



UNIVERSITY OF ROME "LA SAPIENZA"

NANOTECHNOLOGIES ENGINEERING

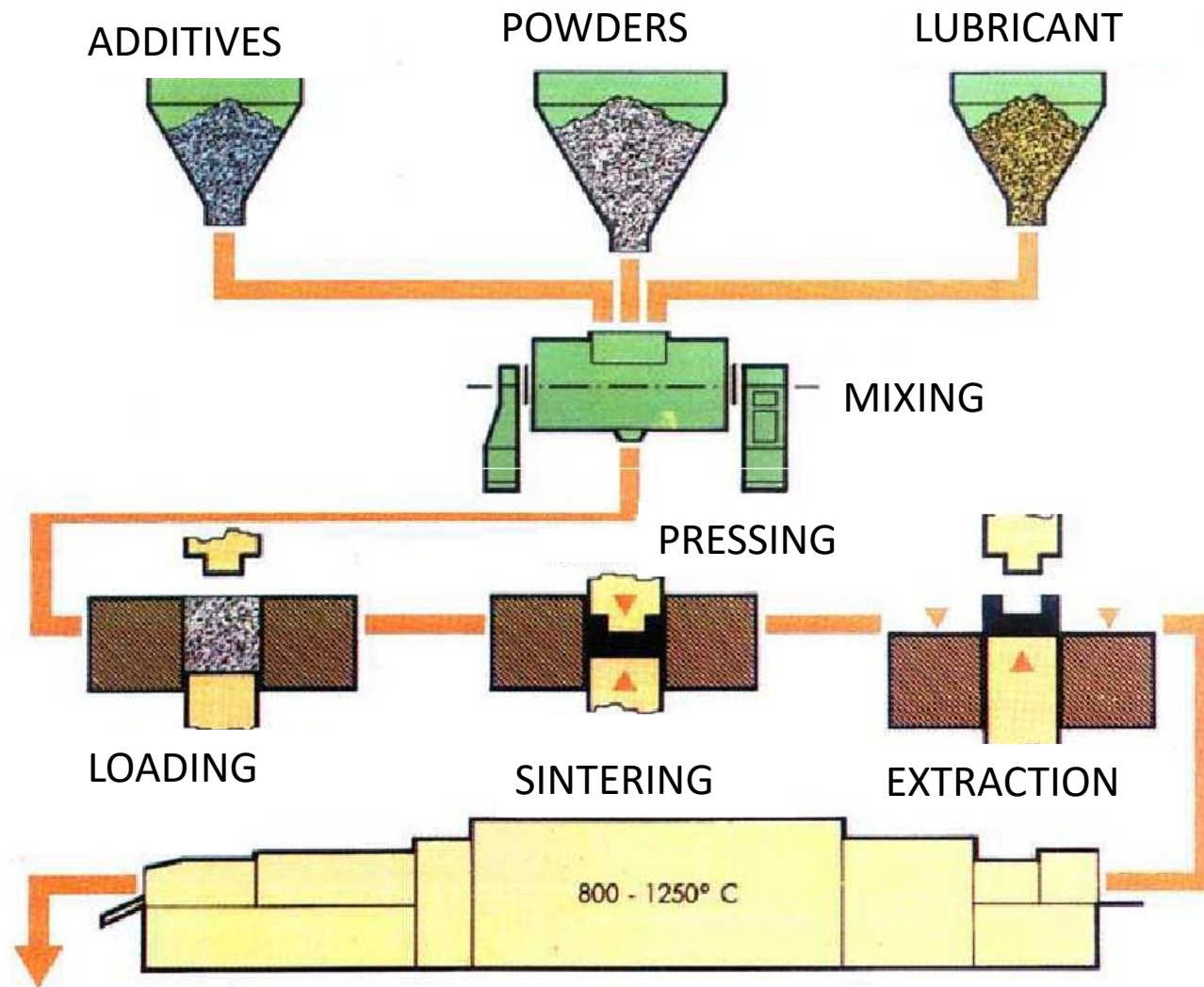
SINTERING

Sintering of materials is a physical mechanical process on powders (or mixed powders) to produce a defined artefact maintaining solid state and without phase transition.

The process is divided in two steps:

Pressing: applying 50-80 atm to the mold containing the powders, these are strongly compressed. The final shape is formed, but the artefact brittles under small application of forces.

Sintering: the artefact enters a furnace at high (below fusion) temperature where the sintering processes take place, that is the physical bonding of the single particles by solid bridges. The resulting artefact is very resisting and behaves like a monolith.



The PSD in the sintering process defines the outcome, since uniform packaging of the powders is desired in order to limit porosity.

A narrow PSD is not desired, since packaging is limited (74%). Smaller particles capable to fill the void spaces are required and/or predominant axial particles.

The sintering process allows solid diffusion in order to form solid necks (bridges) that will bond particles together. The particle material deforms from the original shape to the linked one.

The process is spontaneous and aims to a internal energy reduction. Since no phase transition takes place, the internal energy of the system is determined by the surface area of the solid: by sintering, this area is reduced.

Spherical particles may package up to maximum 74%. When maximum packaging values for a fixed shape is reached, the powder is called “compact”. In order to increase the compactation (surface on volume) of the powder, the shape of the particles must be different.

This can be achieved by particles of different PSD, or by non spherical particles, or by the deformation of spherical ones.

The neck formation transfers material from the surface to the formation of the bridges, thus changing the original shape of the particles.

Sintering requires:

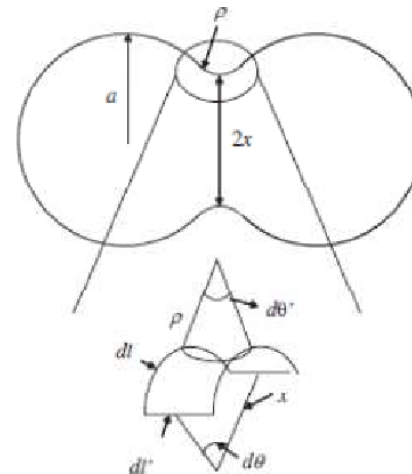
- Solid diffusion
- Energy source

Three types of sintering may be identified:

- Solid-solid
- With presence of a liquid
- Reactive

MECHANISM

High temperatures promotes solid diffusion and possibility of solid rearrangement. The solid will densify (although not reaching fusion). At the contact point of two particles, a energy stressed superficial tension exists. Vacations will increase in this sectors, promoting solid diffusion. Local evaporation-condensation, internal and superficial solid diffusion leads to the neck formation.



Sintering method	Mechanism	Driving force
In presence of melt	Diffusion	Superficial tension Capillarity
Solid state	Diffusion	Internal energy
In presence of vapor	Evaporation and condensation	Vapor pressure
In presence of other phases	precipitation	Superficial tension Capillarity

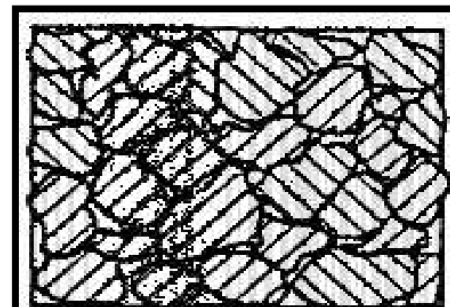
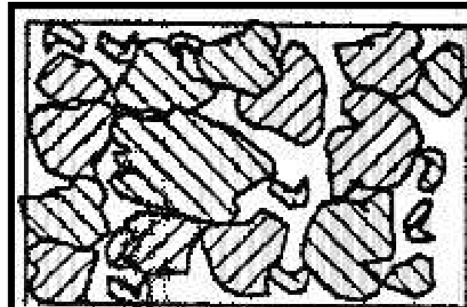
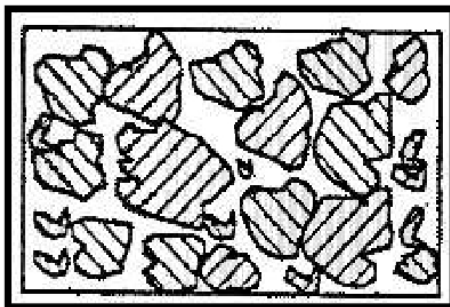
SOLID-SOLID SINTERING

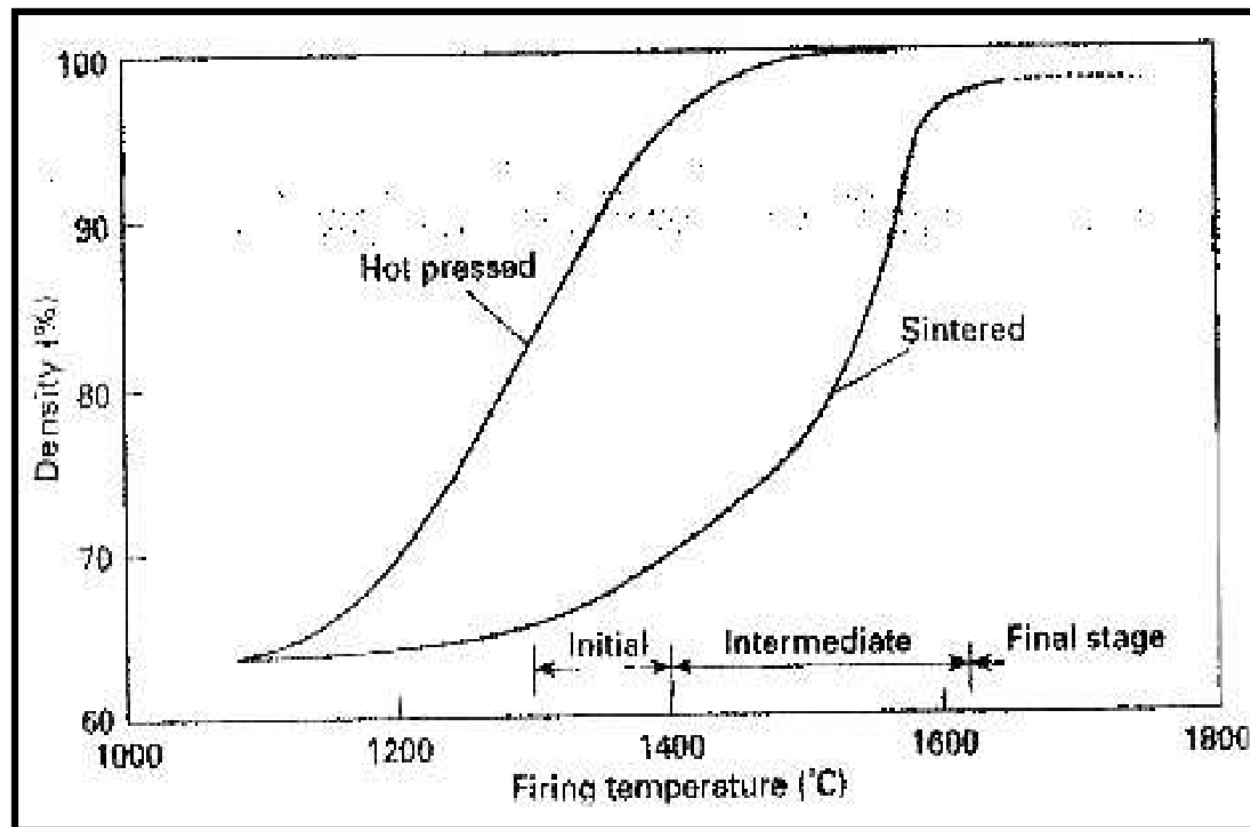
The porosity of the material decreases due to the bridge formation among particles given by the minimization of the internal energy of the system

Porosity 75%

50%

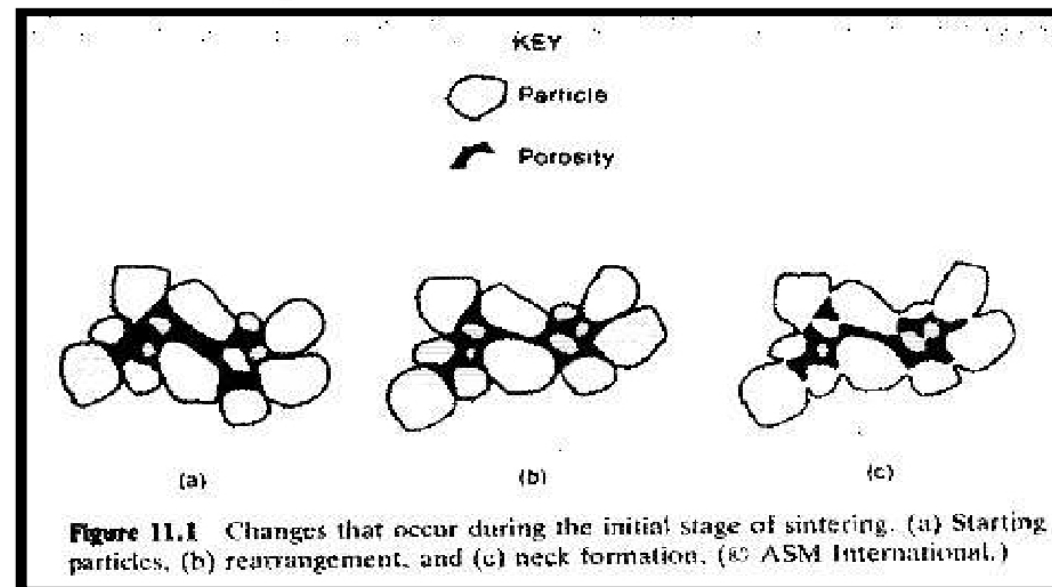
10%





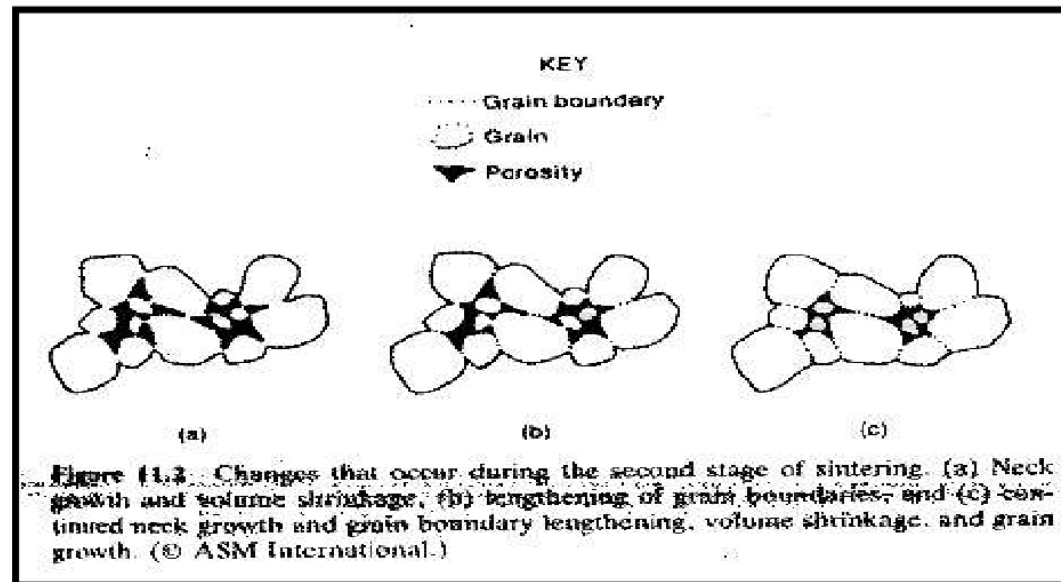
INITIAL PHASE

The rearrangement of the particles and neck formation increases the density from 0.6 to 0.7



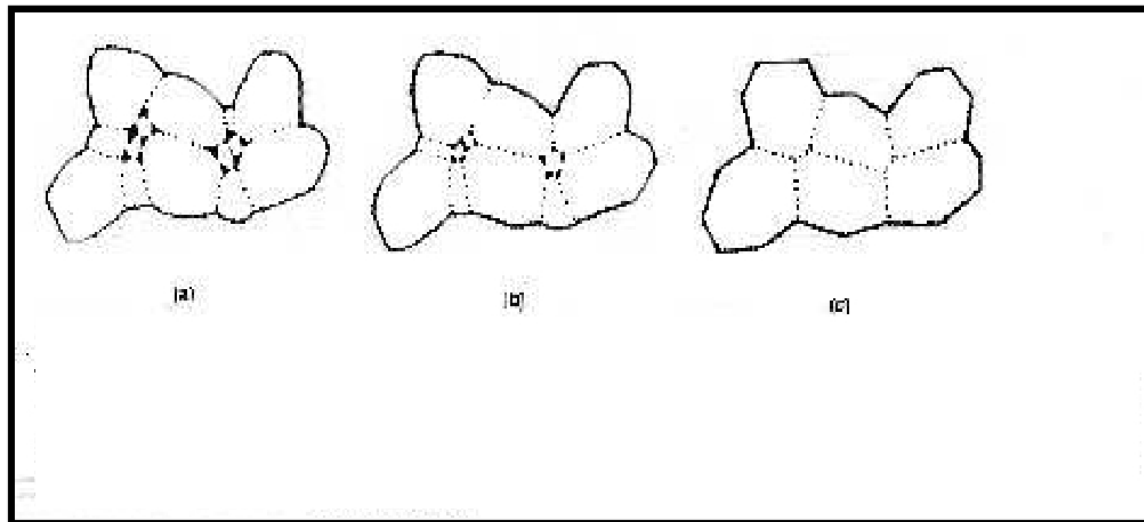
INTERMEDIATE PHASE

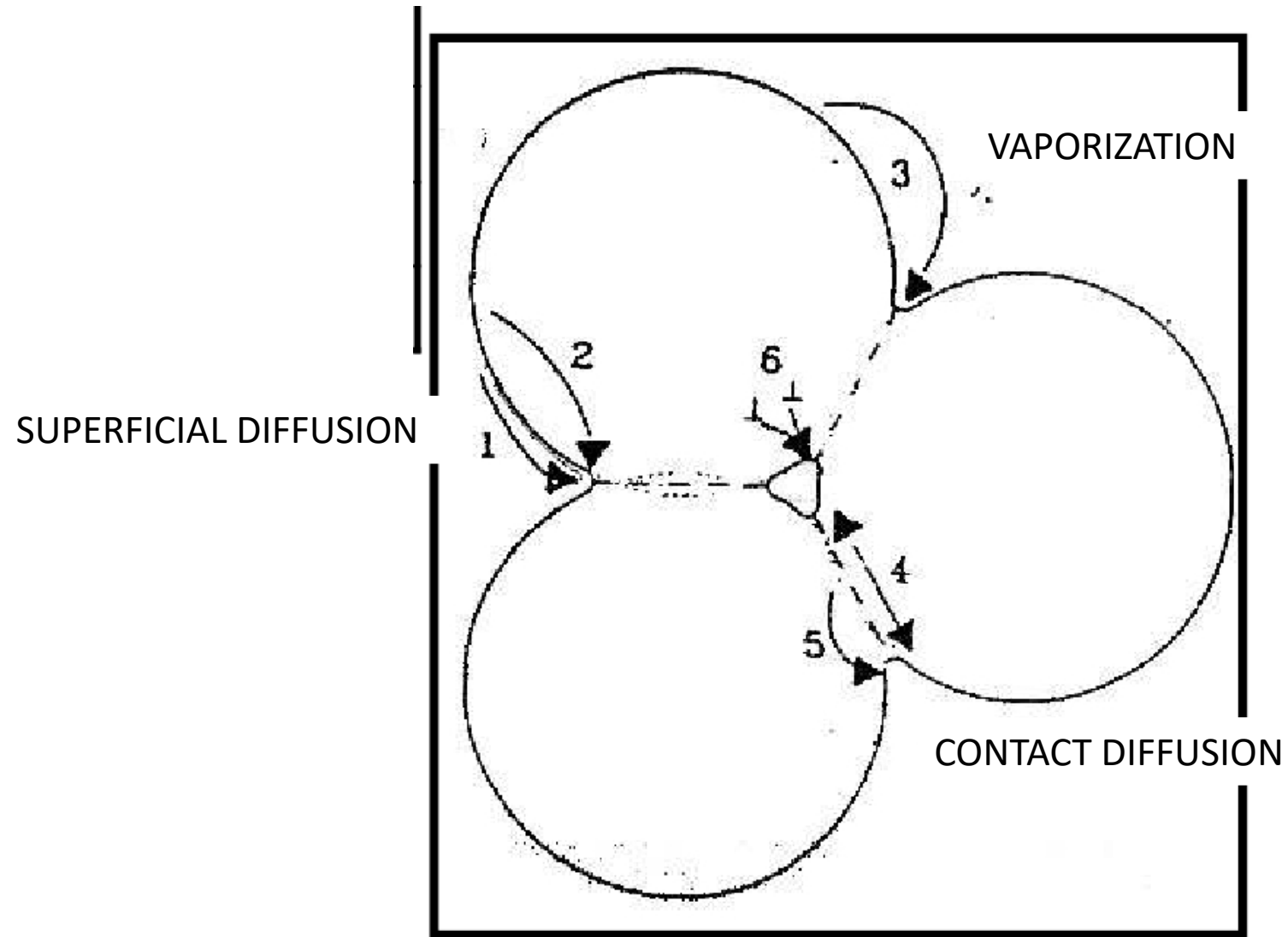
Bridges becomes coarser, porosity becomes closed: density reaches values up to 0.9.

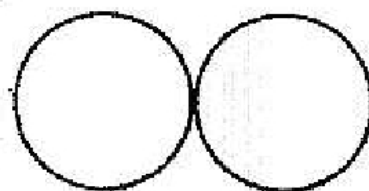


FINAL STAGE

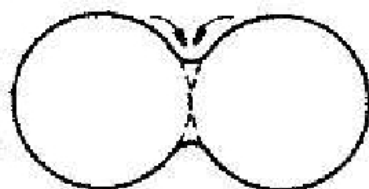
Growth of the granules, elimination of porosity



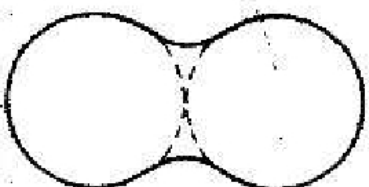




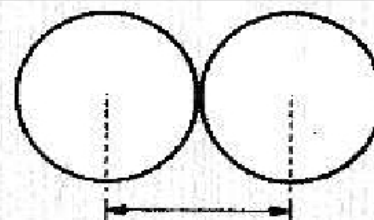
ADJACENT PARTICLES
IN CONTACT



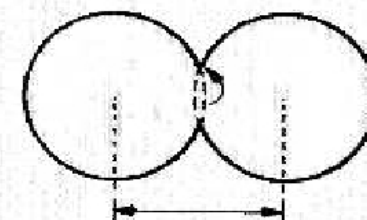
NECK FORMATION
BY VAPOR PHASE
MATERIAL TRANSPORT



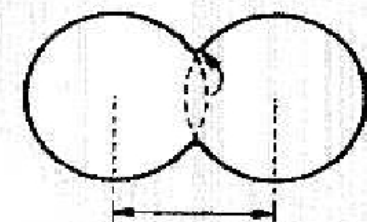
COMPLETION OF VAPOR
PHASE TRANSPORT; PARTICLES
BONDED, PORE SHAPE CHANGED,
NO SHRINKAGE



ADJACENT PARTICLES
IN CONTACT



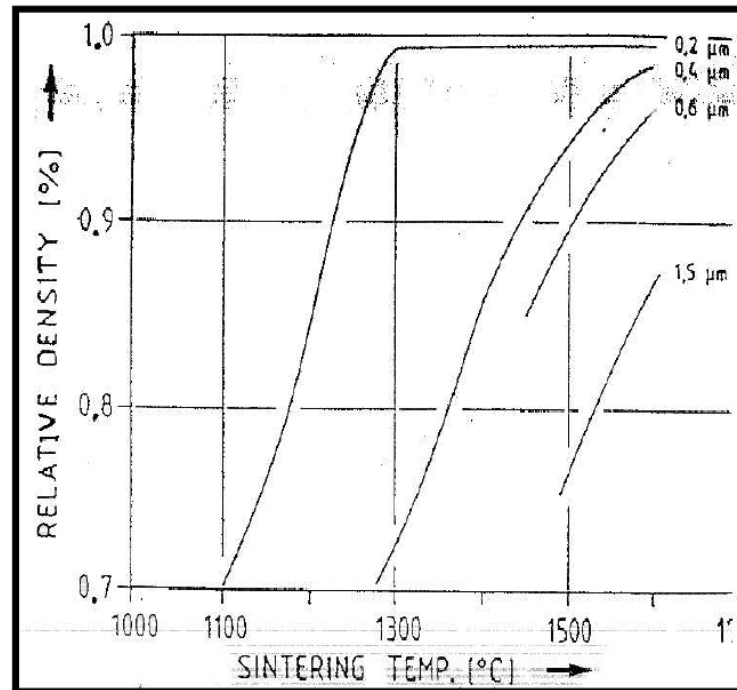
NECK FORMATION
BY DIFFUSION



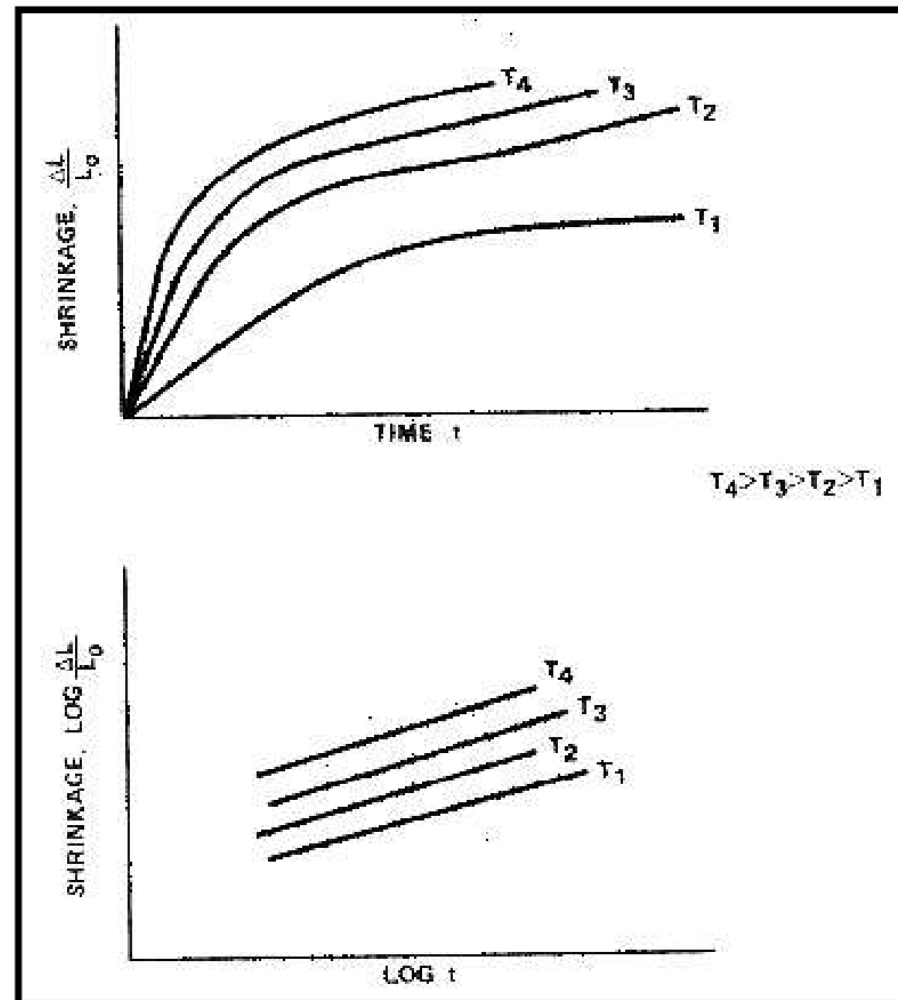
DISTANCE BETWEEN PARTICLES
CENTERS DECREASED, PARTICLES
BONDED, PORE SIZE DECREASED

SINTERING AS A FUNCTION OF TEMPERATURE AND INITIAL PSD

Operating with nanoparticles may reduce sintering temperatures about 200°C.



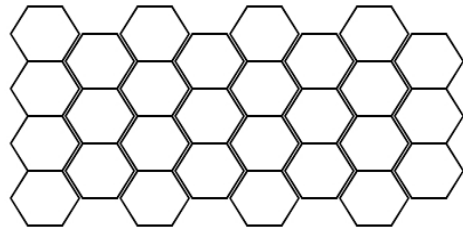
SINTERING AS A FUNCTION OF TEMPERATURE



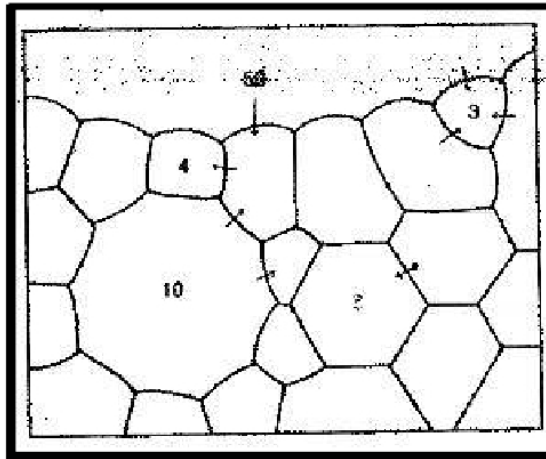
GROWTH

The free energy of a surface is a function of the convexity: higher values correspond to a higher chemical potential value.

The difference of free energy of the surfaces in contact of two particles is the driving force to material migration: the total area of the particles will decrease, and as a consequence, also their total free energy.



In case of symmetric arrangement the system exhibits minimum values of free energy.



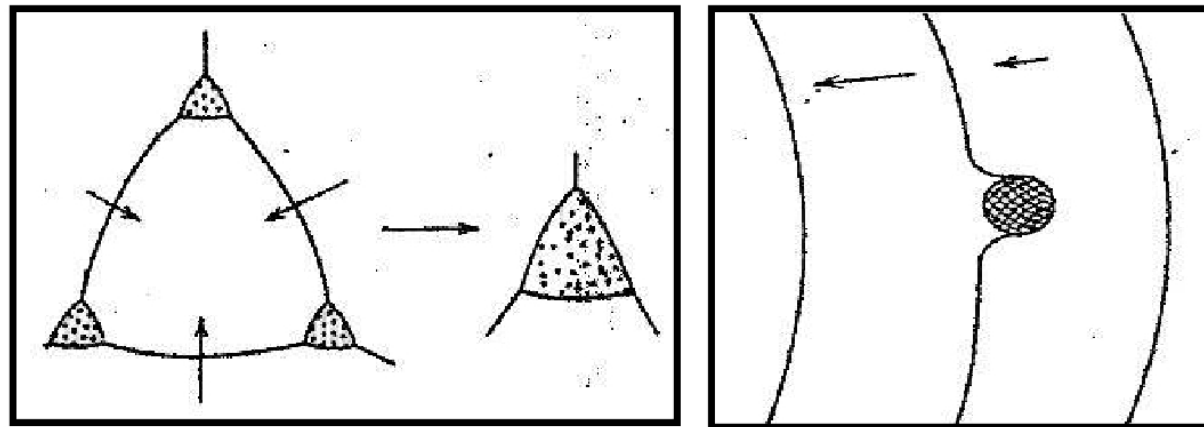
Tending to this, the analysis of the grains permits to identify the direction of the material migration during sintering.

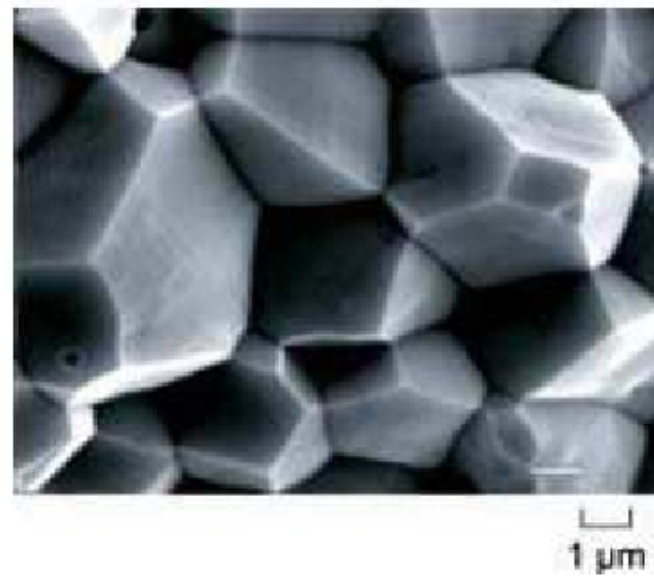
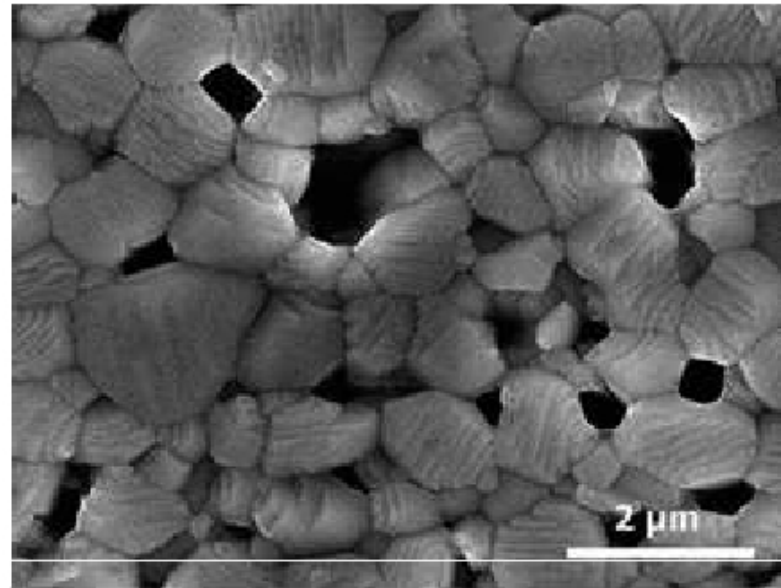
Particles that exhibit more than 6 surfaces have at least one convex; on the contrary, particles with less than 6 surfaces have concave surfaces.

The grains will grow or shrink as a function of the number of surfaces: those having more than 6 will grow, whereas those having less than 6 will shrink.

Bigger particles will grow at the expense of smaller ones.

The porosity of the material will act as a consequence of the grain rearrangement and can be transported on the surface (if the growth rate is slow) or included (if the growth rate is fast). In the first case, porosities will agglomerate and eliminated, in the second case they will survive.





The production of dense ceramics requires therefore slow growth rates, and in order to limit growth, additives are used to influence the grain border behavior (such as MgO).

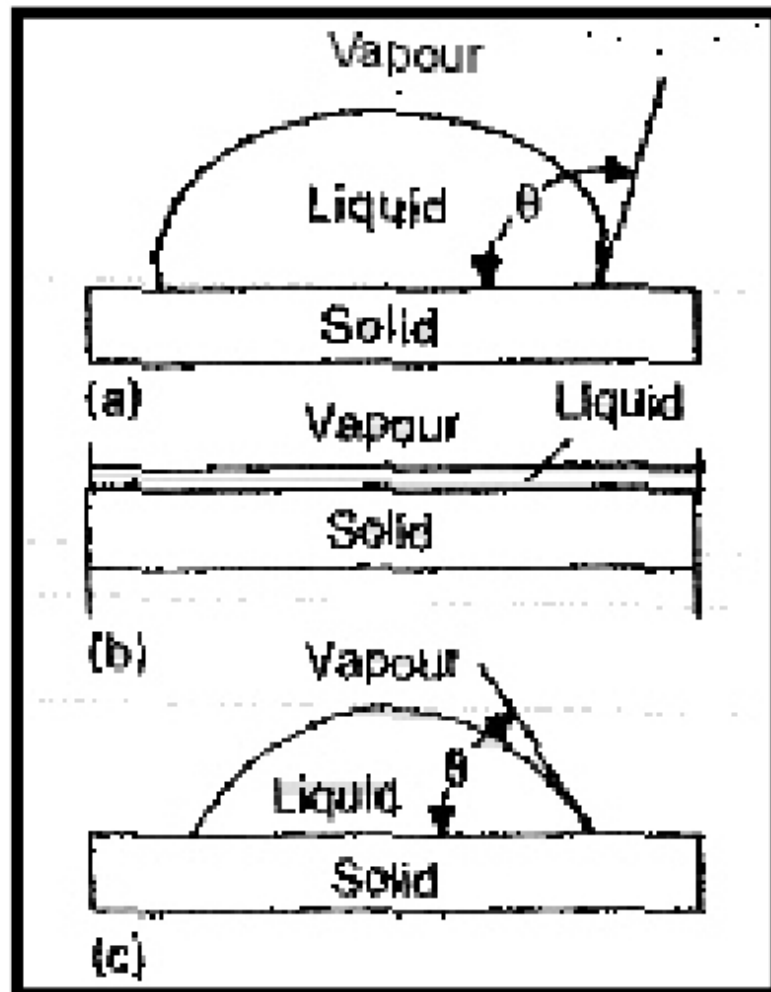
The additives must not exceed solubility values and used at very low concentrations.

LPS (LIQUID PHASE SINTERING)

In this case, sintering is performed in the presence of a liquid phase. This practice is very common since the sintering phenomena are intensified and the operating temperatures lower.

In order to operate the process, the wettability of the solid by the liquid must be high.

The liquid phase are given by additives (up to 5%) which will melt before the powders in order to permit the solidification of the latter in glass state (amorphous). This works well for artifacts at low exercise temperatures, but may give problems on high exercise temperatures where the glass phase may soften and stop to properly bind the grains together.

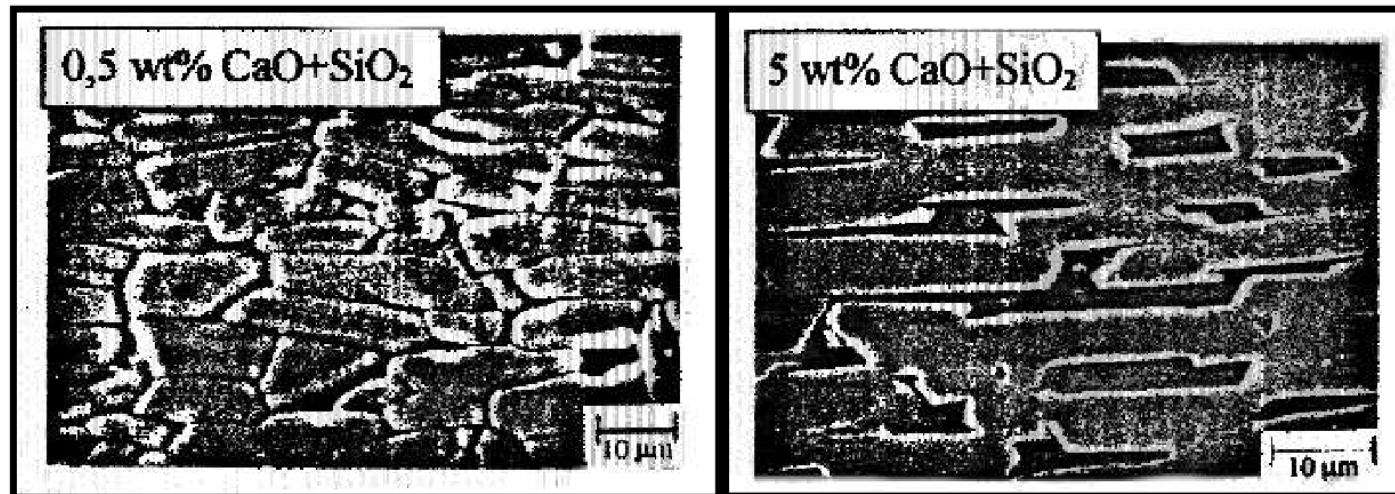


WETTING

Expressed as a function of the contact angle, which should be at least less than 90° .

In case of LPS, the contact angle must be at least lower than 60° in order to guarantee the wettability of the chord and kinks of the particles.

At the end of the process, the particles will be submerged in the glass phase left by the liquid (additives and solids formed by the partial dissolved solid).



Therefore, requirements are:

1. At the operating conditions, that is the sintering temperature, a sufficient amount of liquid must be available
2. The particles must be wetted uniformly on the total chord length
3. The particles requires to be compact and partially soluble in the liquid

LPS – 1st STAGE

In a first stage, the liquid will bind to the particles and necks will start to form. This phase terminates when all the particles are in contact to each other through the liquid bulk.

LPS – 2nd STAGE

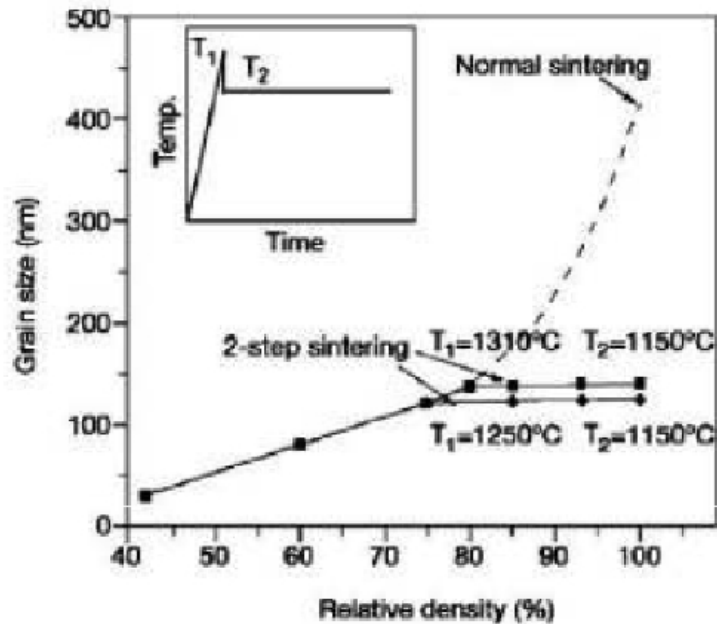
Smaller particles, kinks, necks and convexed surfaces starts to dissolve, and crystallizes on the bigger particles surfaces.

LPS – 3rd STAGE

A solid skeleton is formed. Porosity becomes closed and may be eliminated furthermore.

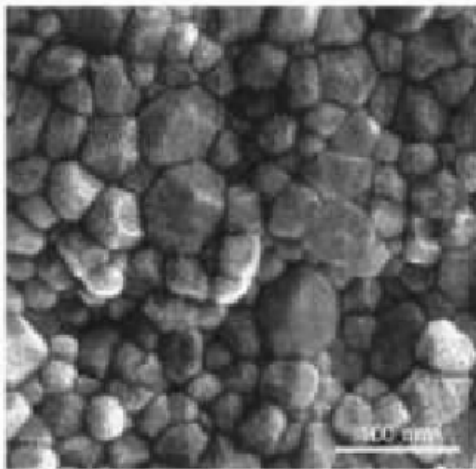
The elimination of the porosity may be of great importance, since the elastic module, the mechanical resistance, the optical transmission and/or the electric conductivity will increase.

Starting from nanoparticles allows to obtain sintered artifacts with almost no porosity!



SINTERING OF Y_2O_3

Performed in two steps, with addition of 1% MgO



OTHER EXAMPLES:

Porcelain: sintered in liquid phase (KF) at 1200°C

Si_3N_4 : sintered in liquid phase (Y_2O_3 , MgO, rare earth oxides) at specific temperatures to obtain a beta phase (needle shaped grains, higher resistance)

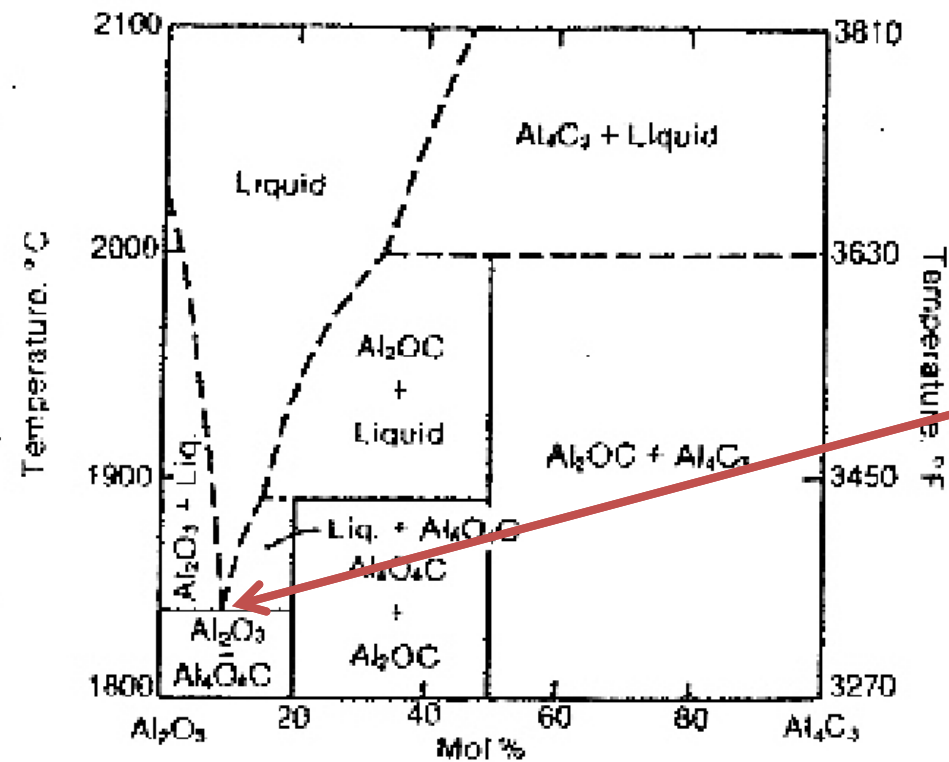
REACTIVE SINTERING

The material migration phenomena will occur in vapor or liquid phase. In this case, the binding phase is reactive and may transform or be eliminated.

In the latter case, the artifact will exhibit good properties even at high exercise temperatures.

The binding phase may be obtained by:

1. A mix of additives that reacts forming products that will melt or vaporize before the melt of the powders
2. A mix of additives that forms a solid solution after having formed a liquid one
3. Perform a LPS forming the glass phase and treat by heating the artifact again to crystallize the glass phase



FORMATION OF SiC
at 1900°C instead of 2150°C

Increase of resistance at high
exercise temperatures

Figure 11.15 Phase equilibrium diagram of the system Al_2O_3 - Al_4C_3 showing the eutectic between Al_2O_3 and Al_4C_3 at about 1830°C (3325°F). (From L. M. Foster, G. Lang, and M. S. Hurter, *J. Am. Ceram. Soc.* 39 [1], 8, 1956.)