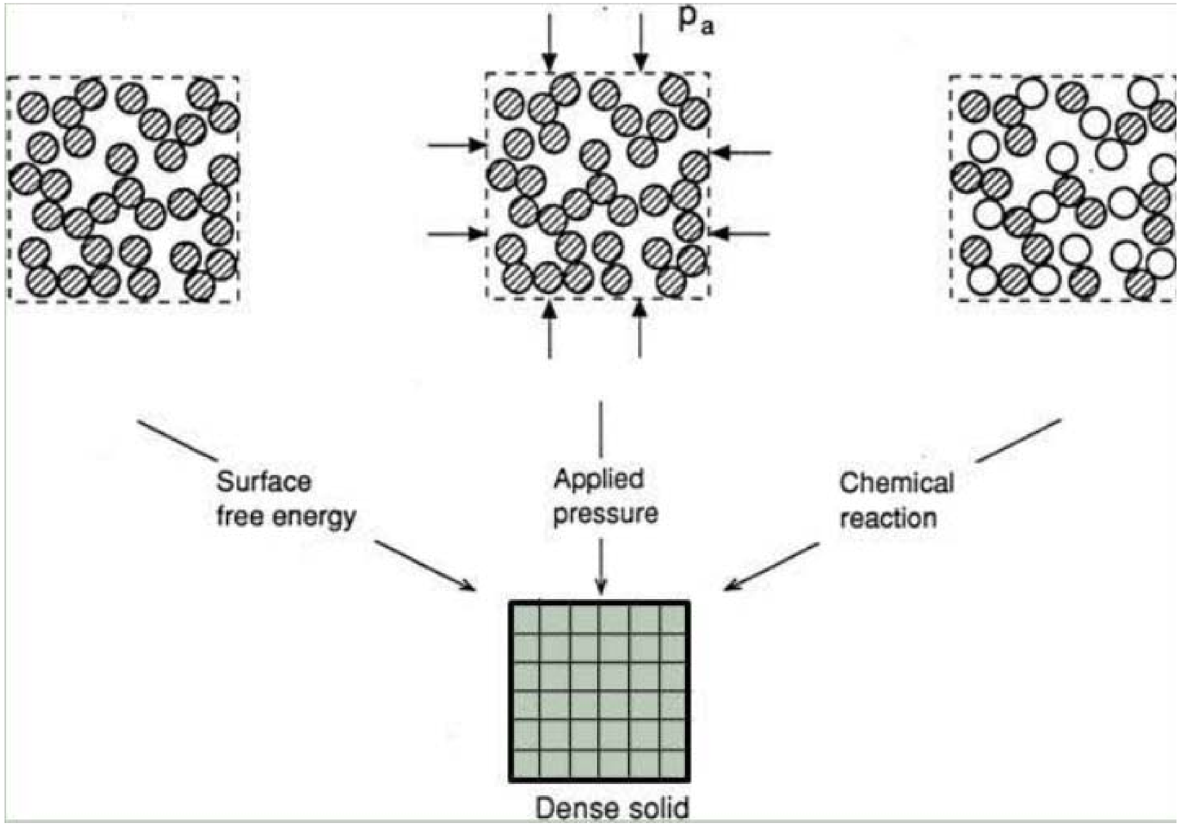
- Driving force for sintering



- Surface curvature

$$\Delta E_S = 3\gamma_{SV} V_m / a$$

75 J/mol

- Applied pressure

$$W = p_a V_m$$

750 J/mol

- Chemical reaction

$$\Delta G^o = -RT \ln K_{eq}$$

20,000 J/mol

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- Surfaces and Grain boundaries

Atoms at the surfaces and grain boundaries have higher energies relative to those in the bulk crystal

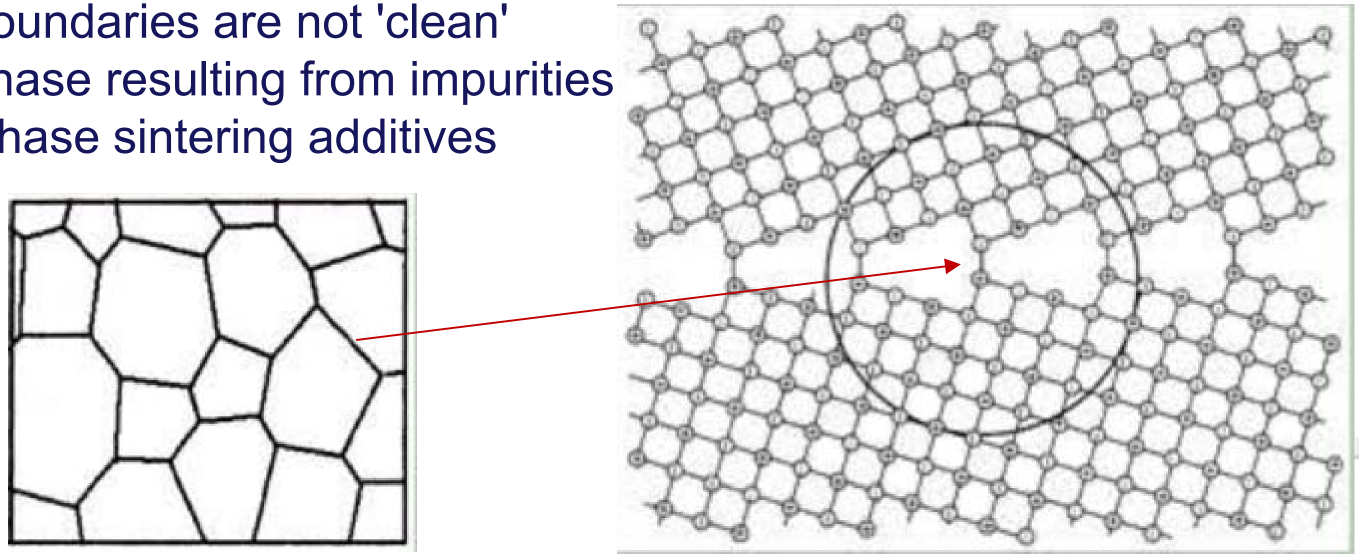
- Surface energy, Γsv (0.5 - 1 J / m2)
- Grain boundary energy, Γgb (0.5 - 1 Γsv)

Grain boundary:

- Thin region of disorder between 2 grains
- Thickness of 'clean' grain boundaries: 0.5-1 nm

Most grain boundaries are not 'clean'

- Second phase resulting from impurities or liquid-phase sintering additives



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- Kinetics

Matter transport to accomplish sintering occurs by diffusion

T > ~0 .5 TM for appreciable diffusion to occur

Diffusion affected by:
-> Defect equilibria
  - Intrinsic
  - Extrinsic (solutes present)
-> Solubility of dopants (solutes)
-> Ambipolar coupling
-> Surf ace and grain boundary segregation

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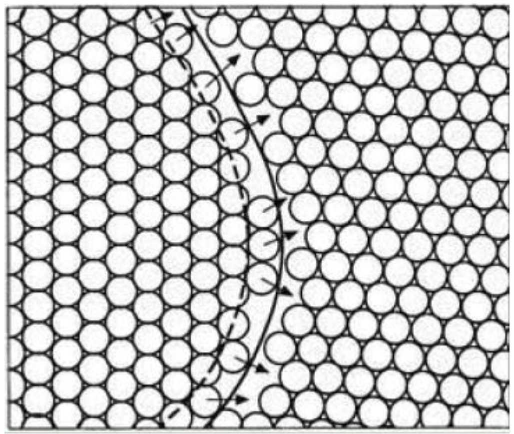
- Grain growth

✓ Grain growth - increase in the average grain size in dense or porous systems

✓ Coarsening - a common situation in porous systems where the average grain size and the average pore size increases

- Driving force for grain growth: - reduction in total grain boundary energy of the system



✓ How grains grow

- diffusion of atoms across the boundary
- from 'convex' side to 'concave' side
- boundary moves toward its center of curvature
- larger grains grow at the expense of smaller grains
- average grain size increases; number of grains decreases

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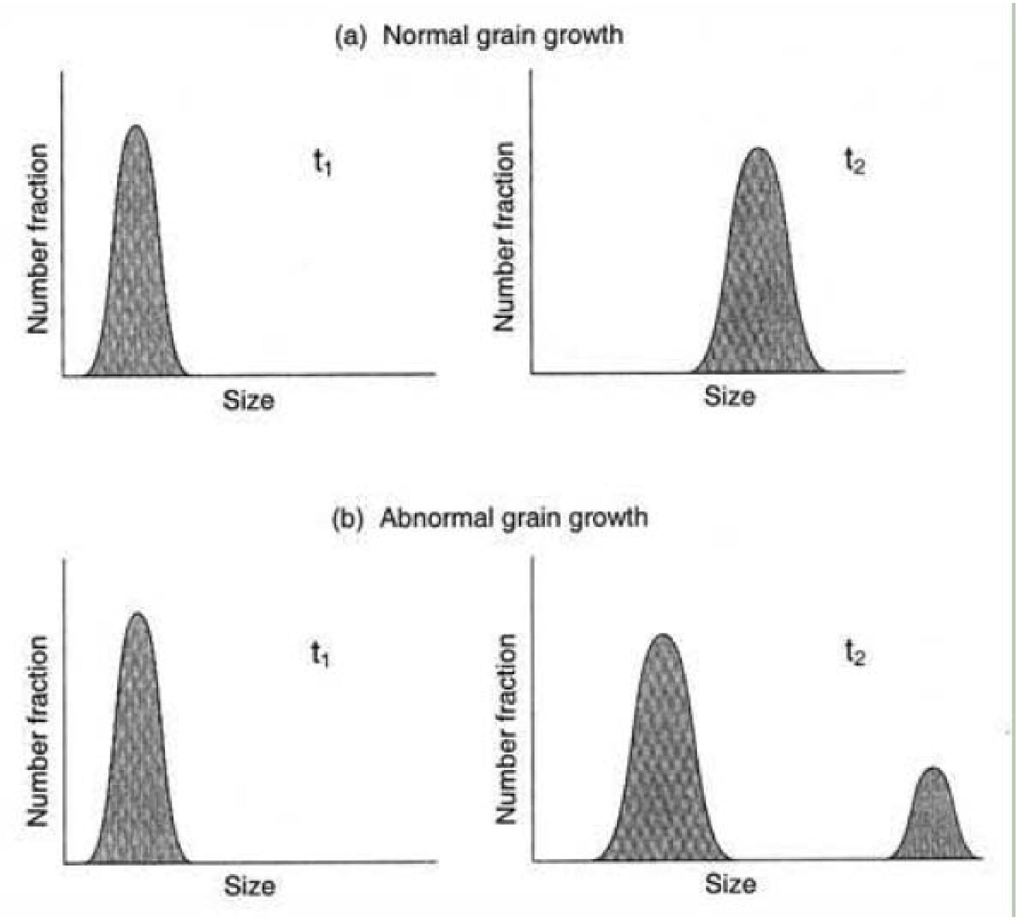
➢ Grain growth

✓Type of grain growth

- Normal: average grain size increases, but no marked change in the grain size distribution
- Abnormal: a few large grains grow rapidly at expense of small grains; bimodal grain size distribution



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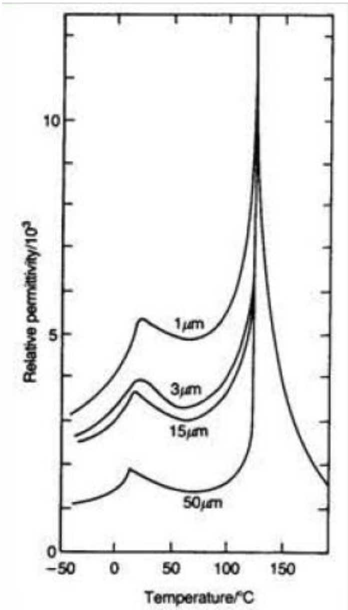
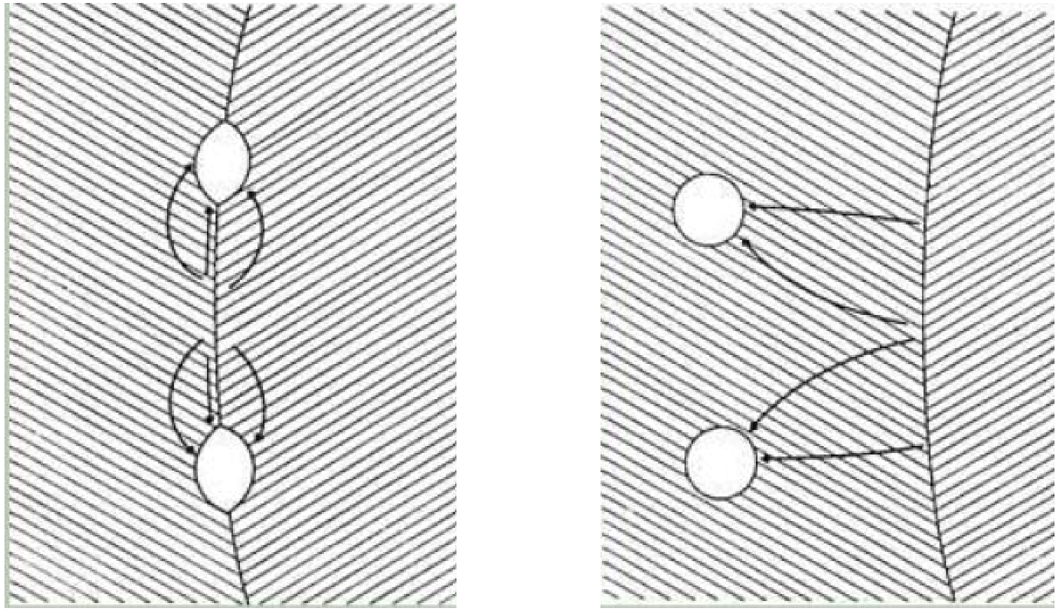
- Grain growth
  - ✓Why control grain growth?
    - Properties depend on grain size: small size often better
    - Grain growth hinders the attainment of high density
    - long sintering times increases the tendency for abnormal growth



Effect of grain size
on dielectric constant of BaTiO3



Pores trapped in grains (abnormal
growth) difficult to remove

Sintering methods

Sintering methods

- Hot pressing Equations

Process

Conventional (pressureless)

- Solid-state
- Liquid-phase
- Viscous

Pressure-assisted

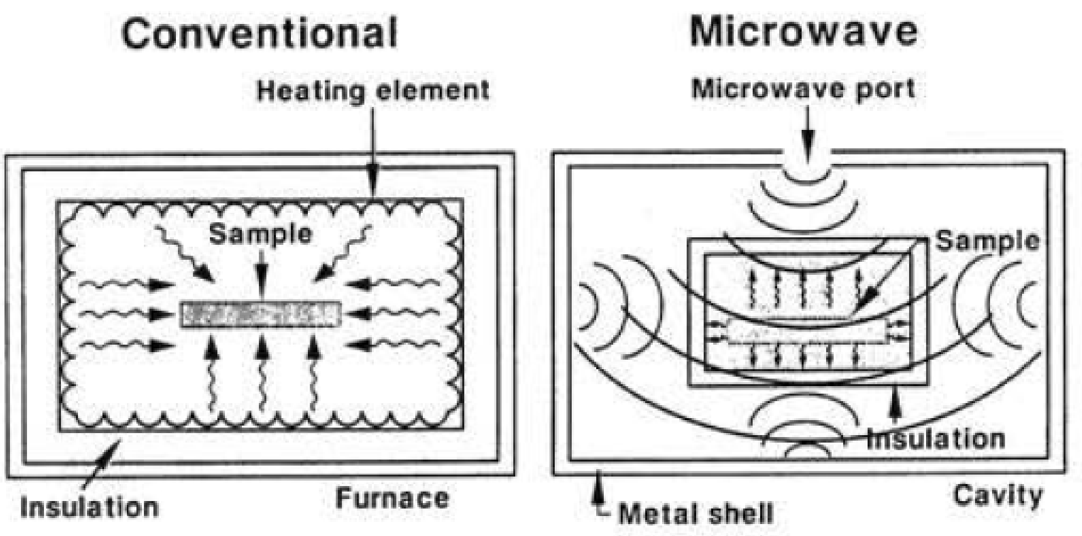
- Hot pressing
- Hot isostatic pressing
- Sinter-forging

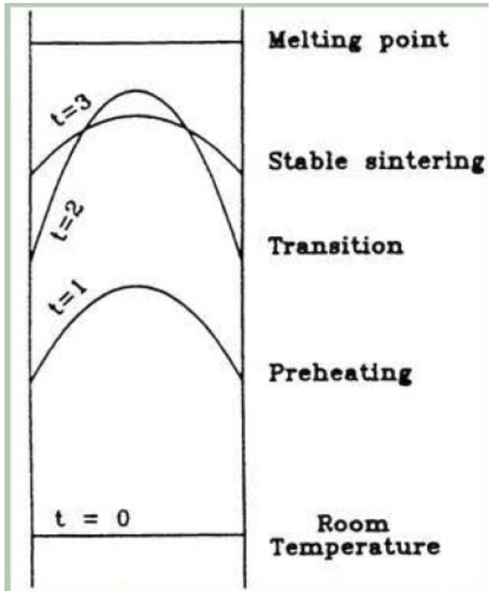
Special technique

- Microwave sintering
- Field-assisted sintering

Sintering methods

- Microwave sintering
  - ✓ Heating results from coupling between electromagnetic radiation and matter (free and bounds changes; dipoles)
  - ✓ Heat generated internally within material
  - ✓ Rapid heating (up to 1000°C/min or more)
  - ✓ Heating profile is 'inside-out'
    - Temperature higher inside material





Radial temperature profile of rod specimen (schematic)

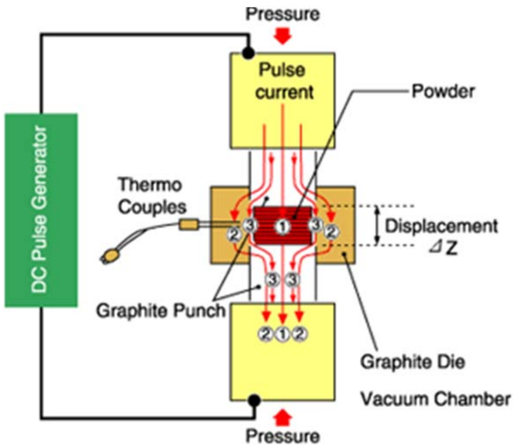
Sintering methods

- Microwave sintering
  - ✓Rapid heating (up to 1000°C/min or more)
  - ✓For the same heating rate as conventional heating:
  - - Faster diffusion (dens if ication and grain growth)
  - ✓Fast dens if ication
  - - Lower sintering temperature
  - - Can lead to finer grain size
  - - Shorter sintering cycles (more energy efficient?)
  - ✓Applicable to microwave-absorbing materials
  - - Many inorganic and polymeric materials
  - ✓Recently shown to be applicable to metal powders

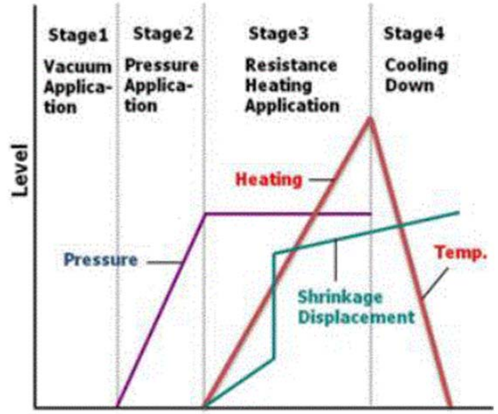
- Potential problems
  - ✓Large temperature gradients due to microwave frequency and shape of the article
  - ✓High heating rates/temperature gradients
  - - enhance density gradients .... non-uniform properties; cracking
  - ✓Thermal runaway due to localized heating
  - ✓High cost of equipment
  - ✓Continuous microwave sintering difficult

연구의 배경 및 필요성

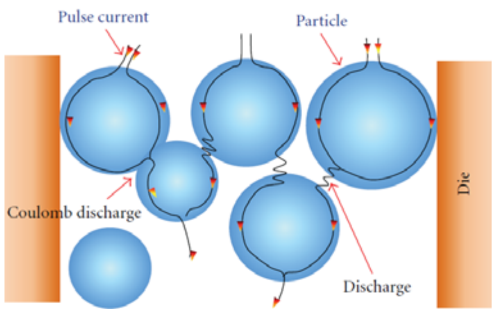
➢ SPS (Spark plasma sintering)



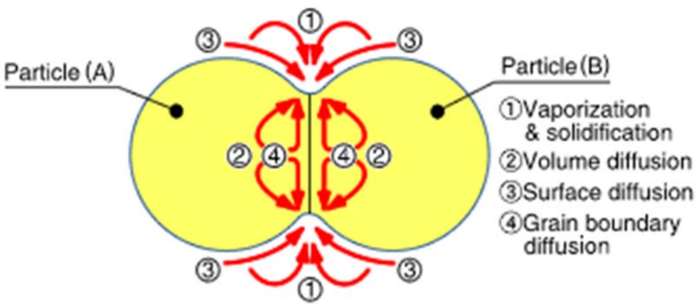
SPS system configuration and pulse current path



Sintering stages with temperature, pressure and shrinkage displacement profile during SPS



DC pulse current flow through the particles



Material transfer path during sintering

SPS system
- uniaxial force
- pulsed DC (direct way of heating)
  -> fast sintering process
  -> Advantages

SPS stages
- create vacuum (remove gases)
- apply pressure
- resistance heating
- cooling

Electric discharge
- discharge at noncontact surface
  -> plasma heating
- discharge at contact surface
  -> joule heating

Material transfer by SPS
- rapid densification by SPS
- selective diffusion mechanisms
- surface diffusion
- plastic deformation (diffusion through the melt, or time-independent processes)
- grain boundary and volume diffusion X

Sintering Applications. InTech, 2013. Int J Innov Res Sci Eng Technol 3 (2014): 15068-15075. Journal of Nanomaterials Volume 2012 (2012), Article ID 983470, 13 pages

Sintering methods

- Spark plasma sitnering
  - ✓ Short sintering cycle (a few minutes; typically <30 min)
  - ✓ Fast densification kinetics (compared to sintering)
  - ✓ Lower temperature onset for sintering
  - ✓ Desirable microstructure (high density; fine grain size)
  - ✓ Particularly useful for nanocrystalline materials; high temperature ceramics

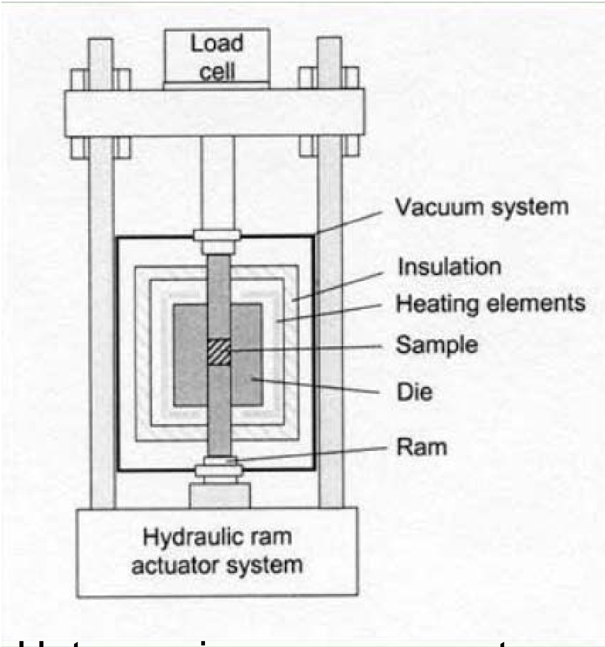
Material	Initial particle size (nm)	SPS Conditions: T(°C); t (min); p (MPa)	Final grain size (nm)
MgO	11	800; 5; 150	52
CeO_2	7	625; 5; 600	12–14
ZrO_2–2.4 mol% Y_2O_3)	13	1150; 5; 70	70
$BaTiO_3$	20–30	850; 2; 70	50
$SrTiO_3$	50	875; 5; 200	80

(Density >98%, except for $BaTiO_3$: 97%)

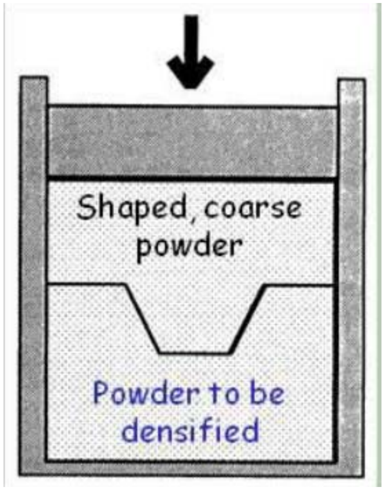
- Difficulties
  - ✓ Accurate temperature measurement of sample difficult: Temperature overshoots (especially for fast heating rate)
  - ✓ Microstructural inhomogeneities
  - ✓ Stoichiometry; C contamination
  - ✓ Net shape fabrication (complex shapes)
    -> Manufacturing potential continuously being improved

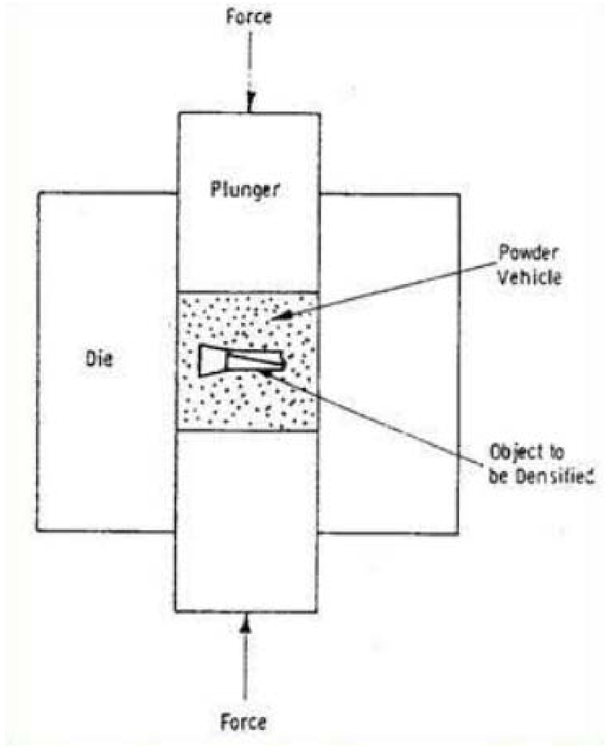
Sintering methods

➢ Hot pressing



Hot pressing arrangement





Powder vehicle method

Applied pressure 10-75 MPa

- Stress in die can be approximated as being isotropic
- Simple shapes: typically disks
- More complex shapes can be produced by 'powder vehicle hot pressing'. method

- use coarse or 'unsinterable' powder (BN , C) as a medium

Sintering methods

- Hot pressing

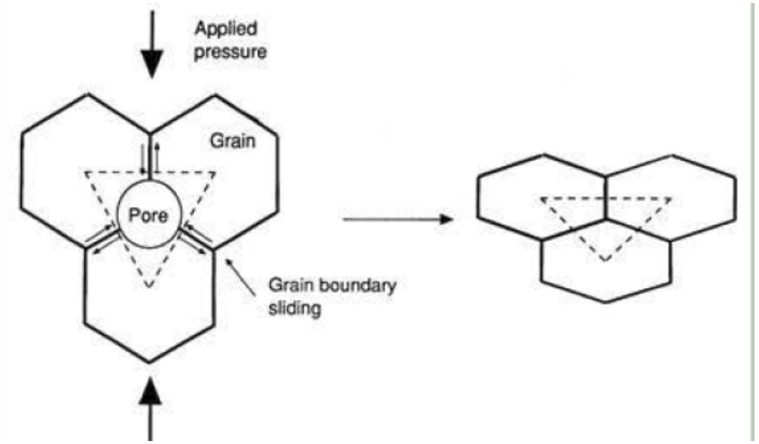
  ✓ Gases trapped in closing pores: substantial pressure can build up in pores during further densification

  ✓ Graphite impurities from die

  -> Ceramic can swell (bloating) or even break when used at elevated temperatures

  ✓ Some grain alignment (texturing) develops

  - can be used to develop anisotropic microstructures



Grain boundary sliding and texturing

Question or Comment