SINTERING

Outlines

- Introduction
- Types of Sintering
- Parameters in Sintering
- Driving Force for Sintering
- Stages of Sintering
- Mechanisms of Sintering
- Advantages of Sintering

Introduction

Sintering is defined as

The thermal treatment of a powder or compact at a temperature below the melting point of the main constituent, for the purpose of increasing its strength by bonding together of the particles.

Types of Sintering

1. **Solid state sintering**

    Only solid phases are present at the sinter temperature

2. **Liquid phase sintering**

    Small amounts of liquid phase are present during sintering

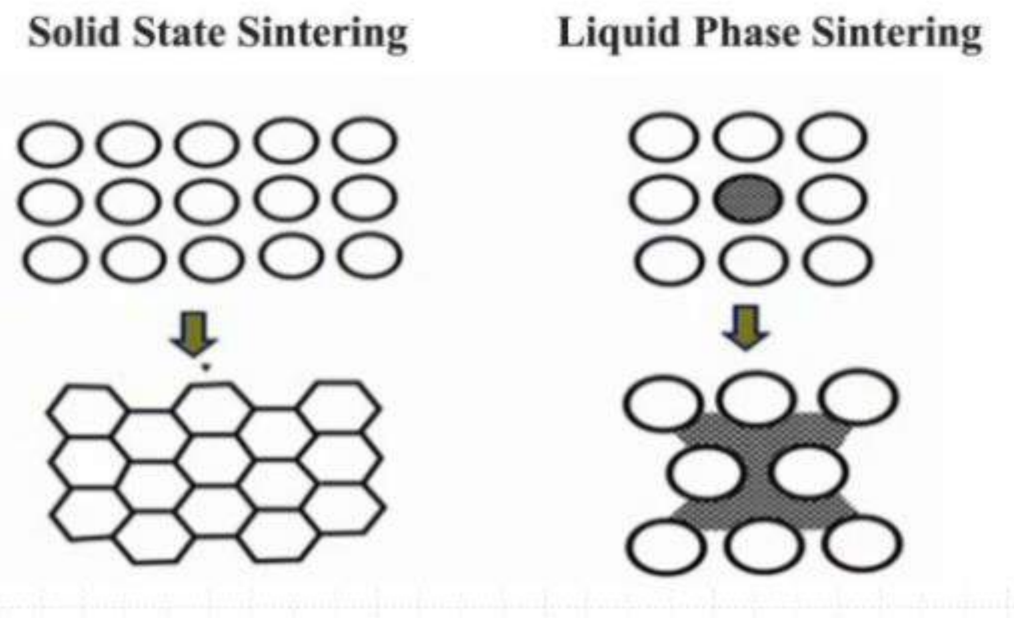
3. **Reactive sintering**

    Particles react with each other to new product phases

Two Most Important Sintering processes

1. **Solid State Sintering** : Direct particle to particle contact

2. **Liquid Phase Sintering** : Presence of a liquid film particularly at high temperature ensures adherence of the solid particles together.



Important Parameters in Sintering

We can divide these parameters into four broad categories

- **Powder preparation:**
  - -- Particle size
  - -- Shape
  - -- Size distribution

Important Parameters in Sintering

- **Distribution of:**
  - -- Dopants
  - -- Second phases
- **Powder Consolidation:**
  - -- Density
  - -- Pore size distribution

Important Parameters in Sintering

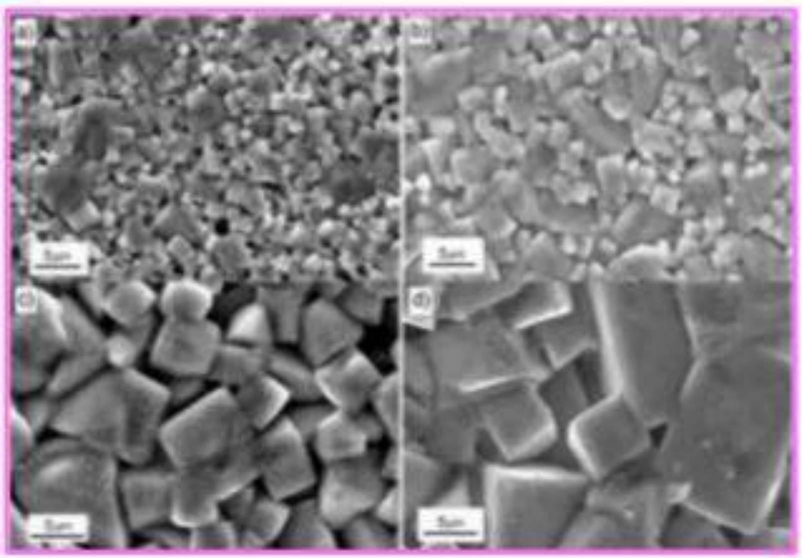
- **Firing:**
  - -- Heating rate
  - -- Temperature
  - -- Applied pressure
  - -- Atmosphere

Rate-Controlled Sintering

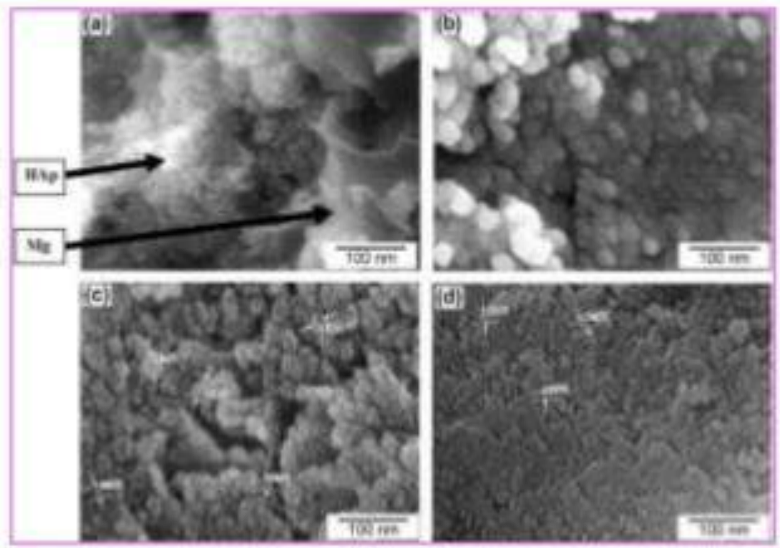
Rate – controlled sintering is done in two ways

I. controlling Heating rate

II. controlling temperature



SEM images of KNN sintered samples at: a) 1060, b) 1080, c) 1100 and d) 1120°C for 2 h



FE-SEM micrograph of Mg sintered at different heating rate, (a) 200 °C/min, (b) 400 °C/min, (c) 500 °C/min and (d)1200 °C/min

Important Parameters in Sintering

- Some parameters, such as the sintering temperature, applied pressure, average particle size and atmosphere can be controlled with sufficient accuracy
- Others, such as the powder characteristics and particle packing are more difficult to control but have a significant effect on sintering

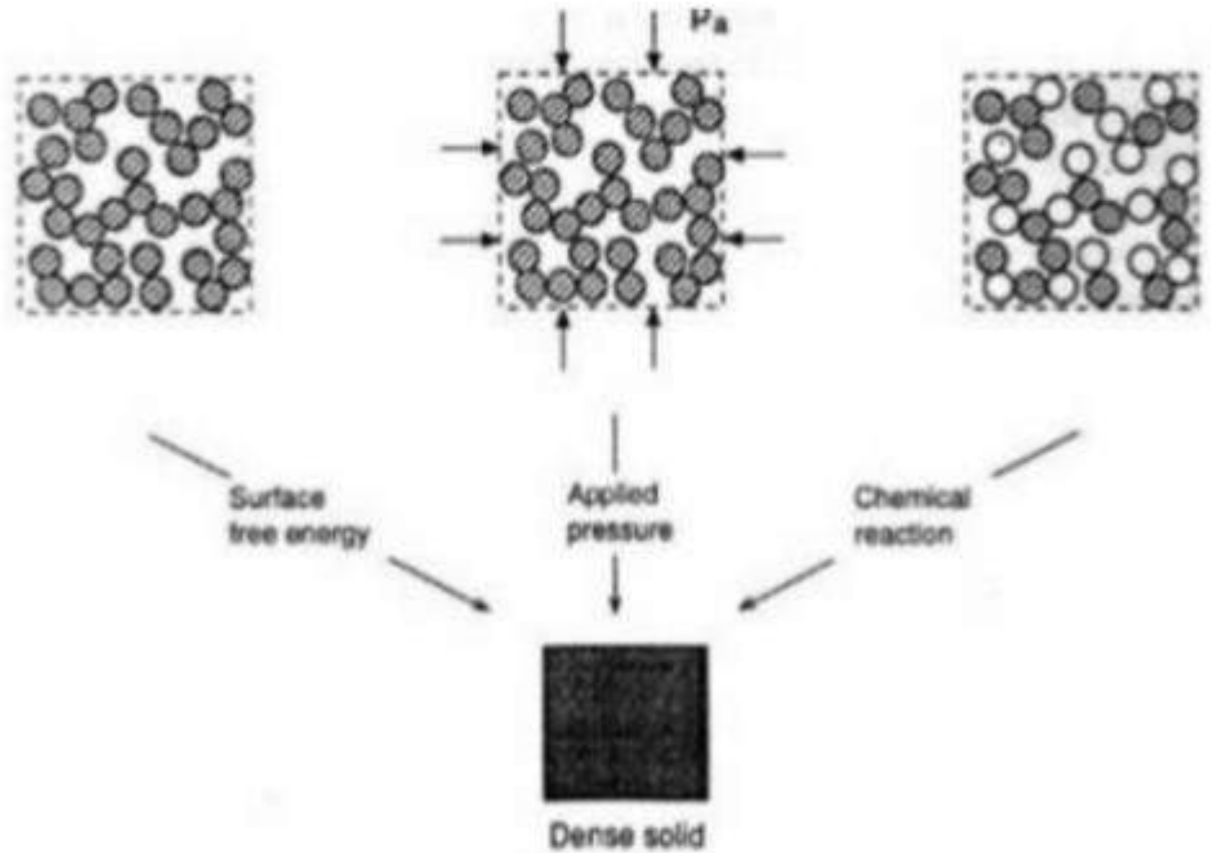
Driving Force for Sintering

As with all processes, sintering is accompanied by an increase in the free energy of the system. The sources that give rise to the amount of free energy are commonly referred to as the driving forces for sintering. The main possible driving forces are

- The curvature of the particle surfaces
- An externally applied pressure
- A chemical reaction

Driving Force for Sintering

Schematically it can be shown as



Driving force of Sintering

- ✓ The macroscopic driving force for sintering is the lowering of excess energy associated with the free surfaces of the fine powders. This may occur in different ways:

  - Reduction of total surface area through increase of the average size of the particles (coarsening of particle size)

  - Replacement of high energy solid-vapour interface by low energy solid-solid interface (formation of grain boundaries)

- ✓ Both the phenomena may occur simultaneously or one may lead the other depending on the local situations.

What Happens During Sintering?

- Atomic diffusion takes place and the welded areas formed during compaction grow until eventually they may be lost completely

- Recrystallisation and grain growth may follow, and the pores tend to become rounded and the total porosity, as a percentage of the whole volume tends to decrease

What Happens During Sintering?

- In the pressing operation the powder particles are brought together and deformed at the points of contact

- At elevated temperature - the sintering temperature - the atoms can move more easily and quickly migrate along the particle surfaces (the technical term is ***Diffusion***)

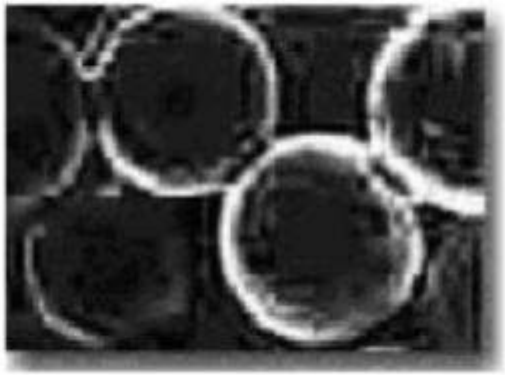
What Happens During Sintering?

Metals consist of crystallites

- At the sintering temperature new crystallites form at the points of contact so that the original inter-particle boundaries disappear, or become recognizable merely as grain boundaries (This process is called Recrystallisation)

What Happens During Sintering?

- The total internal surface area of the pressed body is reduced by sintering



- ***Neck-like*** junctions are formed between adjacent particles as can be seen on the adjoining scanning electron micrograph

Important Outcome of Sintering

- Volumetric Shrinkage
- Densification

(Volumetric Shrinkage and Densification: In most cases)

- Reduction of pore volume and size
- Significant enhancement of mechanical strength
- Grain coarsening (if not controlled)

Stages of Sintering

Three stages are distinguished in sintering

- ***First Stage***

  After burn out of any organic additives, two things happen to the powder particles when the mobility of the surface atoms has become high enough; initially rough surface of the particles is smoothed and neck formation occurs

Stages of Sintering

- ***Second Stage***

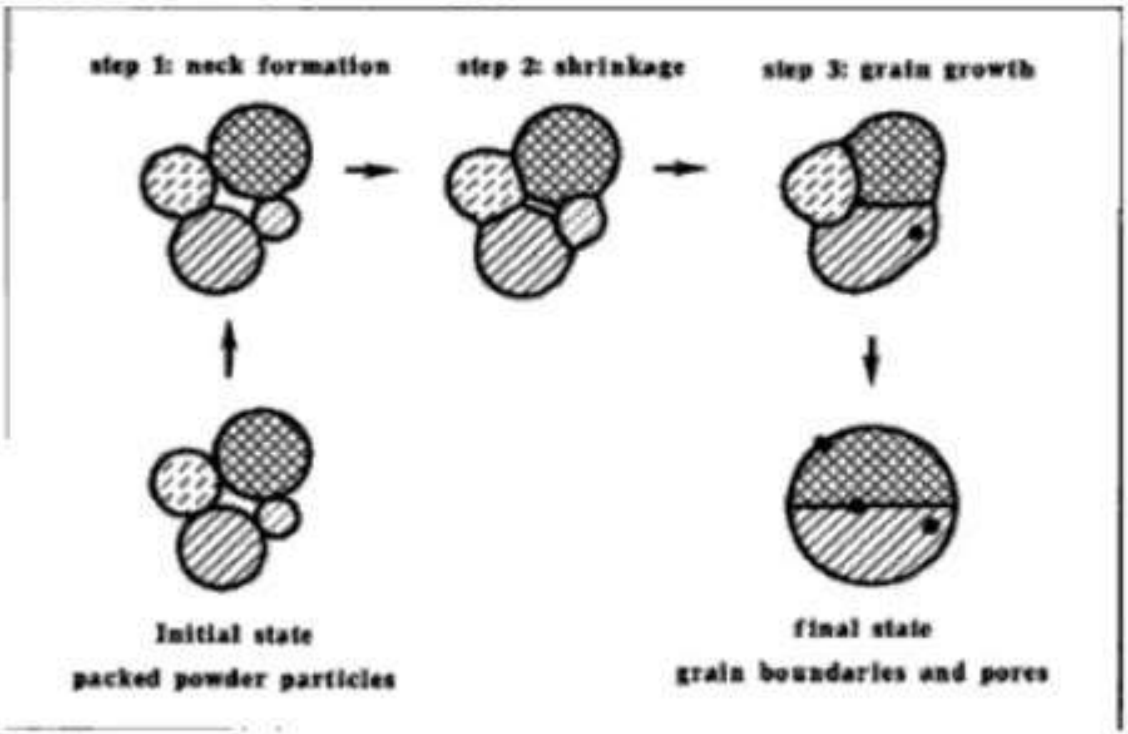
  Densification and pore shrinkage. If grain boundaries are formed after the first stage, these are new source of atoms for filling up the concave areas which diminishes the outer surface of the particle

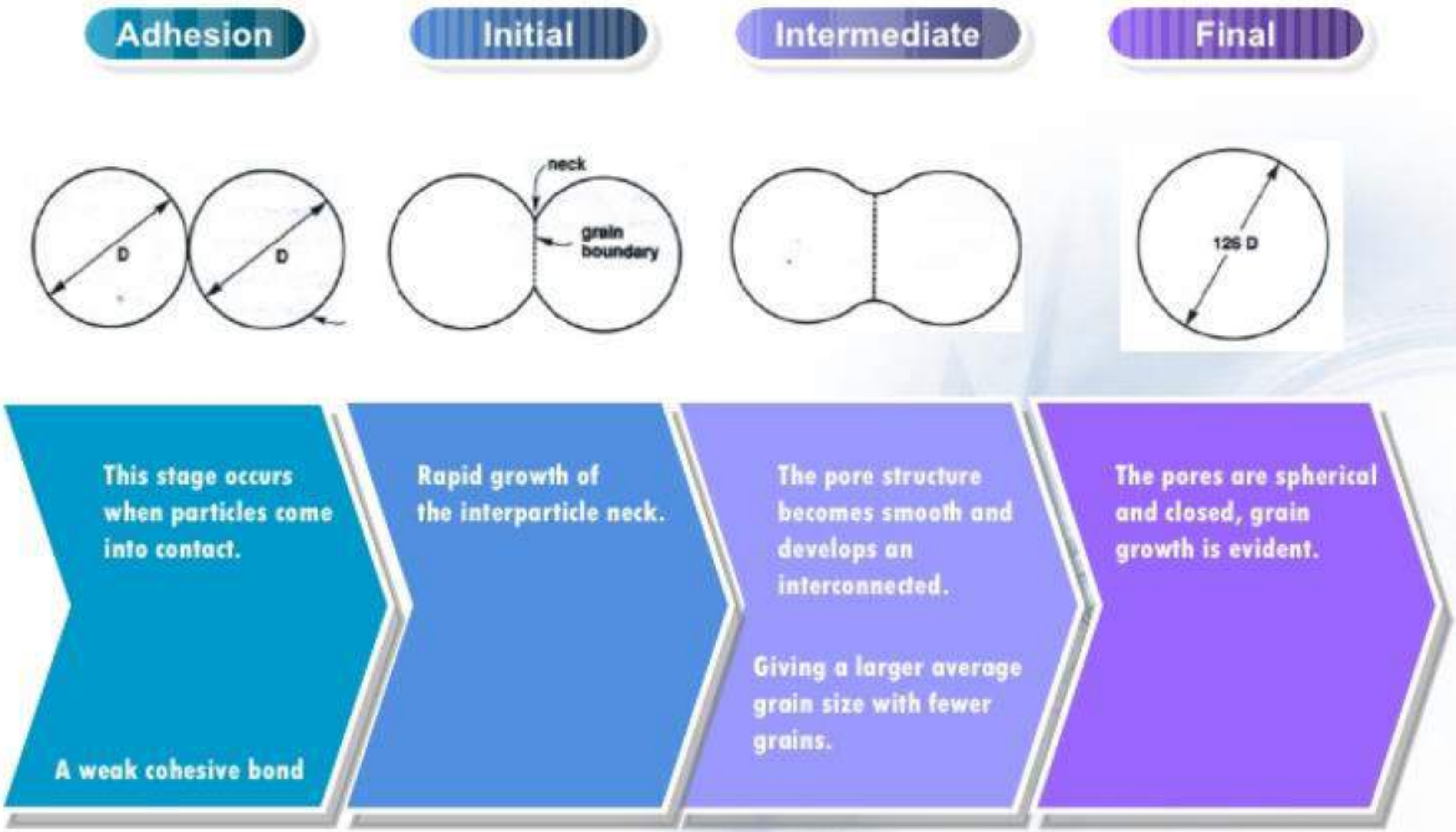
- ***Third Stage***

  Grain growth takes place, the pores break up and form closed spherical bubbles

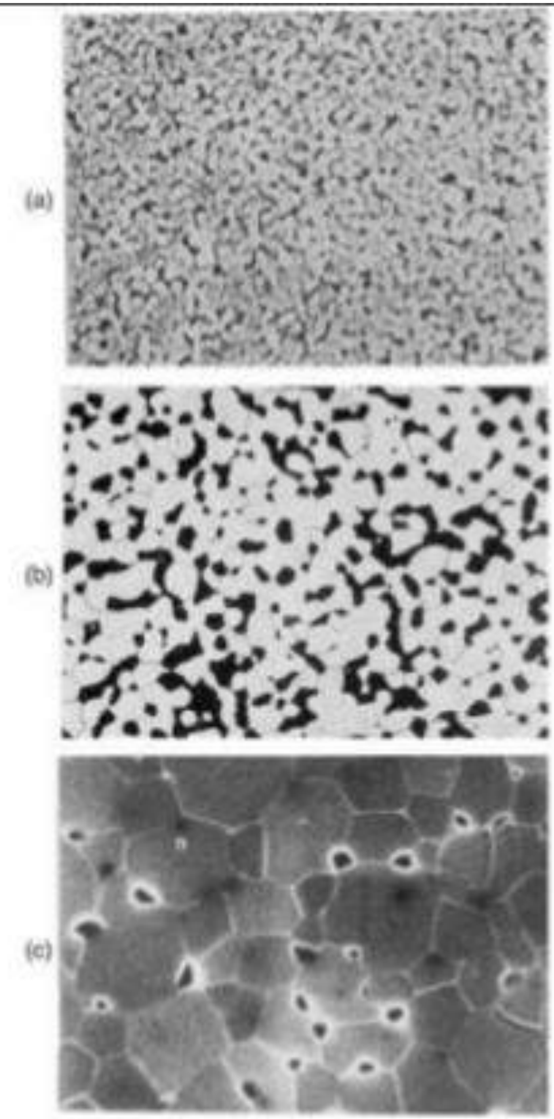
Stages of Sintering

The three stages in the dry sintering can be shown as




Adhesion
Initial
Intermediate
Final
D
D
neck
grain boundary
126 D
This stage occurs when particles come into contact.
A weak cohesive bond
Rapid growth of the interparticle neck.
The pore structure becomes smooth and develops an interconnected.
Giving a larger average grain size with fewer grains.
The pores are spherical and closed, grain growth is evident.

- Initial stage (a)
  rapid interparticle growth (various mechanisms), neck formation, linear shrinkage of 3-5%.
- Intermediate stage (b)
  Continuous pores, porosity is along grain edges, pore cross section reduces, finally pores pinch off. Up to 0.9 of TD.
- Final stage (c)
  Isolated pores at grain corners, pores gradually shrink and disappear. From 0.9 to TD.

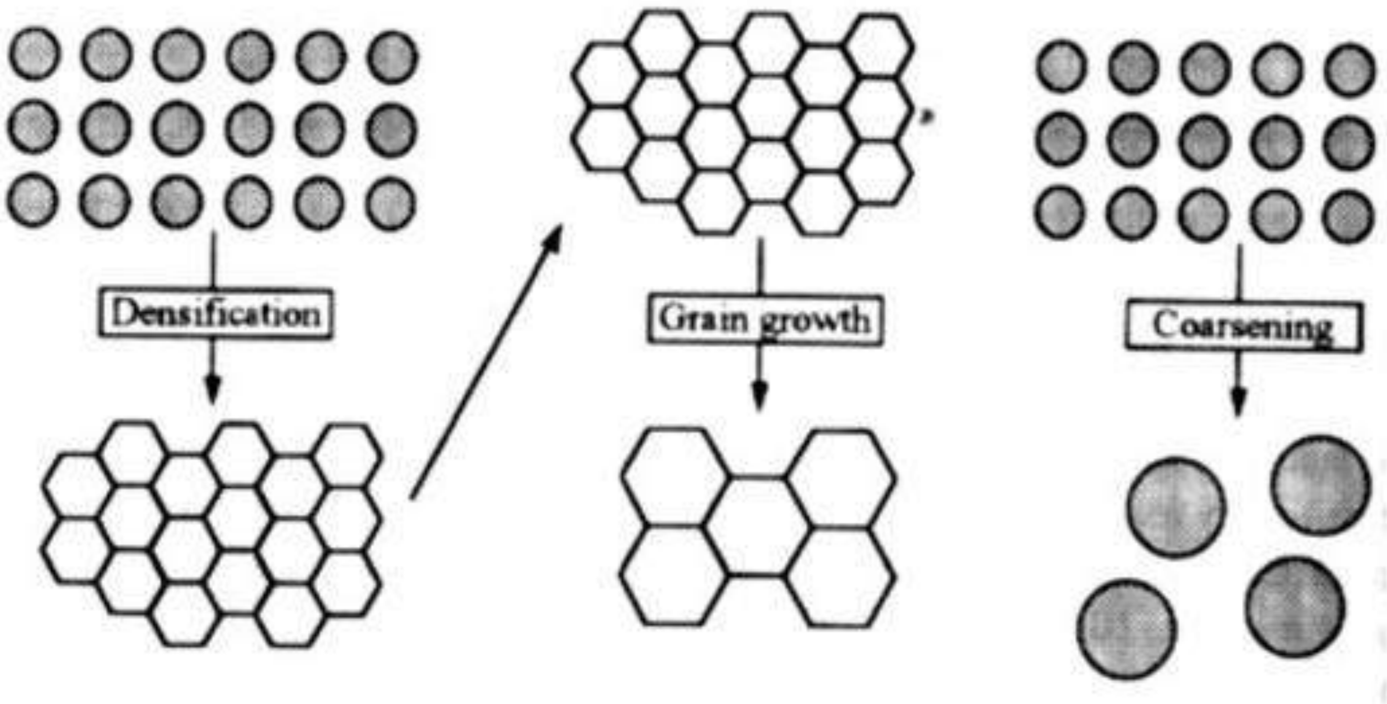


Densification vs. Coarsening I

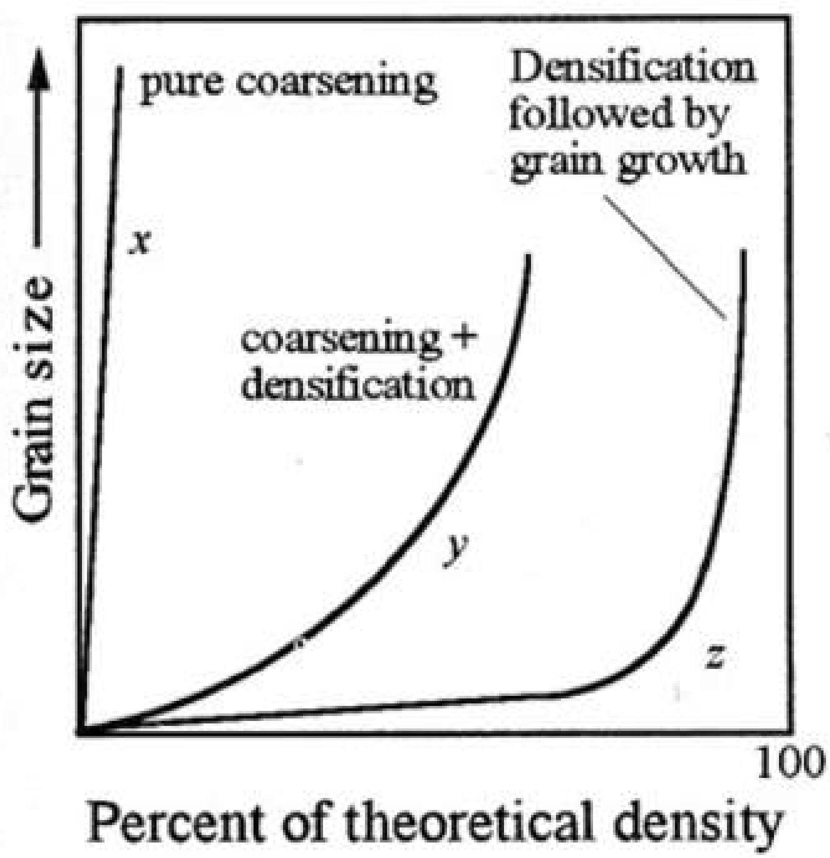
Densification and grain growth occur simultaneously. The resulting textures and density depend on which mechanism is predominant.

a) densification followed by grain growth

b) Coarsening alone



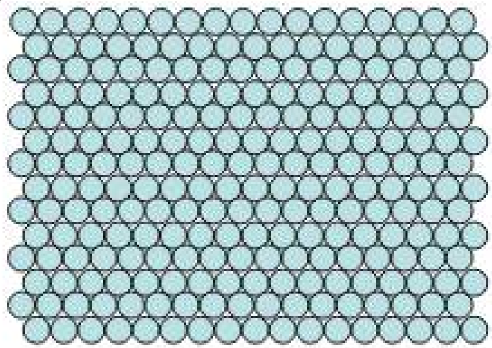
Densification vs. Coarsening II



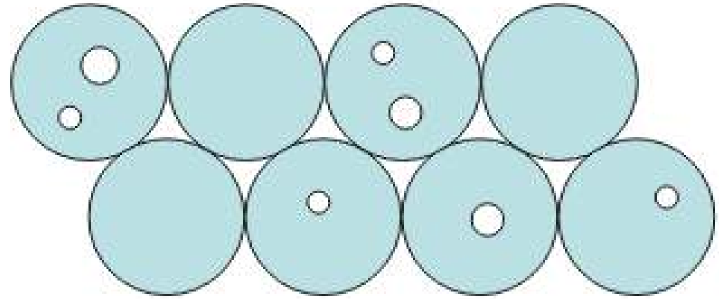
Only densification followed by grain growth will give good final densities.

Porosity of sintered bodies

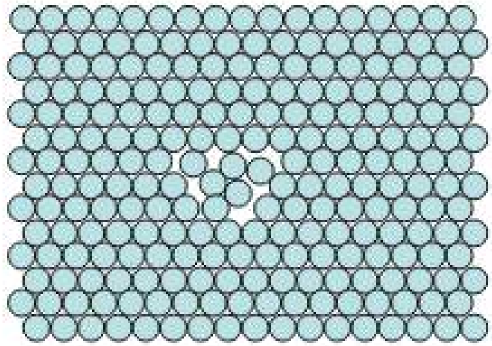
Pores are important and unwanted elements of a ceramic microstructure. The final pore space in an sintered ceramic is mainly a function of the pore volume in the greenbody. Source of pores



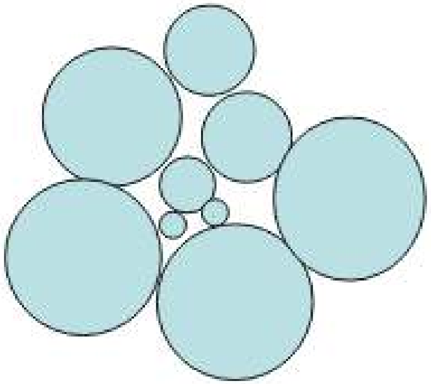
Intergranular pore space. Ordered packing of monodispersed spherical particles minimizes initial pore volume.



Intragranular pore space



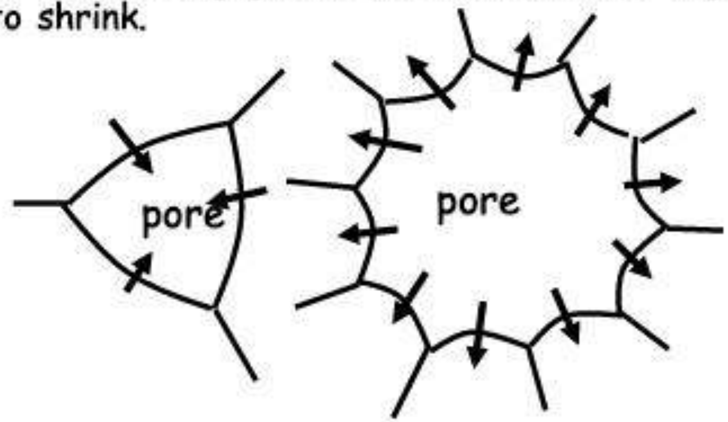
Extra pore space due to hard, disordered agglomerates



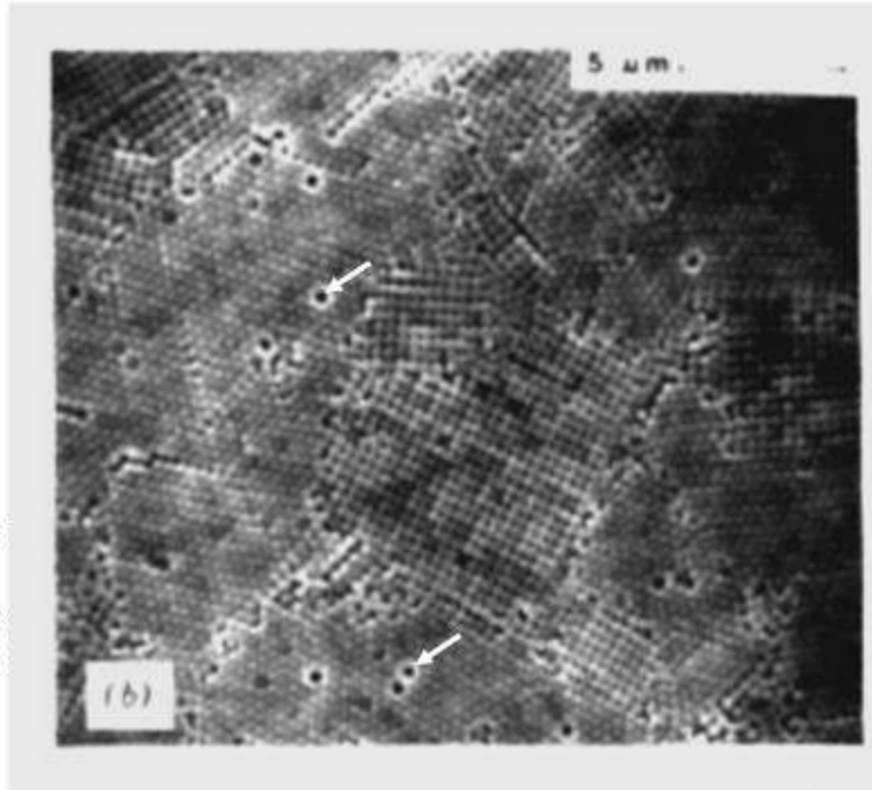
Extra pore space due to polydispersed powders.

Evolution of porosity I

Pores can like grains grow or shrink. The two parameters affecting pore growth is the number of surrounding grains and the dihedral angle. Generally pores with few neighboring grains tend to shrink.



(Small) pores with few neighboring grains have concave surfaces and tend to shrink, whereas (large) pores with many neighboring grains have convex surfaces and tend to grow



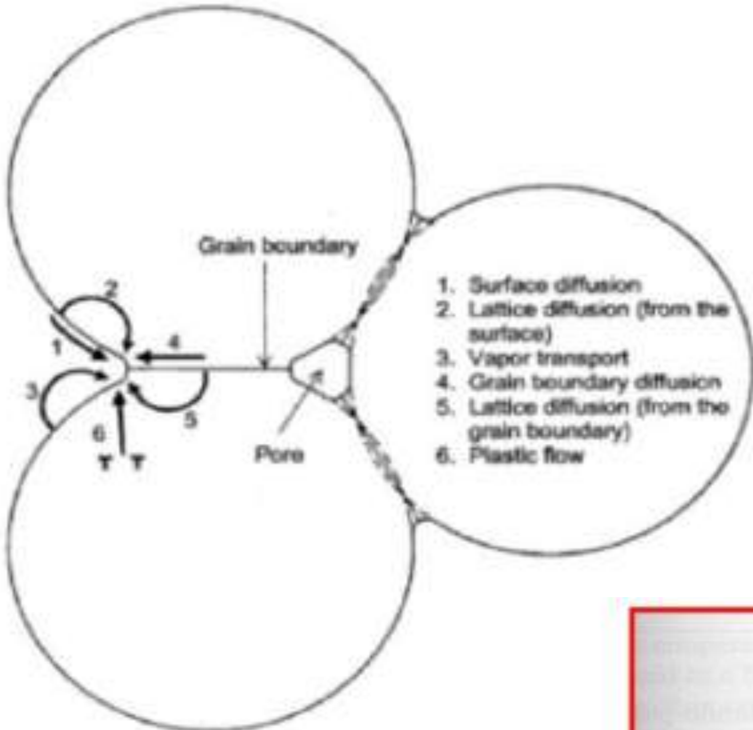
Monodisperse greenbody of boron doped SiO_2. The larger pores may be difficult to evacuate.

Mechanisms of Sintering

Six mechanisms can contribute to the sintering of a consolidated mass of crystalline particles

1. Surface diffusion
2. Lattice diffusion from the surface
3. Vapor transport
4. Grain boundary diffusion
5. Lattice diffusion from the grain boundary
6. Plastic flow

Mechanisms of Sintering



Transport mechanism	Material source	Material sink	Related parameter
Lattice diffusion	Grain boundary	Neck	Lattice diffusivity, D_l
Grain boundary diffusion	Grain boundary	Neck	Grain boundary diffusion, D_b
Viscous flow	Bulk grain	Neck	Viscosity, η
Surface diffusion	Grain Surface	Neck	Surface diffusivity, D_s
Lattice diffusion	Grain Surface	Neck	Lattice diffusivity, D_l
Gas phase transport 1. Evaporation/ condensation 2.Gas diffusion	Gas surface Gas surface	Neck Neck	Vapour pressure difference Δp Gas diffusivity, Dg

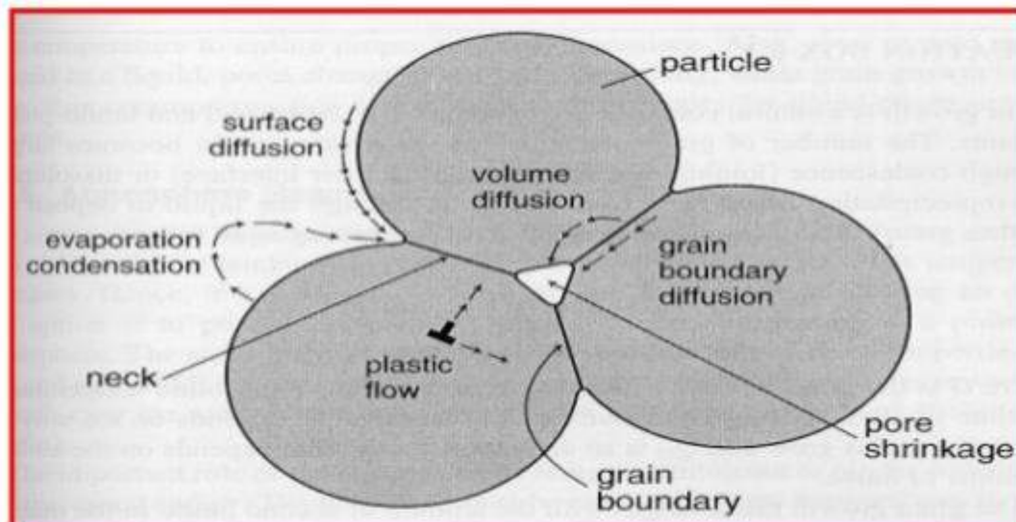
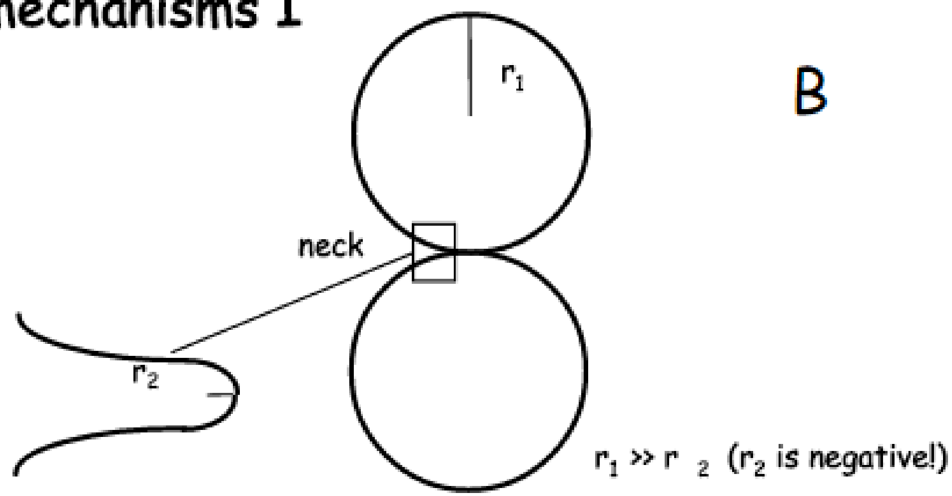
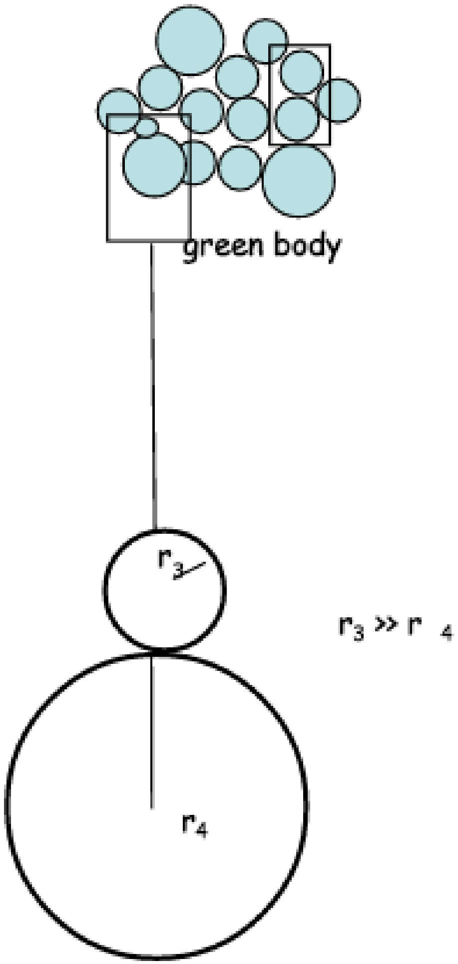


Fig: A three particle sketch of sintering, showing several possible paths of atomic motion involved with particle bonding (neck growth) and pore shrinkage (densification).

Sintering mechanisms I



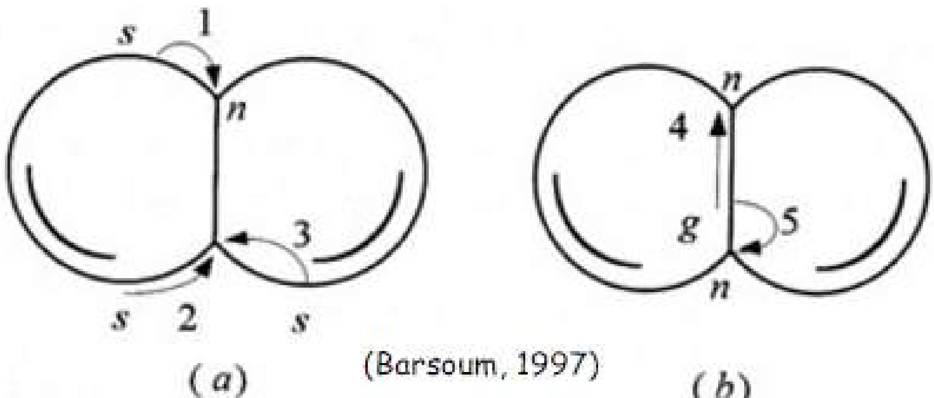


Due to the fine nature of the powders used as raw materials, the green bodies have a high internal surface area and, therefore, a high excess surface free energy. During the heat treatment the internal surface will be reduced and the necessary material movement is driven by the differences in surface curvature

A) between different sized grains, the big grains getting bigger, the small ones disappear = grain growth/shrinkage = overall coarsening of the texture

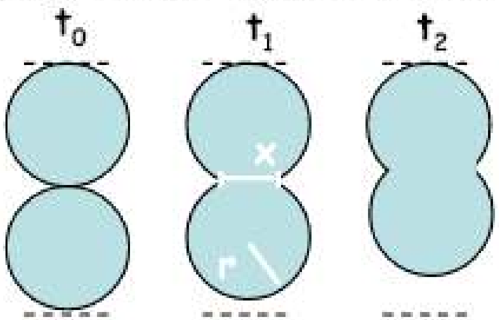
B) between the surface of two grains and the neck region between them = elimination of pore volume = densification

Sintering mechanisms II



(Barsoum, 1997)

Mechanisms that can lead to a) coarsening and change in pore shape and b) densification



Any mechanism in which the source of material is the srface of the particles and the sink is the neck area cannot lead to overall densification, because such a mechanism does not allow the particle centers to move closer together. For densification to occur, the source of the material has to be the grain boundary or region between powder particles, and the sink has to be the pore or the neck region.

Transport paths and mechanisms active during the sintering process:

1) diffusion through the gas phase in the porespace towards the neck area, evaporation - condensation

2) diffusion along the surface solid - gas towards the neck area

3) volume diffusion from the surface to the neck area

4) grain boundary diffusion from the the interface between the necks to the neck

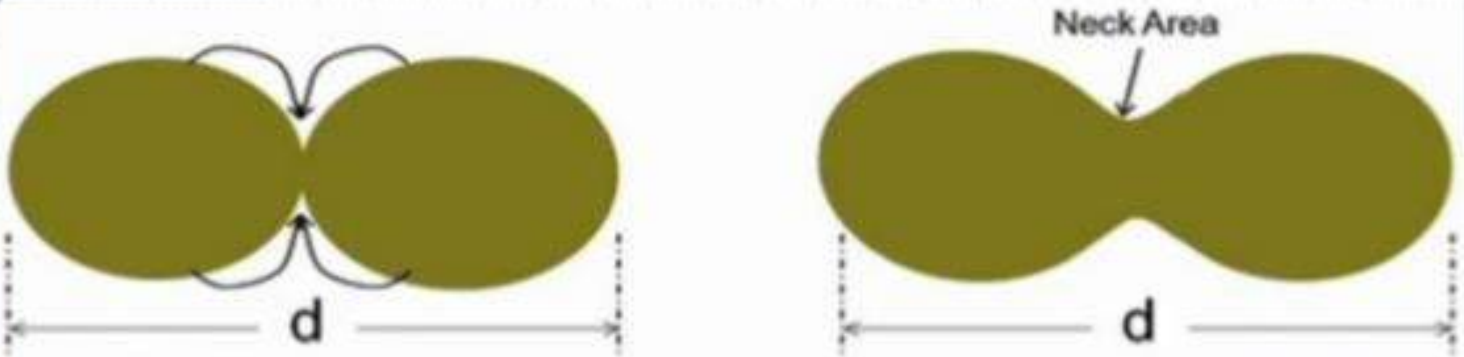
5) Viscous flow of material from area of highstress to areas of low stress

Atomic mechanisms of Mass Transport During Solid State Sintering (Initial Stage)

Three Distinctly Different Mechanisms:

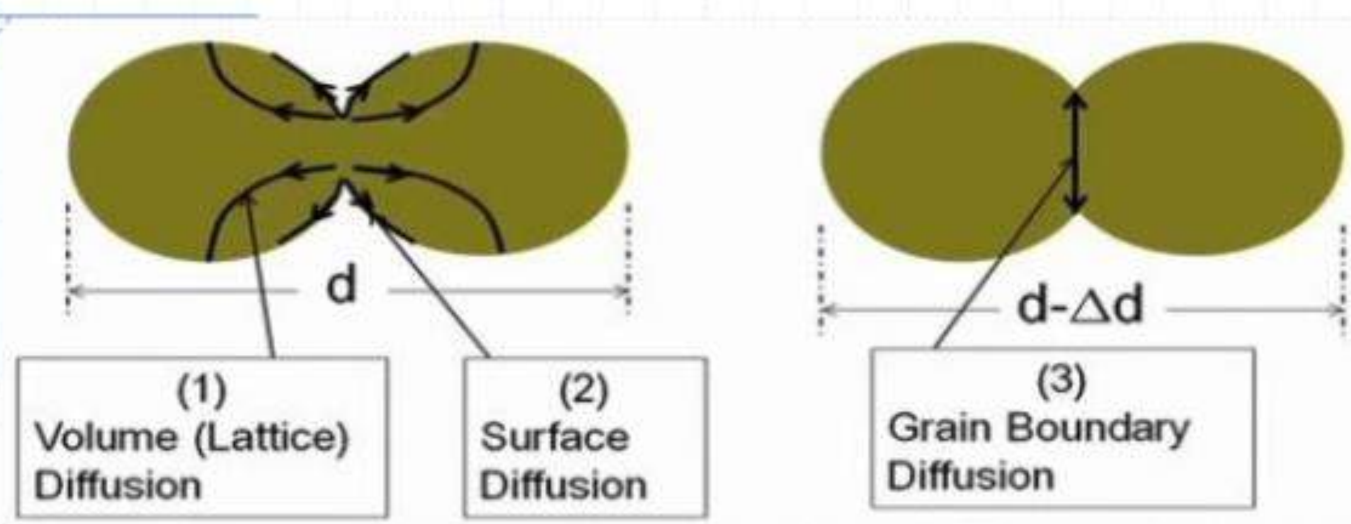
1. Evaporation and Condensation
2. Diffusion by Vacancy mechanism
3. Viscous Flow (Creep)

Evaporation and Condensation Mechanism



- Driving Force: Difference of vapour pressure between the convex and concave surfaces.
- No change in dimension > No shrinkage > No densification
- Increase of bond area > Enhancement of strength

Vacancy Mechanisms of Solid State Sintering



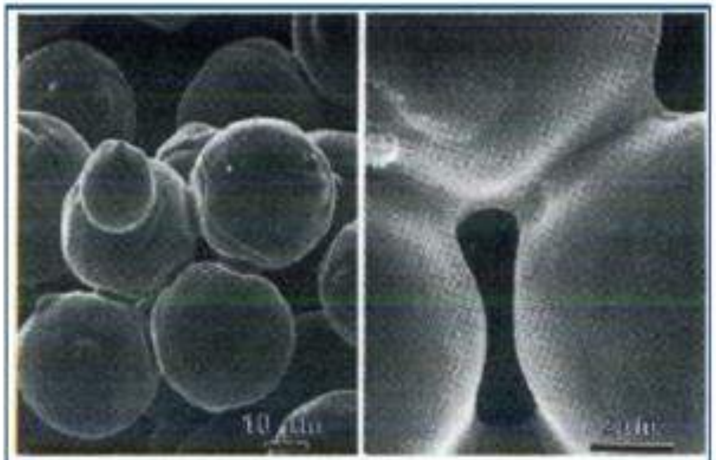
- Direction of the arrow indicates the direction of vacancy migration. Mass transport is in the opposite direction.

Viscous Flow Mechanisms of Sintering

In this mechanism, the particle surfaces gets softened at the temperature of sintering and the mass transport takes place by viscous flow facilitates by the internal stress of the particles aggregate. The pores are filled up by the flow of the viscous mass.

Grain Growth/ Abnormal Grain Growth

- During the final stage of sintering, in addition to pore elimination, grain coarsening takes place.
- Average grain size increases with time
- Larger grain grow at the expense of the smaller ones.
- Abnormal grain growth refers to a process whereby a small number of grains grow much faster than the others such that their size becomes an order of magnitude larger than the average.



ure 3.3. Scanning electron micrographs of neck formation due to sintering. The nickel spheres
-µm diameter) were sintered at 1030°C for 1 h in vacuum. At a high magnification the grain
undary groove is apparent in the neck.

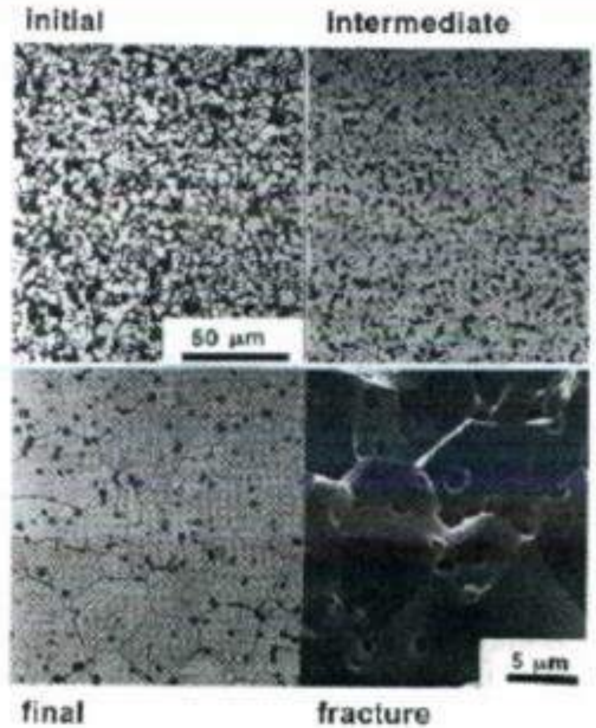
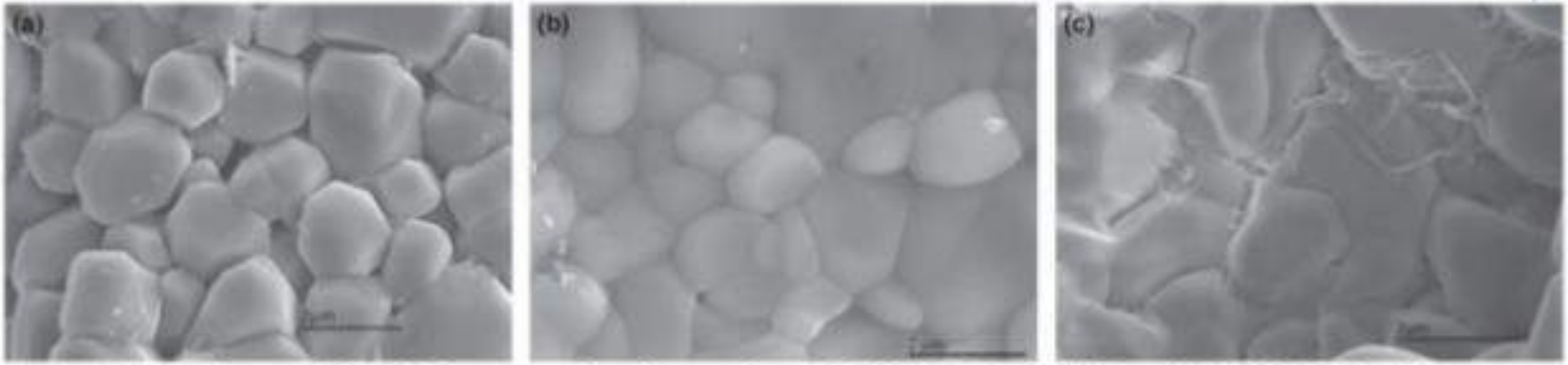
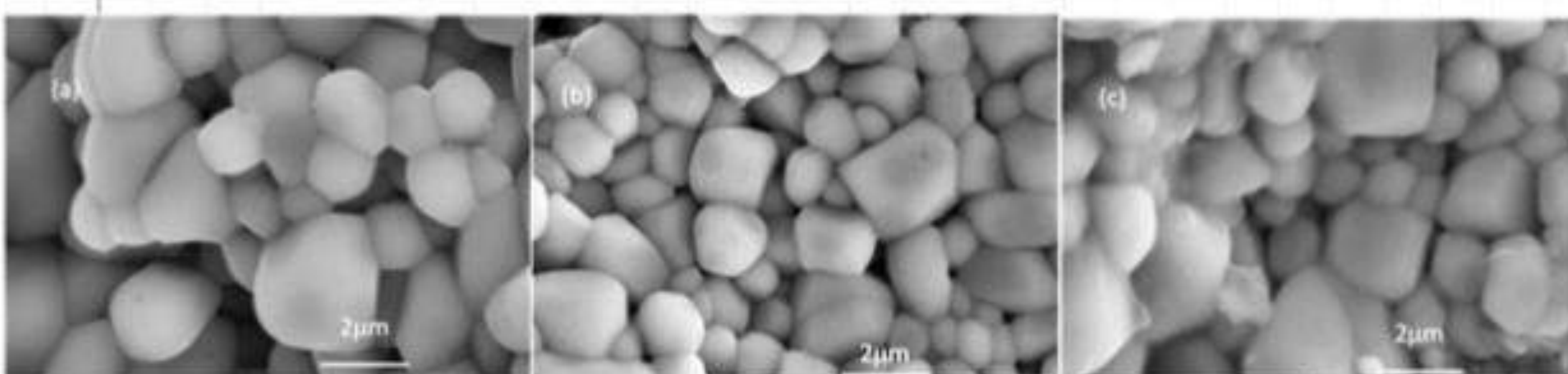


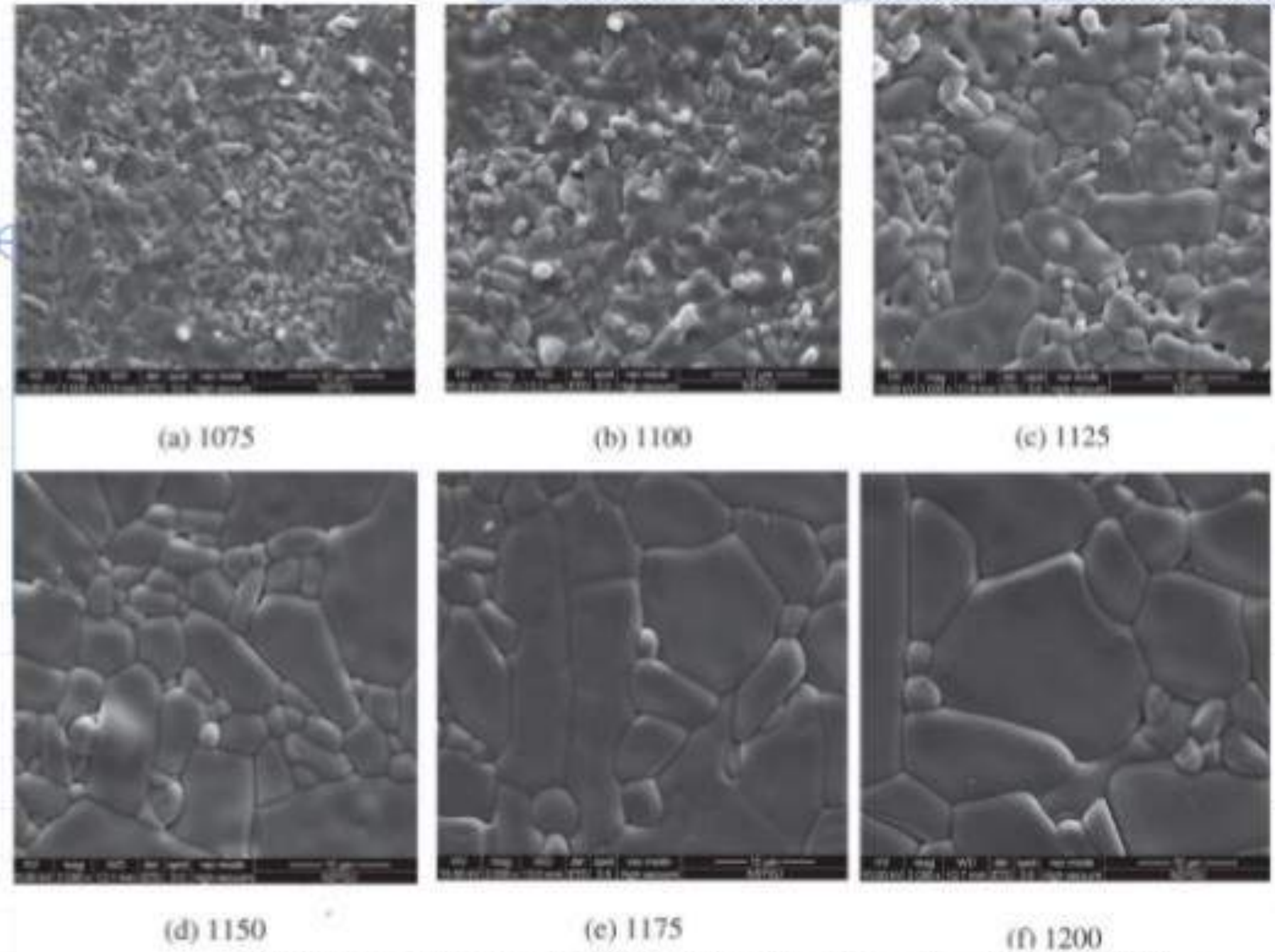
Figure 3.4. Micrographs of tungsten powder during solid-state sintering, showing the (
in porosity (black regions) and microstructure growth. A fracture surface after sinterin
spherical pores on the grain boundaries, a condition that is desirable for continued final-st
sification.



SEM picture of $Ba_3V_4O_{13}$ ceramics sintered at (a) 580 °C, (b) 600 °C and (c) 620 °C for 1 h



SEM picture of BaV_2O_6ceramics sintered at (a) 540°C (b) 550°C and (c) 560°C



SEM photographs of $[(Mg_{0.7}Zn_{0.3})]_{0.95}Co_{0.05}]_{1+\delta}(Ti_{1-x}Sn_x)O_{3+\delta}$ ($\delta = 0.02$) ($x = 0.05$) ceramics (a) 1175, (b) 1200, (c) 1225, (d) 1250, (e) 1275°C sintered at various temperatures for 4 h.

Types of sintering process

1.Conventional Sintering Process

Dense nanostructured ceramic materials are usually obtained by pressing and conventional sintering of nano powders using pressure assisted methods, such as hot pressing, hot isotactic pressing

2. Advanced sintering process

Show great potential in ceramics processing
Overcomes the problem of grain growth

1.Microwave sintering

Microwave energy is a form of electromagnetic energy with the frequency range of 300MHz to 300 GHz. Microwave heating is a process in which the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform into heat.

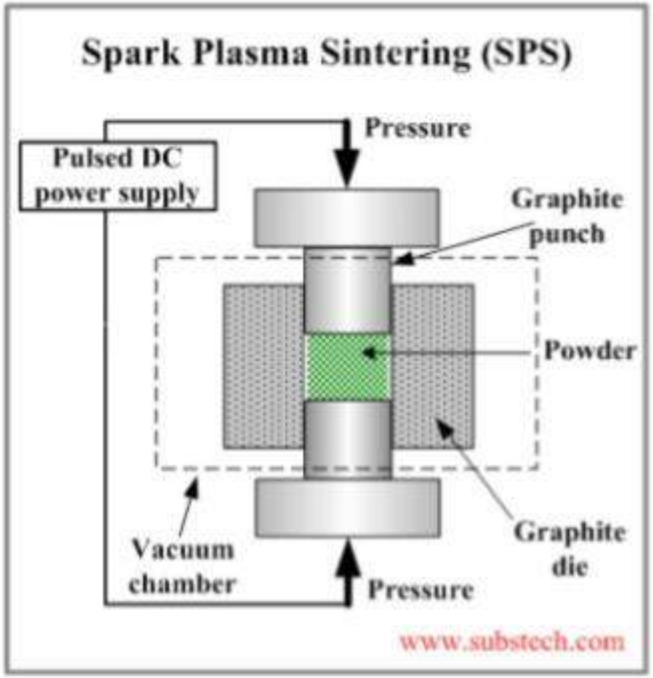
Advantages

a)reduced energy consumption
b)very rapid heating rates
c)decreased sintering temperatures
d)improved physical and mechanical properti

Simple microwave ovens used in microwave sintering

2.Spark plasma sintering

Instead of using an external heating source, a pulsed direct current is allowed to pass through the electrically conducting pressure die and, in appropriate cases, also through the sample. Die also acts as a heating source and that the sample is heated from both outside and inside.



Advantages of Sintering

Allows making complex geometries

High precision

Green technology

Products ready for assembly

Disadvantages

Large material quantity is required.

High initial capital cost relative to some alternative molding processes.

Size limitation based on size of chamber of machine.

High temperature leads to high energy costs.

Summary

- Sintering is the process by which a powder compact is transformed to a strong, dense ceramic body upon heating
- The driving force behind sintering is lowering of free energy.
- Three stages of sintering depends of different parameters.
- Rate controlled sintering basically done in Temperature and heating rate controlling methods.