SINTERING PROCESS

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.

Introduction

- ✓ Sintering is one of the most important steps and a unique process in manufacturing of ceramic products.
- ✓ Ceramic materials have high melting point and brittle so that sintering can be employed for their preparation rather than applying high pressure or other techniques.
- ✓ Fortunately, for the ceramic community, sintering provides an alternative and useful process for the shaping and consolidation of ceramic materials.
- ✓ Ceramic material are preparing from powder raw materials and sintering is the easiest and better method.

✓ Powdered raw materials provide certain advantages:

- They can be suspended in a liquid and the suspension can be used for casting to give them shape.
- Powders can be directly fed into a mould and pressed to a shape under high pressure.
- Making available sufficient activation energy, powders tend to loose the excess energy associated with their free surface. This advantage is made use of in sintering.

Driving force of Sintering

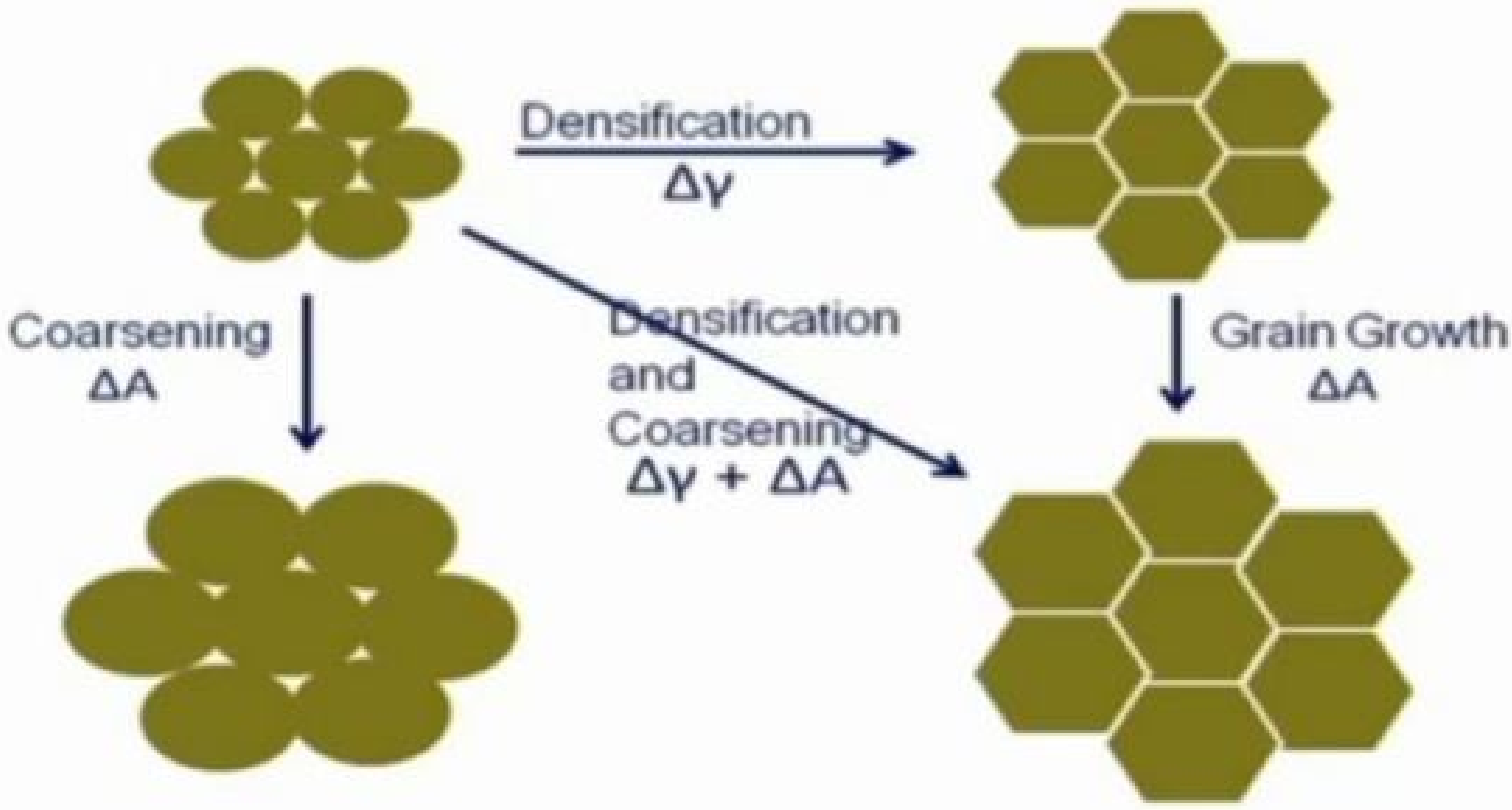
- ✓ The macroscopic driving force for sintering is the lowering of excess energy associated with the free surfaces of the fine powders. This may occur in different ways:

- 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)

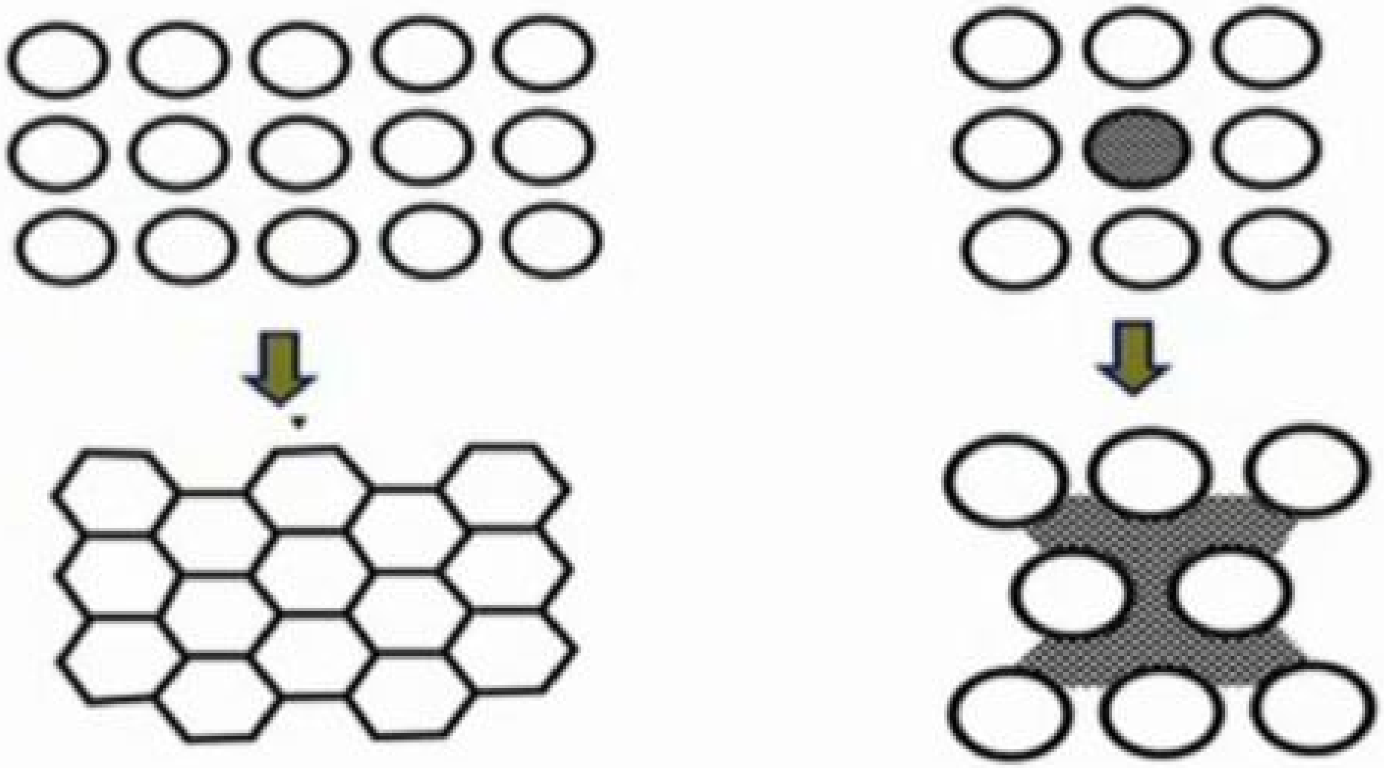
- ✓ Both the phenomena may occur simultaneously or one may lead the other depending on the local situations.

Schematics of particles coarsening and grain boundary formation (Densification)



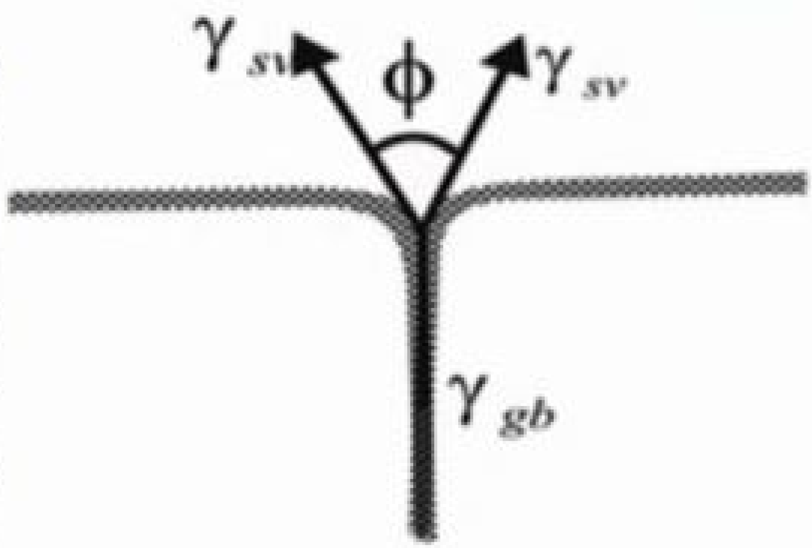
Schematic of the two Sintering Processes

Solid State Sintering | **Liquid Phase Sintering**



Surface Energy and Dihedral Angle
(Solid – Vapour Interface)

A necessary condition for sintering process is that the grain boundary energy (γ_{gb}) or in other words solid/solid surface energy should be less than twice the solid/vapour surface energy (γ_{sv}). This implies that the equilibrium dihedral angle (Φ) is required to be less than 180^o for sintering to take place.



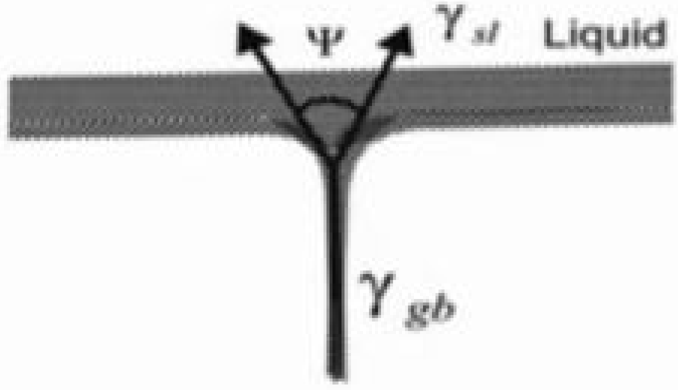
Equilibrium condition

$$\gamma_{gb} = 2\gamma_{sv}\cos\frac{\emptyset}{2}$$

Surface Energy and Dihedral Angle

(Solid – Liquid Interface)

Similar to the previous situation, sintering of the solid particles can take place in presence of a liquid if the corresponding dihedral angle (Ψ) is less than 180^o as per the adjoining figure.



Equilibrium condition

$$\gamma_{gb} = 2\gamma_{sl}\cos\frac{\varphi}{2}$$

Other Variations of the Process

1. High Pressure Sintering

2. Reactive Sintering

3. Microwave Sintering

4. Spark plasma Sintering

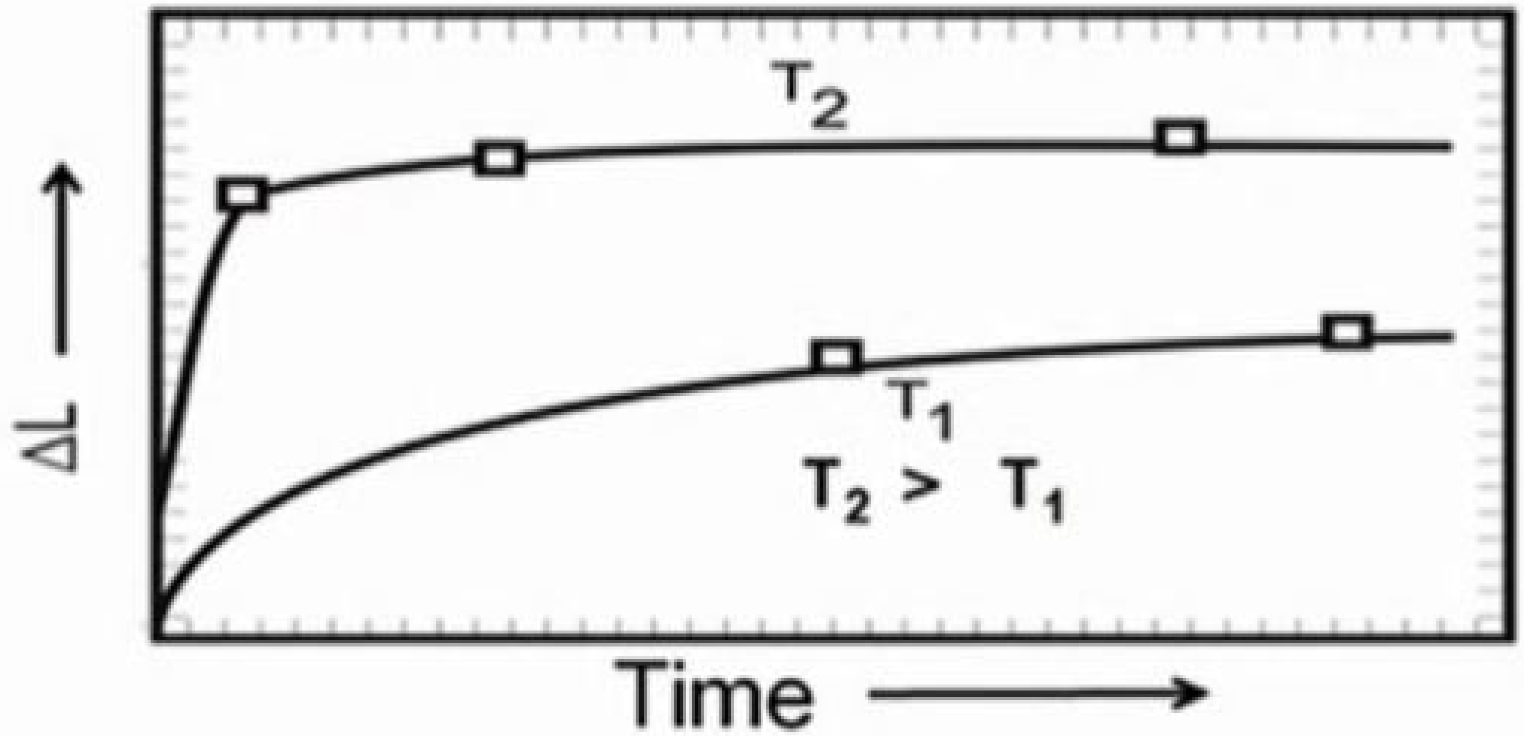
Important Outcome of Sintering

- Volumetric Shrinkage
- Densification

} In most cases

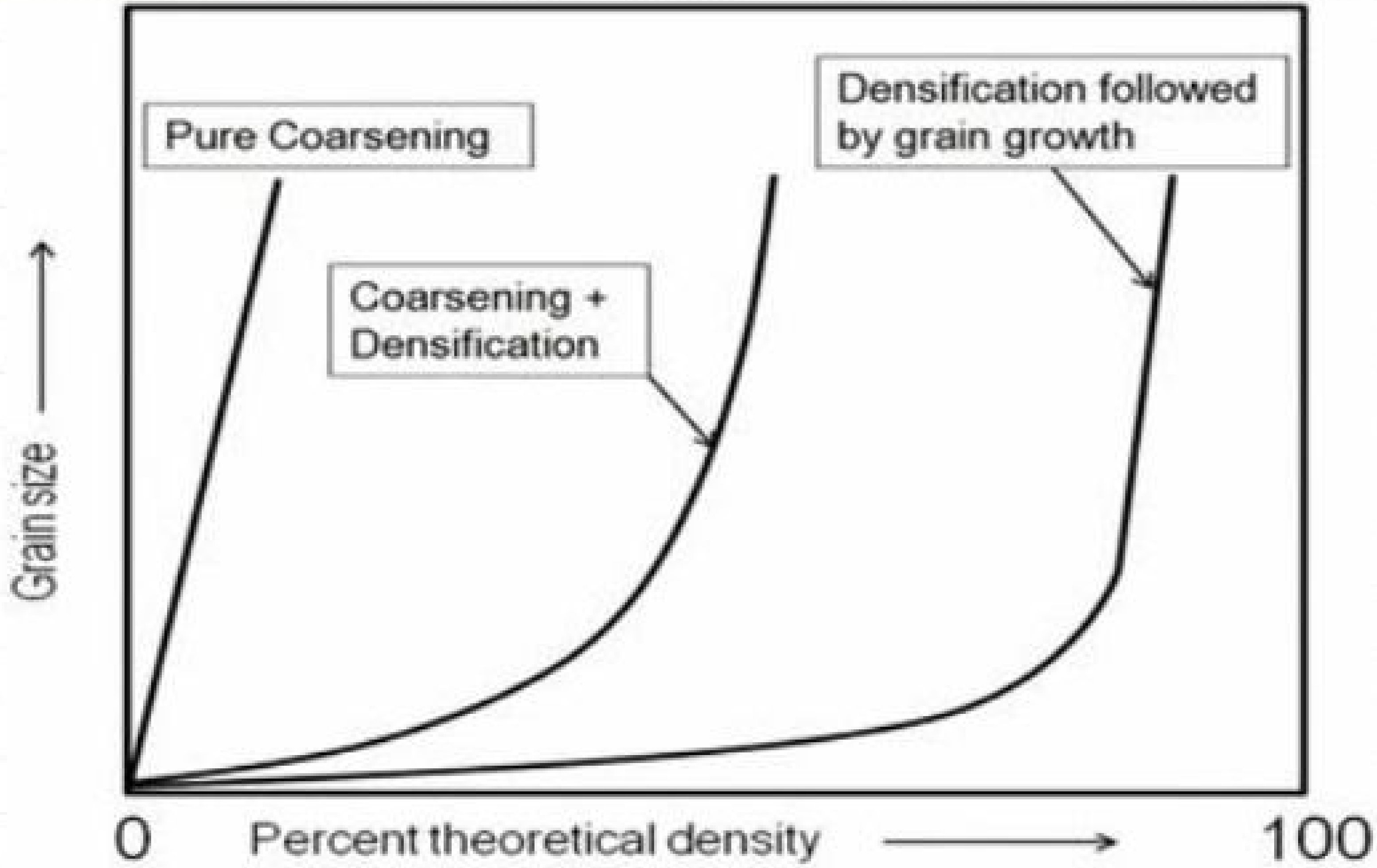
- Reduction of pore volume and size
- Significant enhancement of mechanical strength
- Grain coarsening (if not controlled)

Typical Shrinkage Behaviour



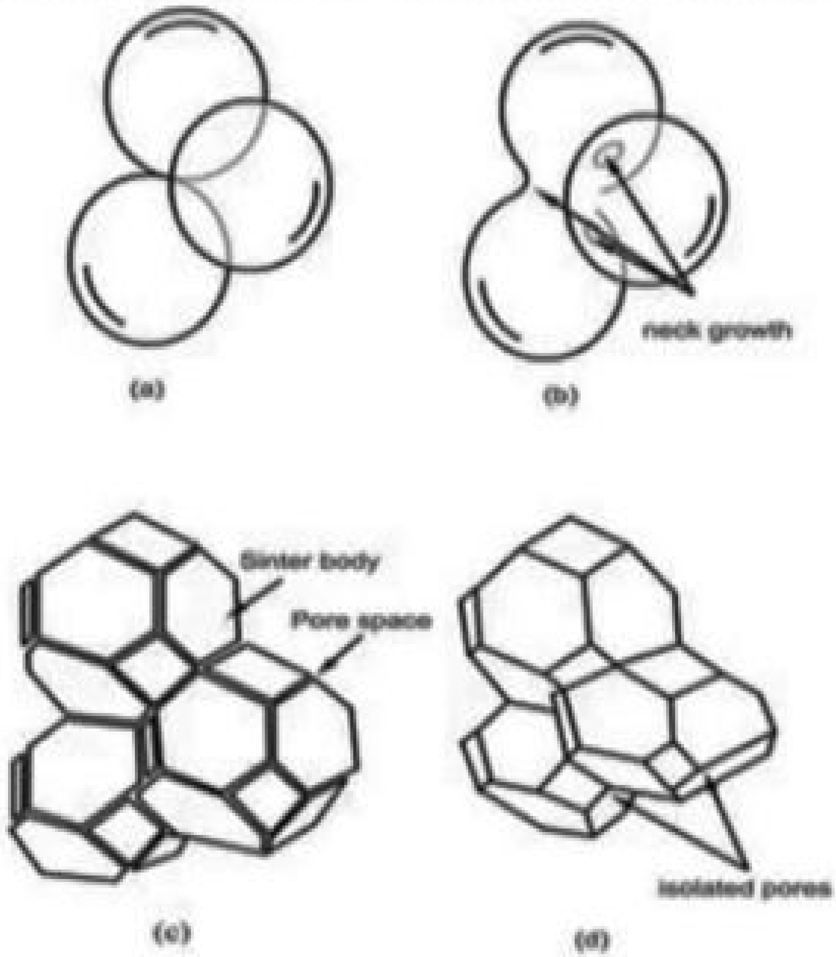
Axial shrinkage as a function of time and temperature

Schematic grain size V/S density variation under different conditions



Pictorial Representation of Different Stages of Sintering

a) Initial stage
b) End of the Initial stage
c) Intermediate stage: Both pores and the solid phases are continuous.
d) Final Stage: Pores are at the corners of the polyhetra.



Stages of Sintering

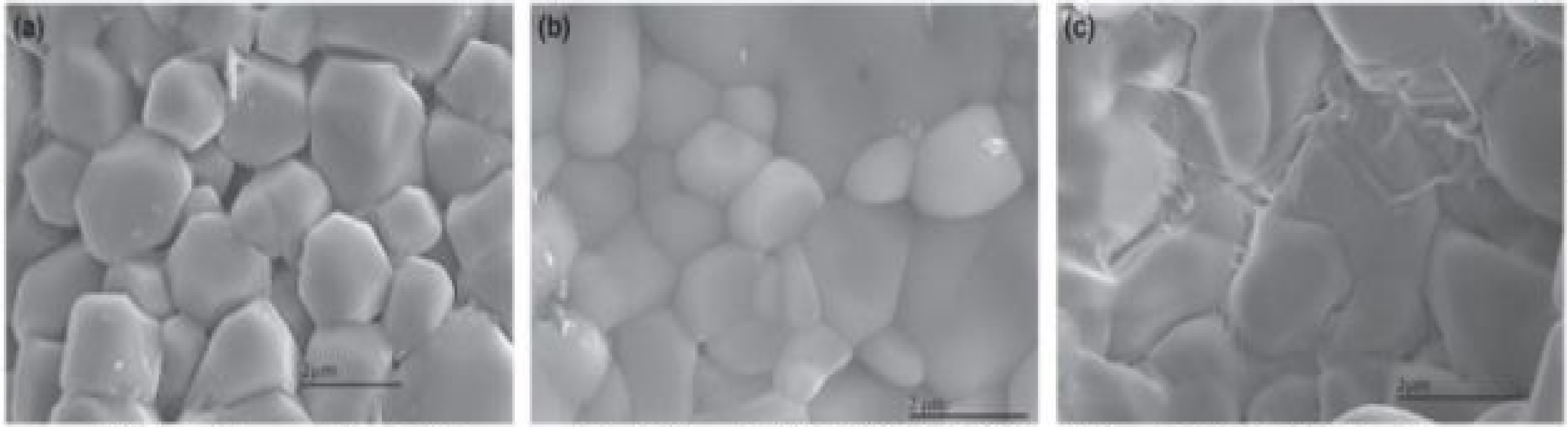
The complete process of sintering can be divided into three distinct stages depending on the geometrical changes (particularly in terms of pore shapes and size) that the sample undergoes during sintering process

1. Initial stage: contact area increases by neck-growth from 0 to ≈ 0.2 and the relative density is up to a maximum of 65%

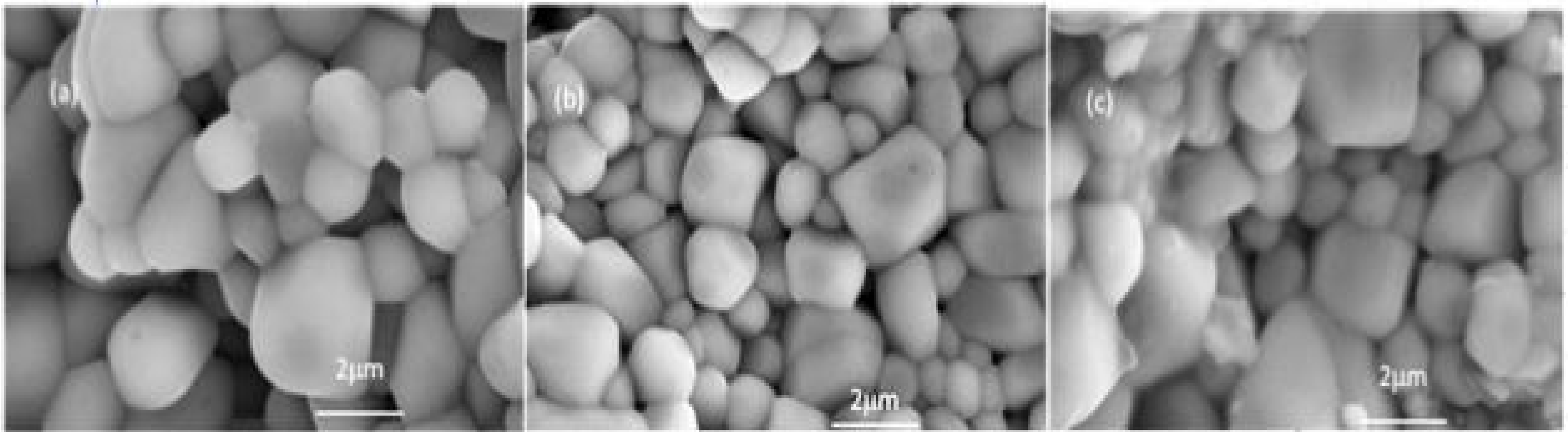
2. Intermediate stage: This is the longest stage of sintering, during which the relative density increases from around 65% to around 90%. Pores remain continuous.

3. The final stage of sintering: It begins when the continuous pore gets separated into a large number of isolated pores, which may be lenticular in shape if they are along the grain boundaries or nearly spherical if they are away from the grain boundary (within the grains).

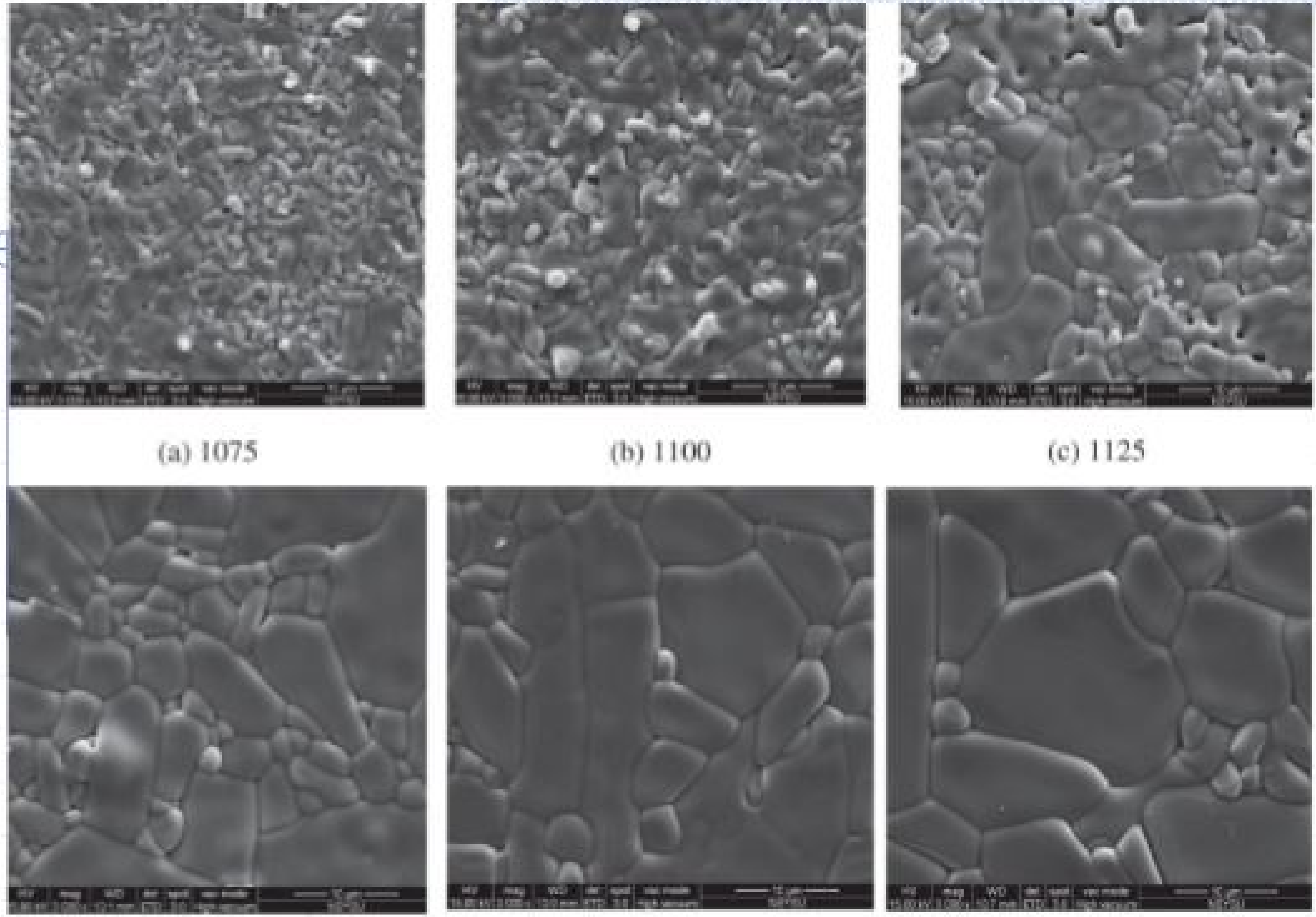
Sintering kinetics are different during the different stages of sintering. Different atomic mechanisms of mass transport may be operative at different stages of sintering.



SEM picture of $Ba_3V_4O_{13}$ ceramics sintered at (a) 580 ^{0}C, (b) 600 ^{0}C and (c) 620 ^{0}C for 1 h



SEM picture of BaV_2O_6ceramics sintered at (a) 540^{0}C (b) 550^{0}C and (c) 560^{0}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.

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

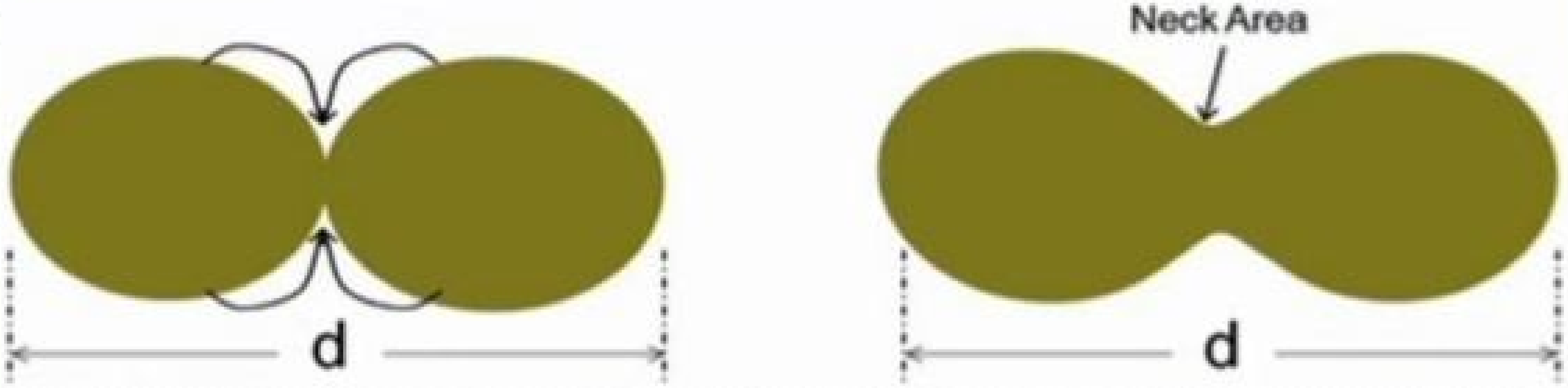
Three Distinctly Different Mechanisms:

1. Evaporation and Condensation

2. Diffusion by Vacancy mechanism

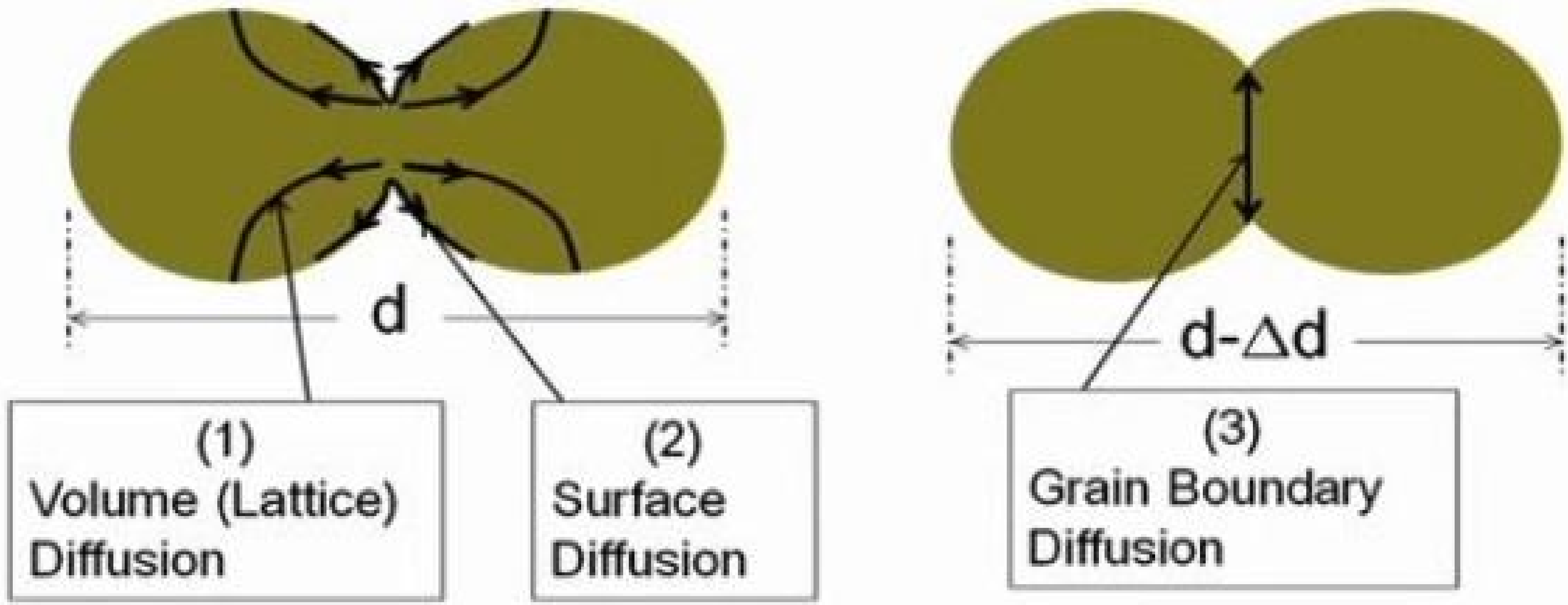
3. Viscous Flow (Creep)

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.

The linear shrinkage is expressed as:

$$\frac{\Delta L}{L} = \frac{3\gamma_{sv}}{4\eta}t$$

Where η is the viscous of the softened 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.

Consolidated List of factors influencing the Solid State Sintering

- Temperature
- Vapour Pressure/ Diffusion Coefficient etc.
- Initial particle size
- Particle size distribution
- Presence of agglomerates(needs to be avoided)
- Green density
- Uniformity of initial microstructure
- Atmosphere
- Impurities(nature and concentration)
- Sintering aids

Liquid Phase Sintering

- Sintering in presence of liquid phase
- Composition of the starting material is such that it generates a small amount of liquid phase on heating.
- This liquid should be able to dissolve a small amount of the solid phase and thereby wet the surface, there will be liquid-solid as well as liquid-vapour surfaces.
- Wet ability of the liquid has a very important role to play.
- Capillary forces of liquid also play a very important role.

Liquid Phase Sintering

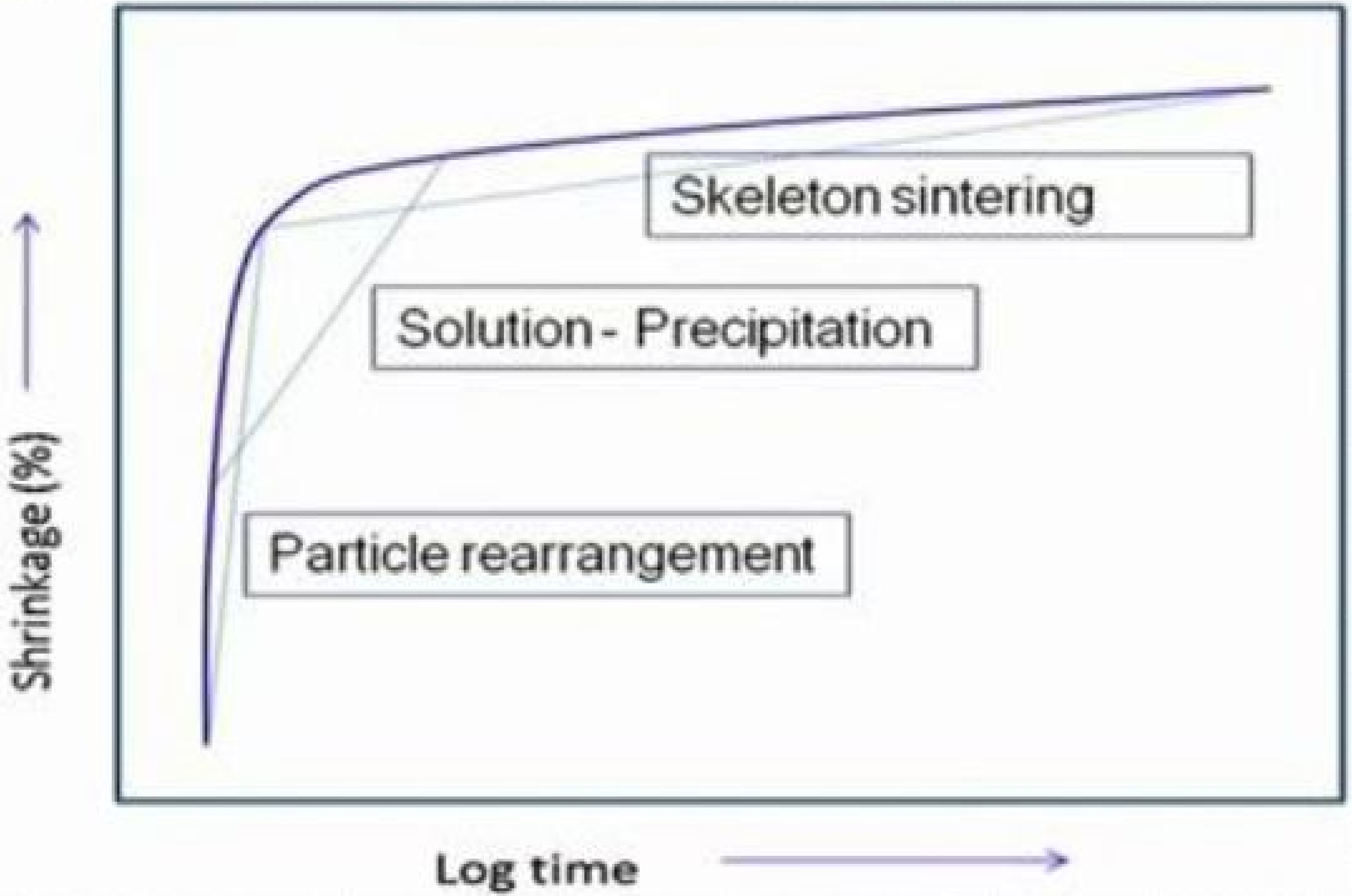
- **Mechanism:**

✓ Particles rearrangement

✓ Solution precipitation

✓ Solid state sintering(Skeleton Sintering)

Liquid Phase Sintering



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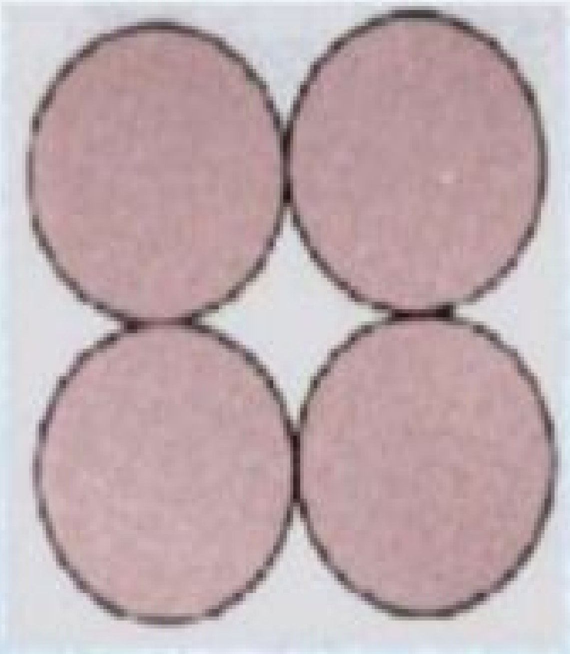
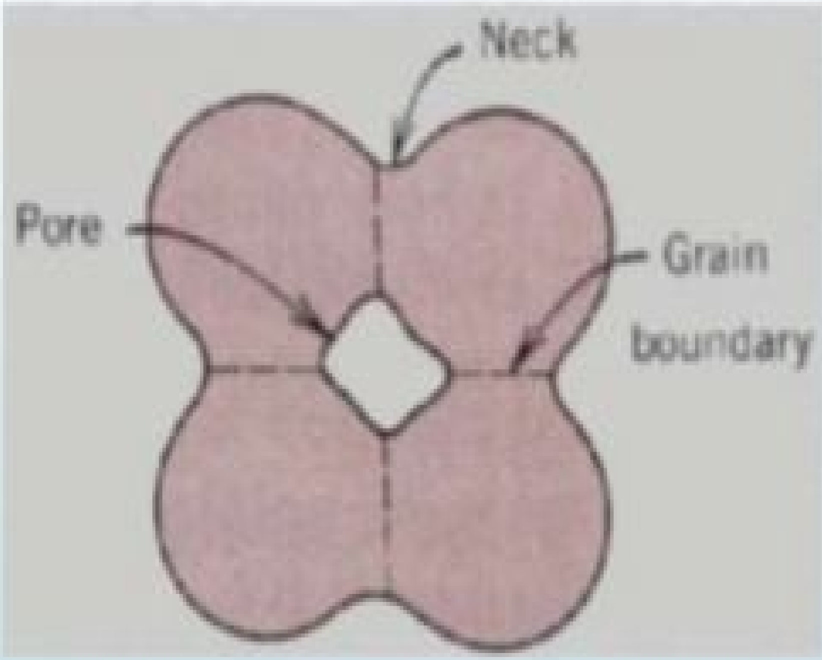
Sintering process

Before sintering



After sintering



What Happens During Sintering?

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

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

Why Do We Need Sintering

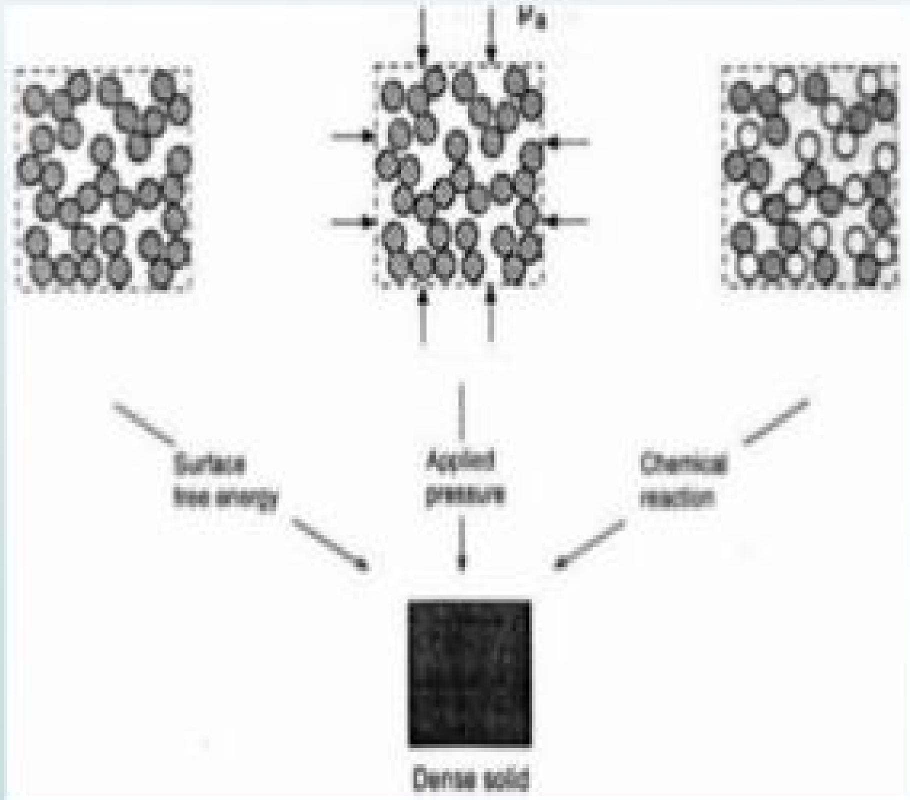
The principal goal of sintering is the reduction of compact porosity. Sometimes the initial spaces between compacted grains of ceramics are called "voids", to differentiate them from the isolated spaces = pores, which occur in the final stages of sintering. The sintering process is usually accompanied by other changes within the material, some desirable and some undesirable. The largest changes occur in

- strength, elastic modulus
- hardness, fracture toughness
- electrical and thermal conductivity
- permeability to gases and liquids
- average grain number, size and shape
- distribution of grain size and shape
- average pore size and shape
- distribution of pore size and shape
- chemical composition and crystal structure

Driving Force For 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



Why Ceramics have to be sintered?

Ceramic processing is based on the sintering of powder compacts rather than melting/solidification/cold working (characteristic for metals), because: ceramics melt at high temperatures, solidified microstructures can not be modified through additional plastic deformation and re-crystallization due to brittleness of ceramics, thus resulting coarse grains which act as fracture initiation sites.

Types of Sintering

1. Solid state sintering
2. Liquid phase sintering
3. Reactive sintering

Solid State Sintering

The majority of non-silicate ceramics are processed through high-temperature treatment and sintering of powder compacts with little (<2 vol%) or no liquid phases. This is defined as Solid State Sintering, with predominant mass transport (i.e. densification mechanism) through solid-state diffusion.

Liquid Phase

Liquid phase sintering is commonly used for materials which are difficult to sinter. Liquid phase sintering is the process of adding an additive to the powder which will melt before the matrix phase. The process has three stages:

Rearrangement – As the liquid melts capillary action will pull the liquid into pores and also cause grains to rearrange into a more favorable packing arrangement.

Solution-Precipitation – In areas where capillary pressures are high, atoms will preferentially go into solution and then precipitate in areas of lower chemical potential where particles are not close or in contact. This is called "contact flattening". This densifies the system in a way similar to grain boundary diffusion in solid state sintering.

Final Densification – densification of solid skeletal network, liquid movement from efficiently packed regions into pores.

Reactive Sintering

Particles react with each other to form new product phases

Parameters Of Sintering

- **Powder preparation:**
  - -- Particle size
  - -- Shape
  - -- Size distribution
- **Distribution of:**
  - -- Dopants
  - -- Second phases
- **Powder Consolidation:**
  - -- Density
  - -- Pore size distribution

Stages Of Sintering

- Initial neck growth
- Intermediate stage sintering
- Final stage sintering

Initial Neck Growth

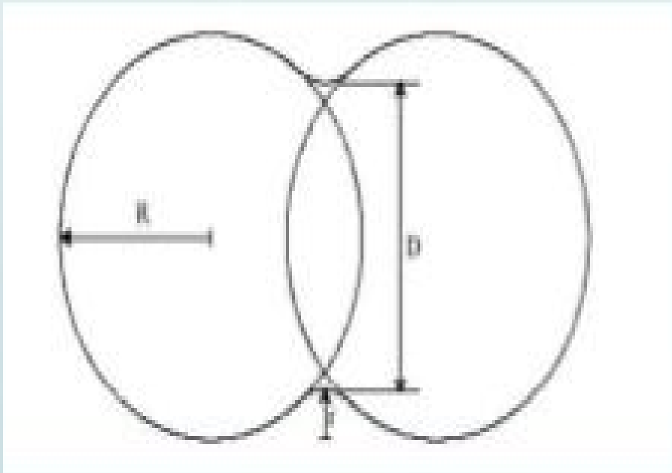
Sintering initially causes the particles that are in contact to form grain boundaries at the point of contact through diffusion. This is the point contact stage and does not result in any dimensional changes. The greater the initial density of compaction (increased particle contact and potential grain boundary area), the higher the degree of coherency in the material

In this initial stage of sintering, necks begin to form at the contact points between adjacent particles see Figure 3-5. This stage is therefore referred to as the "neck growth" stage .No change in the dimensions is observed nor does porosity decrease .

Initial Neck Growth

Neck formation is driven by the energy gradient resulting from the different curvatures of the particles and the neck, Surface diffusion is usually the dominant mass-transport mechanism during the early stages of neck growth, as the compact is heated to the sintering temperature

Figure 3-5 neck formation



Intermediate Stage Sintering

The intermediate stage is pore channel closure where interconnected pore charnels are closed off isolating porosity. One of the causes of pore channel closure is neck growth. Another cause is the creation of new contact points by pore shrinkage within the pore itself . Very low green packing densities (around 40%), which are also associated with low coordination numbers, can lead to coarsening (increase in mean grain size) without densification (decrease in porosity). In extreme cases, this may lead to open-pore structures lacking in structural integrity, See Figure 3-6 . At the beginning of the intermediate stage, the pores form a network of interconnected cylindrical pores broken up by necks. By the end, the pores are smoother and begin to pinch off and become isolated from each other.

Bulk transport mechanisms, such as grain boundary diffusion and volume diffusion, dominate the sintering process during this stage. As stated previously, these bulk transport mechanisms cause material to migrate from inside the particles to the surface, resulting in contact flattening and densification .

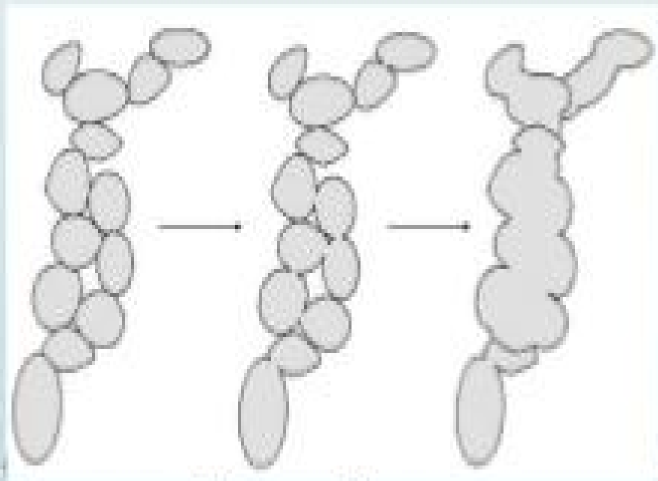


Figure (3- ... tion number

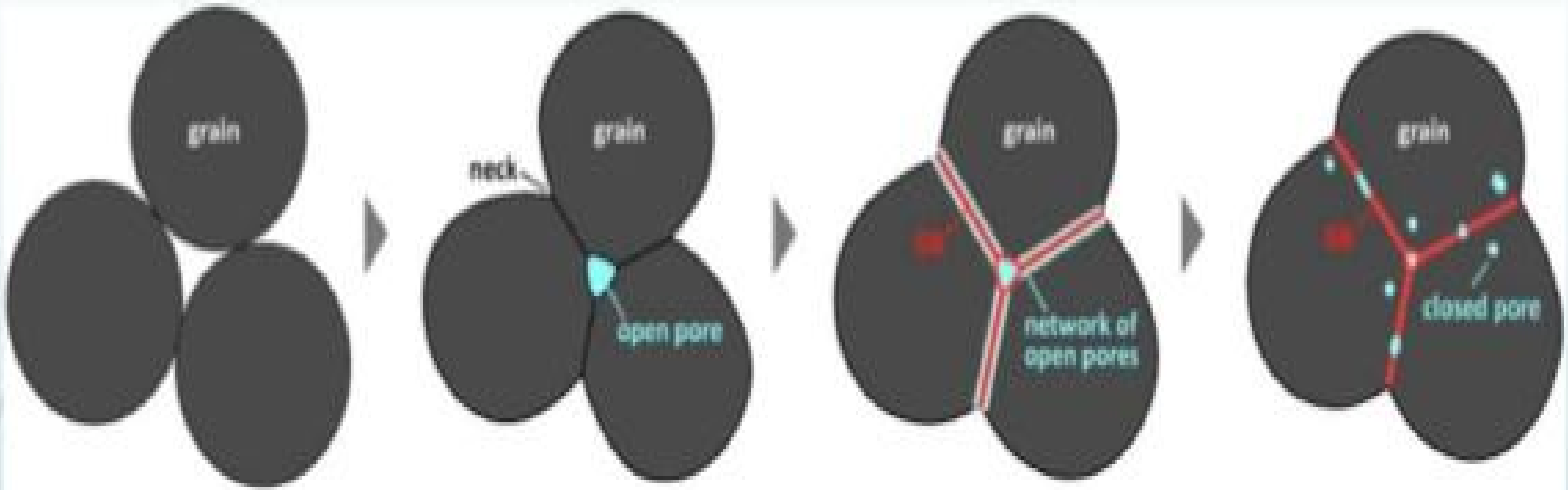
Final Stage Sintering

Final stage sintering begins when most of the pores are closed. As sintering proceeds, the pores, which during intermediate stage sintering form a network, have become isolated from each other.

Final stage sintering is much slower than the initial and intermediate stages. As grain size increases, the pores tend to break away from the grain boundaries and become spherical . Pore shrinkage is the most important stage in sintering. For this stage to occur; solids must be transported into the pores and a means must exist by which the gas in the pores can escape to the surface. The resultant effect is to decrease the volume of the sintering mass .

Smaller pores are eliminated, while larger pores can grow, a phenomenon called Ostwald ripening. In some cases, pore growth during final stage sintering can lead to a decrease in density, as gas pressure in the larger pores tends to inhibit further densification .

Final Stage Sintering



Stage I: before sintering

Stage II: formation of necks

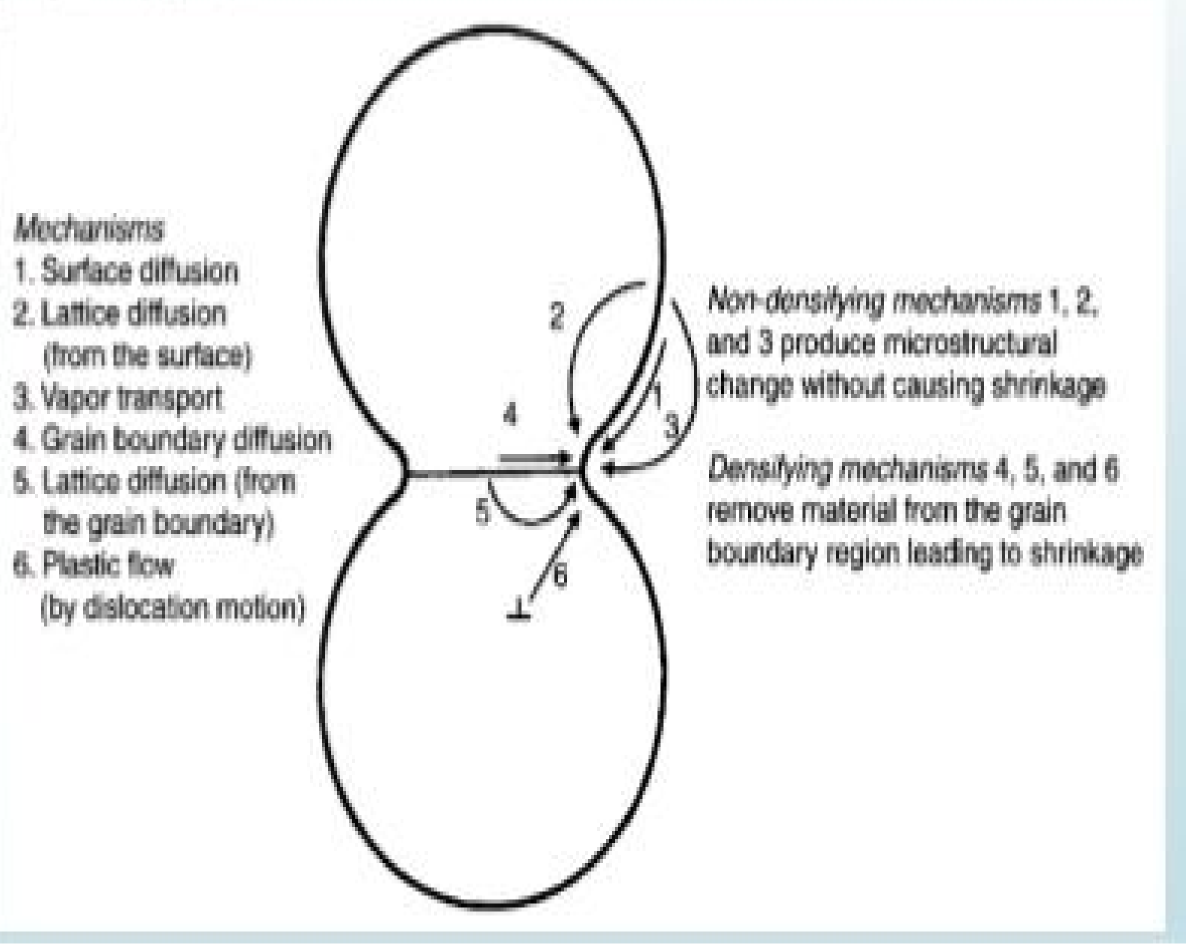
Stage III: evolution of necks and GBs and elimination of pores

Stage IV: isolation of pores

Mechanism Of Sintering

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

1. S
2. L
3. V
4. G
5. L
6. P



Surface Diffusion

This process involving (as in the case of bulk diffusion) the movement of particles (atoms, molecules or atomic clusters) occurring at solid material surfaces within the first layer of atoms (molecules) or at top of this layer.

Both atoms being a part of the solid and adsorbed particles (atoms, molecules or clusters) can move by means of surface diffusion. Typically, surface particles become mobile due to random thermal fluctuations of, usually, atoms or molecules. In the presence of a concentration gradient (surface concentration), random wandering of a large number of particles leads to an average diffusion motion in the opposite direction to that of the gradient.

The diffusion process is affected by many factors, such as the interaction between the diffusing particles, the formation of surface phases (surface reconstructions), the presence of defects, etc. Surface diffusion plays a decisive role in the growth of thin films, the formation of nanostructures on the surface of the substrate and sintering of ceramics.

Lattice Diffusion From The Surface

Atoms from surface diffuse through lattice

Vapor transport

Evaporation of atoms which condense on a different surface

Grain boundary diffusion

diffusion in solid polycrystalline bodies concentrated in narrow (having the thickness of several atomic layers) zones at the boundaries of the grains having different crystallographic orientations.

Due to the high concentration of defects in the grain contact area resulting from their crystallographic misalignment, diffusive transfer along the grain boundaries occurs much faster than in their bulk, where the defect concentration is much smaller (bulk diffusion), but slower than in the boundary between the solid and the atmosphere (surface diffusion). Grain-boundary diffusion is one of the main mechanisms of low-temperature sintering used in ceramics manufacturing and powder metallurgy; increase in its contribution is usually thought to be the reason of a lower sintering temperature when finely-dispersed raw materials are used. Grain-boundary diffusion is also one of the deformation mechanisms in solids

Types of Sintering Processes

- 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

- Advanced sintering process

Show great potential in ceramics processing

Overcomes the problem of grain growth

Advance Sintering Process

- 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.

- 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.

Advance Sintering Process

- **High frequency induction heat sintering**

It is similar to hot pressing, which is carried out in a graphite die, but heating is accomplished by a source of high frequency electricity to drive a large alternating current through a coil. This coil is known as the work coil. The passage of current through this coil generates a very intense and rapidly changing magnetic field in the space within the work coil.

Disadvantages Of Sintering

1. Large material quantity is required.
2. High initial capital cost relative to some alternative molding processes.
3. Size limitation based on size of chamber of machine.
4. High temperature leads to high energy costs.

Powder metallurgy – basics & applications

Powder metallurgy – science of producing metal powders and making finished /semifinished objects from mixed or alloyed powders with or without the addition of nonmetallic constituents

Steps in powder metallurgy: Powder production, Compaction, Sintering, & Secondary operations

Powder production:

Raw materials => Powder; Powders can be pure elements, pre-alloyed powders

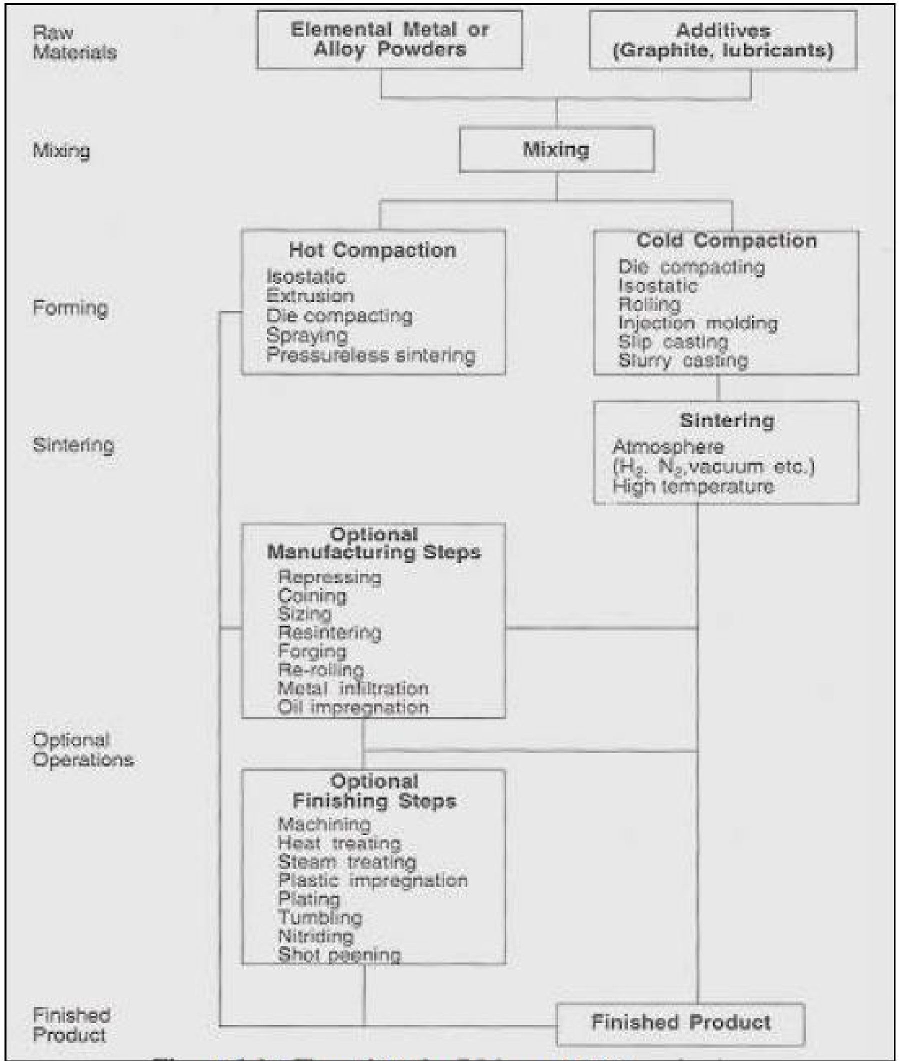
Methods for making powders – Atomization: Produces powders of both ferrous and non-ferrous powders like stainless steel, superalloys, Ti alloy powders; Reduction of compounds: Production of iron, Cu, tungsten, molybdenum; Electrolysis: for making Cu, iron, silver powders

Powders along with additives are mixed using mixers

Lubricants are added prior to mixing to facilitate easy ejection of compact and to minimize wear of tools; Waxes, metallic stearates, graphite etc.

Powder characterization – size, flow, density, compressibility tests

Secondary operations: Operations include repressing, grinding, plating can be done; They are used to ensure close dimensional tolerances, good surface finish, increase density, corrosion resistance etc.

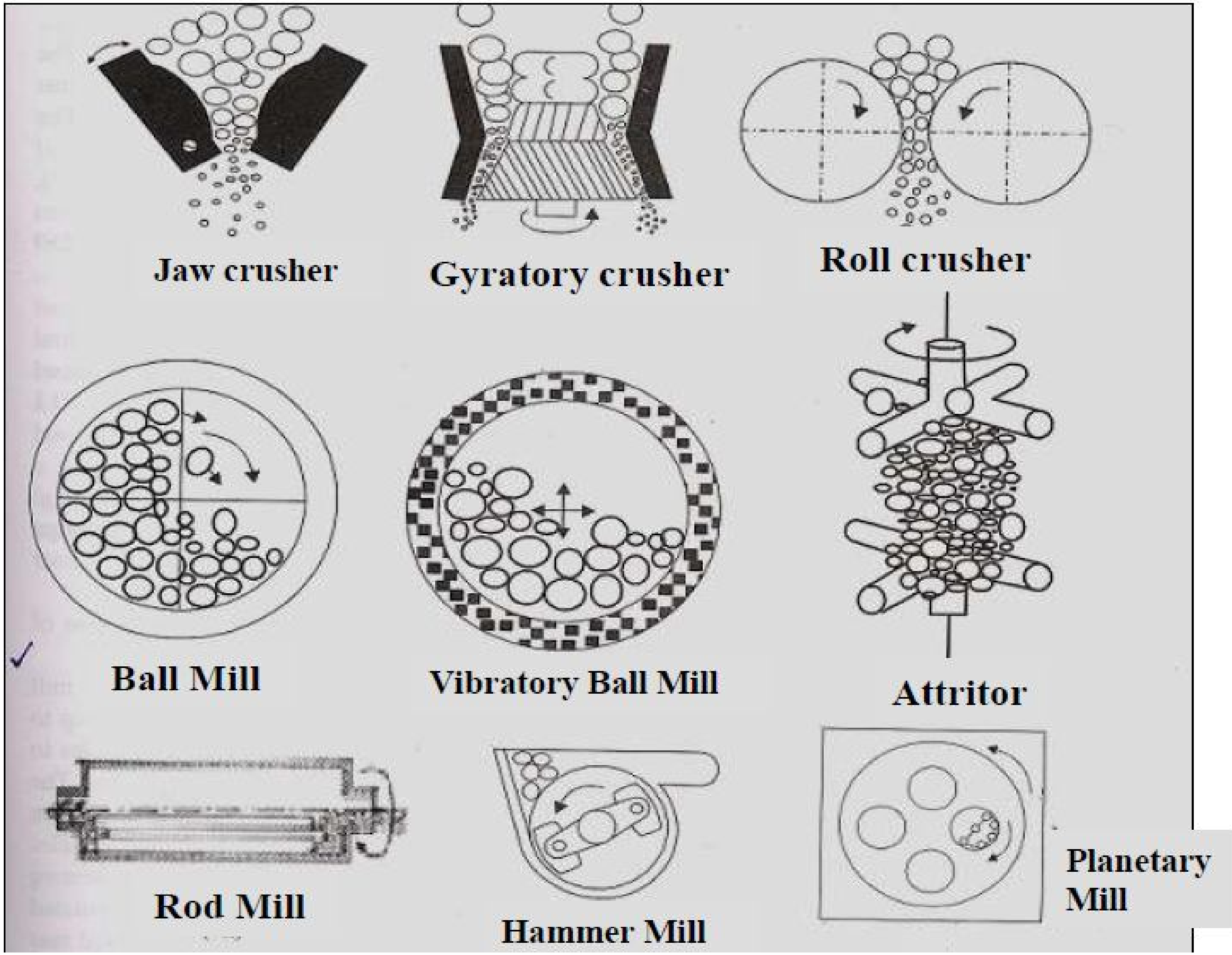


Flow chart for making P/M components

Advantages & limitations

- Efficient material utilization
- Enables close dimensional tolerances – near net shape possible
- Good surface finish
- Manufacture of complex shapes possible
- Hard materials used to make components that are difficult to machine can be readily made – tungsten wires for incandescent lamps
- Environment friendly, energy efficient
- Suited for moderate to high volume component production
- Powders of uniform chemical composition => reflected in the finished part
- wide variety of materials => miscible, immiscible systems; refractory metals
- Parts with controlled porosity can be made
- High cost of powder material & tooling
- Less strong parts than wrought ones
- Less well known process

Grinding: Different types of grinding equipments/methods are shown in the fi



Making powder & subsequent processing