

INTRODUCTION TO CERAMICS, GLASS AND REFRACTORIES

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8) Densification and Sintering



Sintering (Firing): The conversion of a compact powder to a coherent solid at temperature below the melting point of the major phase.

Firing of compact result in	An increase in grain size	Firing may cause	New Phase	
	Change in pore shape		Polymorphic transformation	
	Change in pore size and number (decrease porosity)		Decomposition	New phase
				Gases

Important Variables in the Sintering Process

- The processing temperature
- The rate of heating and time spent in each stage of the sintering process
- The particle size and size distribution of the ceramic powder
- The composition of the system including the additives and atmosphere
- The processing temperature for cases where hot pressing or controlled atmospheres used.

Types of Sintering

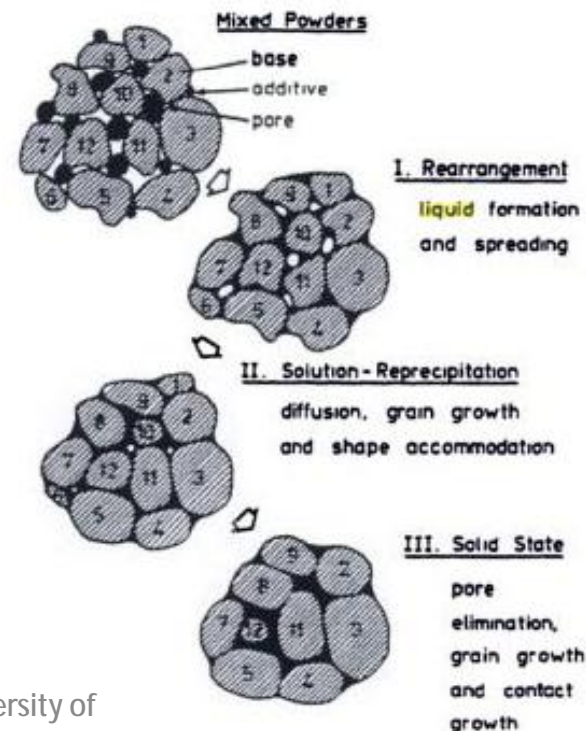
Vitrification: Where the composition and chosen processing temperature are such that liquid forms to fill completely the porous spaces in the original powder compact. It is important in the production of porcelain and clay based ceramics.

surface made shiny and nonporous by fusing a vitreous solution to it



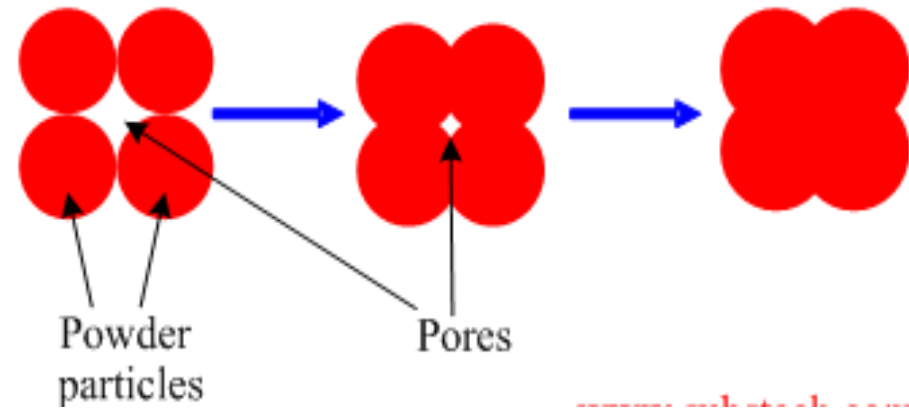
Liquid Phase Sintering:

The composition is such that some liquid forms at firing temperature to allow easy arrangement of the particles but not enough to fill the initial porosity, changes in grain shape are therefore required if full density is to be achieved.



Solid State Sintering:

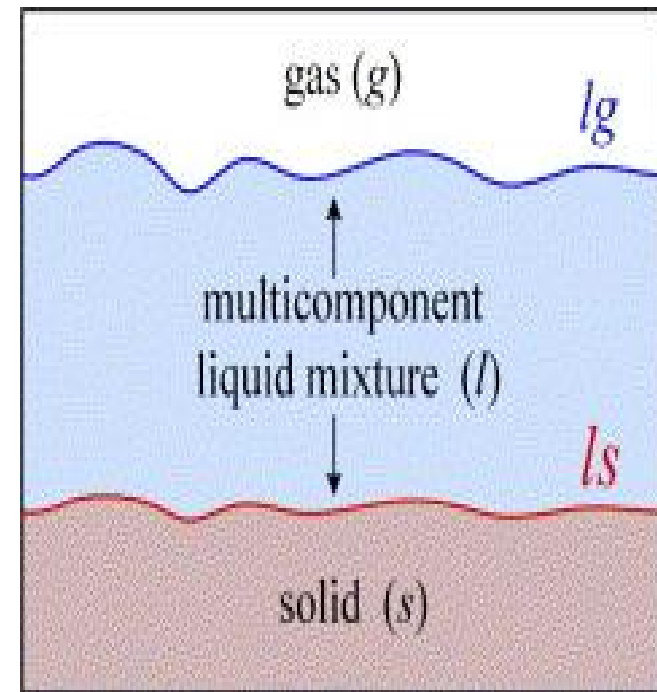
In which no liquid phase is produced at sintering temperature, consequently all densification is achieved by change in grain shape.



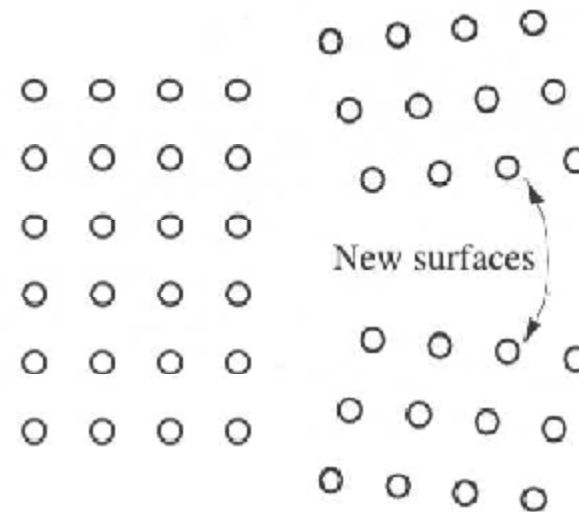
Surface Energy:

The **'surface'** is defined as the plane between condensed matter and a vapour phase or vacuum, such as solid/vapour and liquid/vapour interfaces.

The **'interface'** is used for the dividing plane between any two different phases. The existence of an interface means, by itself, the presence of an excess interface energy over the bulk energy.



The surface energy (γ) of a solid is the amount of energy (work) needed to create a unit area of new surface. The process is shown in the figure where two new surfaces are created by cleavage or cutting a solid in two.



The surface energy (γ) or surface tension can also be expressed as the change in the total internal energy (E) of the system. For the formation of unit area (A) the surface energy can express as

$$\gamma = \left(\frac{\partial E}{\partial A} \right) \text{ At constant temperature } (T) \text{ and pressure } (P)$$

Units of surface energy:

Energy (work) per unit area (J.m^{-2}) or Force /unit length (N.m^{-1}) since $\text{J} = \text{N.m}$

Contact angles

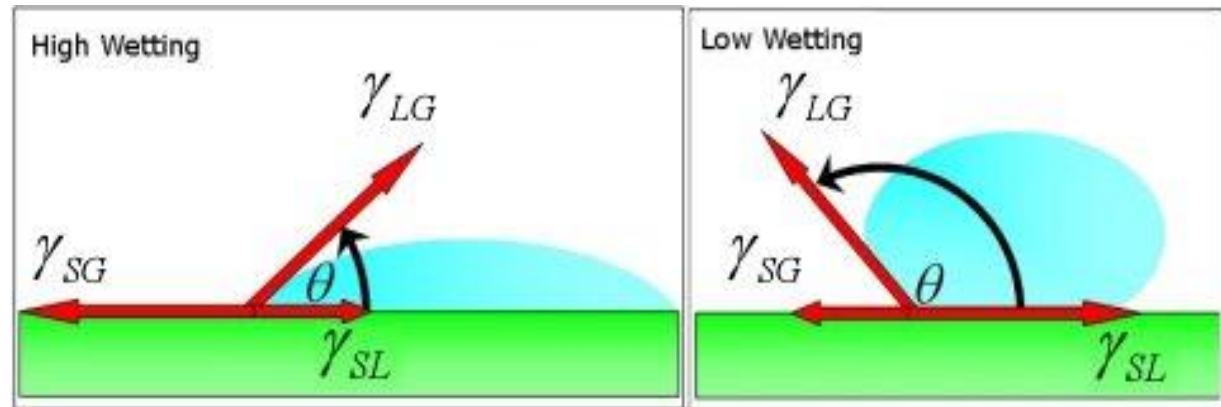
a) Solid – Liquid wetting: The stable configuration of a liquid placed on a solid surface (the equilibrium shape) conforms to the minimum total interfacial energy for all the phase boundaries present.

The contact angle θ (the angle created between the outer surface of the liquid and the surface on which it lies, depends on three surface tensions: the surface tension between the liquid and the solid surface γ_{SL} , between the surface and the air γ_{SG} , and between the liquid and the air γ_{LG} . Where

$$\gamma_{SG} = \gamma_{LG} \cos\theta + \gamma_{SL}$$

If γ_{SL} is high, the liquid tend to form a ball

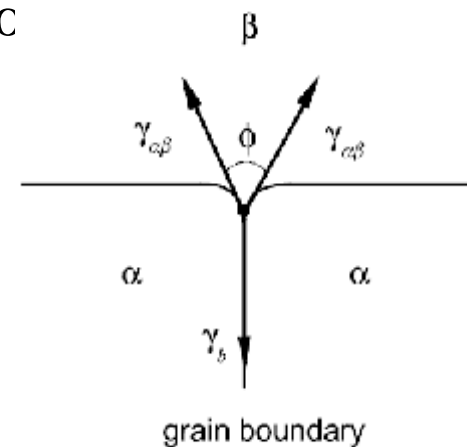
If γ_{SG} is high, the liquid tend to spread out



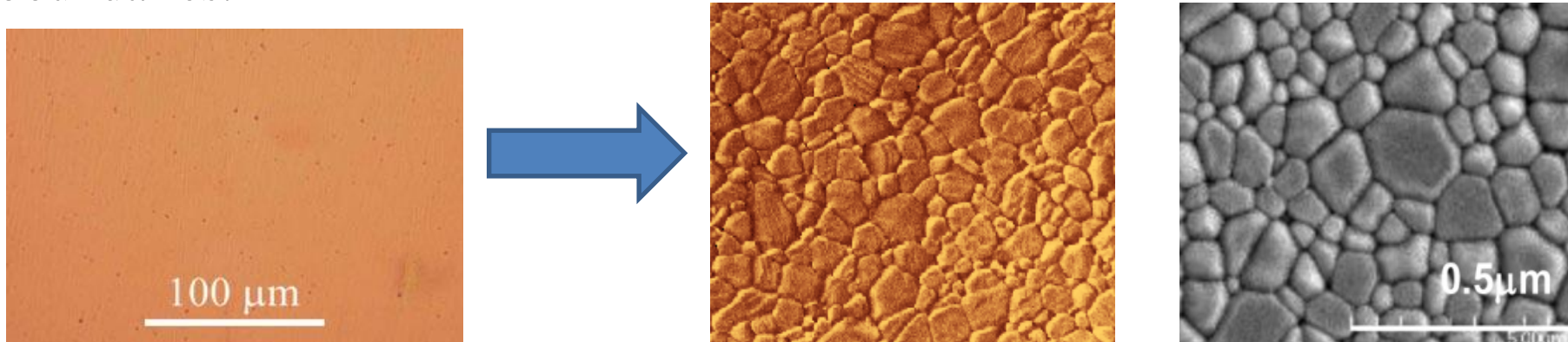
b) Solid – Solid (grain boundaries)

The angle at the junction between two grains is referred to as the dihedral angle. If the interfacial tensions are in equilibrium at this junction, is satisfied, where γ_b is the grain boundary energy of α , $\gamma_{\alpha\beta}$ the interfacial energy between α and β and ϕ the dihedral angle.

$$\gamma_b = 2\gamma_{\alpha\beta} \cos\frac{\phi}{2}$$



In thermal etching of polished surface γ_b become larger than the vertical components of $\gamma_{\alpha\beta}$ and leading to groove formation and revealing grain boundaries.

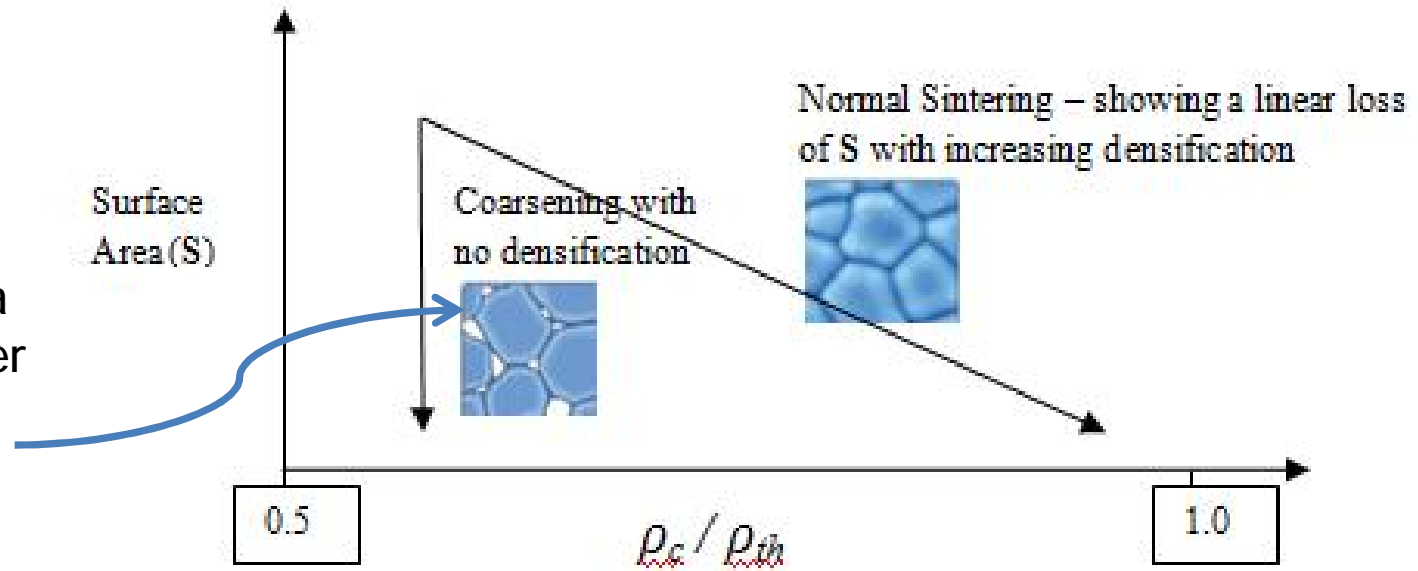


Driving Force of Sintering:

The primary driving force for sintering is reduction in the free surface energy of the system. This is accomplished by reducing the area of surfaces and interfaces of compact by

- Conversion of many small particles into fewer larger one (Coarsening)
- Replacement of the gas/solid interface by lower energy solid/solid interface (Densification)

The grains are growing bigger (thus surface area reduced), however pores are still present and densification still hasn't occurred.



ρ_c compact density and ρ_{th} is the theoretical density

Sintering Mechanisms:

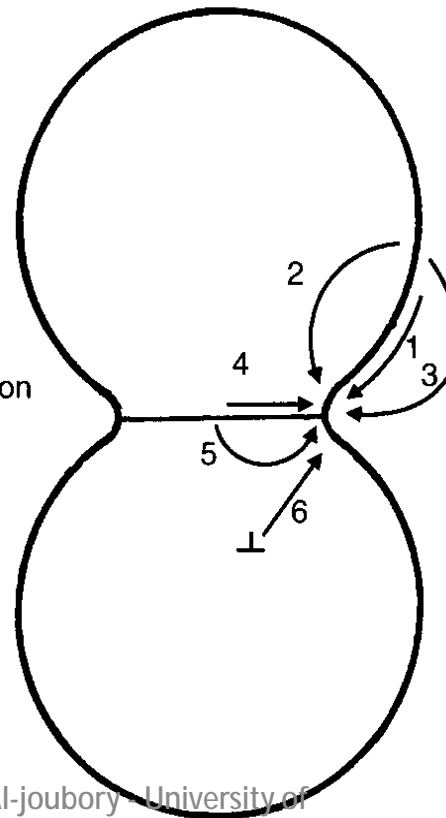
Sintering of crystalline materials can occur by several mechanisms. Material transport through viscous flow and atomic diffusion are caused by pressure difference across curved surfaces and the difference in surface energy (γ) or chemical potential between the neck area and surface of the particle.

Coarsening with no densification	Densification (Shrinkage)
Vapour transport (evaporation /condensation)	Grain boundary diffusion
Surface diffusion	Lattice diffusion from the grain boundary to the neck are the most important densification mechanisms in polycrystalline ceramics
Lattice (volume) diffusion from the particle surface lead to neck growth	

Diffusion from grain boundaries to the pores permits neck growth as well as shrinkage (densification)

Mechanisms

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 (by dislocation motion)



Non-densifying mechanisms 1, 2, and 3 produce microstructural change without causing shrinkage

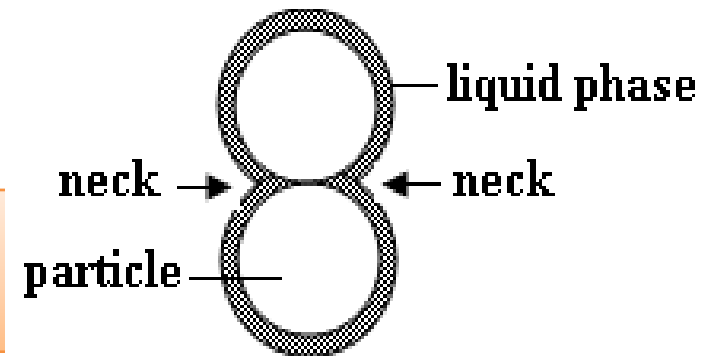
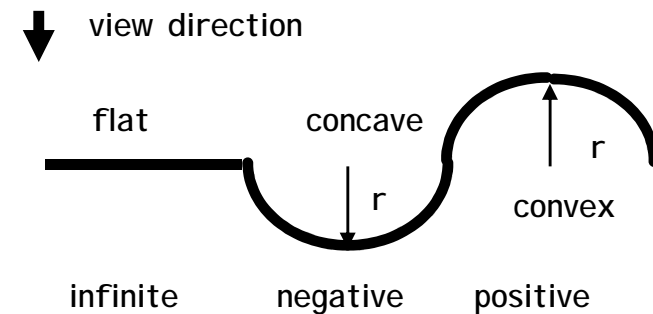
Densifying mechanisms 4, 5, and 6 remove material from the grain boundary region leading to shrinkage

The average bonding of an atom is decreasing from concave over flat to convex surfaces, the partial pressure over the surfaces is increasing in the same order.

Decrease of the porosity, caused by the sintering process, is determined by the level of the initial porosity of the “green” compact, sintering temperature and time.

Sintering is enhanced if a liquid phase takes part in the process (liquid phase sintering).

For glass powders, which cannot have grain boundaries, densification and neck growth occurs by viscous flow, involving deformation of the particles. Sintering (firing) of pure oxide ceramics require relatively long time and high temperature because the diffusion proceeds in solid state. Applying pressure decreases sintering time and the resulted porosity. Sintering process may be conducted in different atmospheres: air, inert atmosphere



Spark Plasma Sintering (SPS/DCS)

Is a revolutionary and new high speed powder consolidation process. SPS sintering technique utilizes high amperage pulsed DC current to activate the consolidation and reaction-sintering of materials.

The spark plasma sintering process proceeds through three stages

Plasma heating: The electrical discharge between powder particles results in localized and momentary heating of the particles surfaces up to several thousands °C

Joule heating: At this stage the pulsed DC electrical current flows from particle to particle through the necks connecting them.

Plastic deformation: The heated material becomes softer and plastic deform under the uniaxial force.

An SPS system processes conductive, non-conductive and composite materials to any level of density. The clear benefit of SPS is the significant savings of time and energy and the ability to retain nanostructures

