CERAMICS MATERIALS MANUFACTURING

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SINTERING

INTRODUCTION

After binder burnout, we have a ceramic compact that consists of an aggregation of ceramic particles giving a porous ceramic green body.

At this stage the ceramic green body is at its most fragile state and must be handled with care or, better yet, simply not handled at all.

The next step, sintering, are done either:

(1) In the same furnace but at different temperatures and different atmospheres.

(2) In the same kiln in different sections.

(3) Other furnace

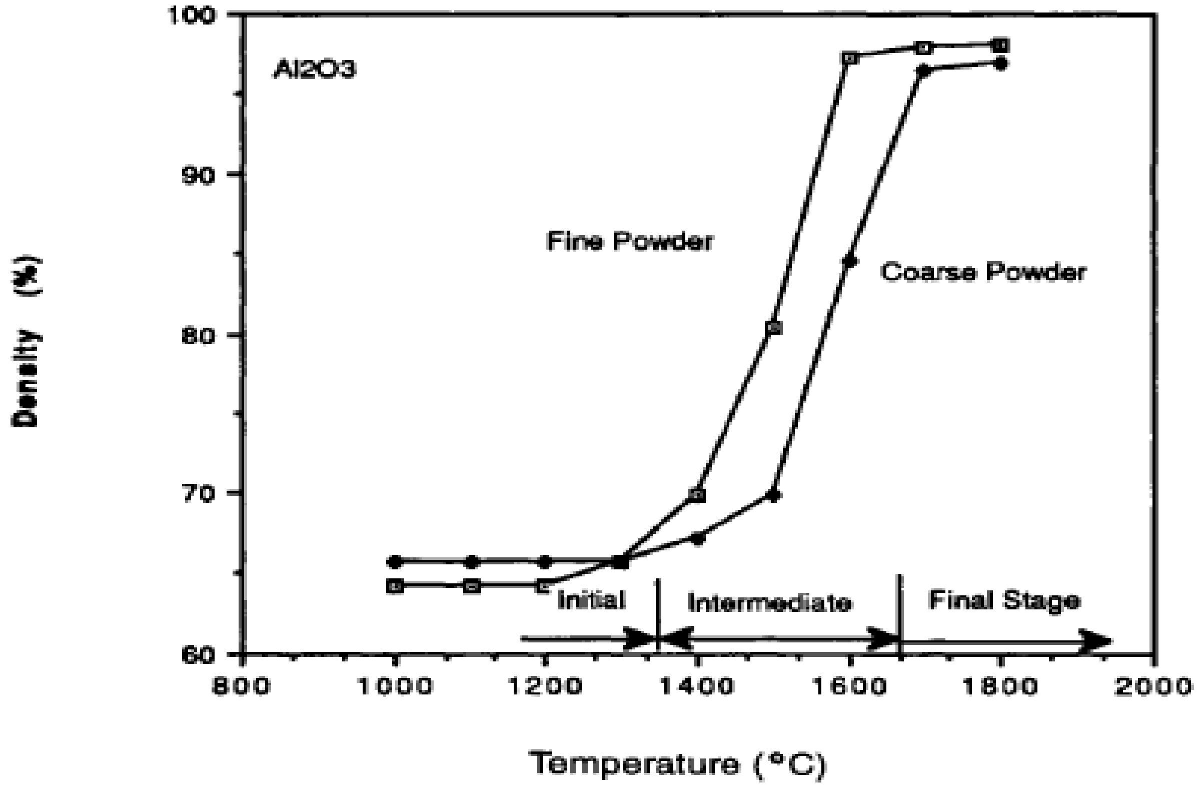
Figure 2. Nanopowder (left) to green ceramic (middle) to optical ceramic YAG (right)

How to change the optical properties of nano-powders after sintering

PROPERTY CHANGES

Figure 1 show the sintered density obtained after 4 hr at each temperature for two log-normal sized distribution $A1_2 0_3$ powders.

In this figure, the finer powder, which has the lower density initially, sinters to a higher density at a lower temperature because it has a higher specific surface area.



{*FIGURE 1* shows two log-normal alumina powders (d = 1.3 and 0.8 μm) showing the initial, intermediate, and final stages of sintering.}

Sometimes the density does not increase even though the pores change shape.

This is called coarsening. The difference between sintering and coarsening is schematically shown in Figure 2.

If the inter-particle separation distance remains the same , coarsening takes place.

If the inter-particle separation distance decreases, sintering takes place. Only sintering leads to an increase in density, which is referred to as densification.

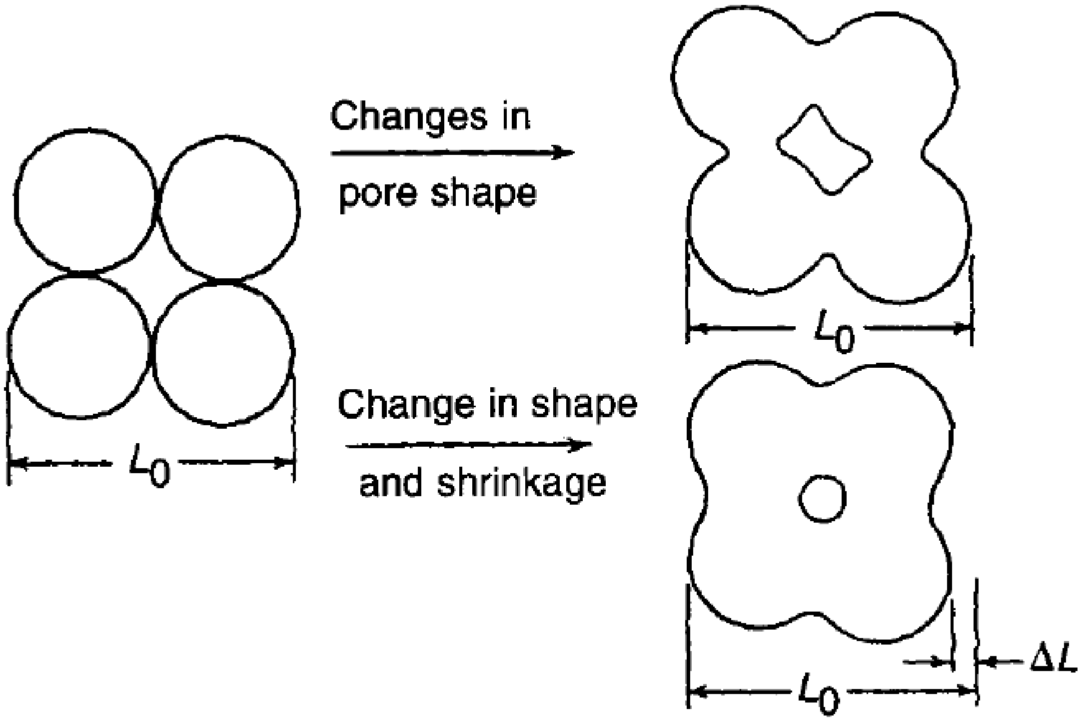
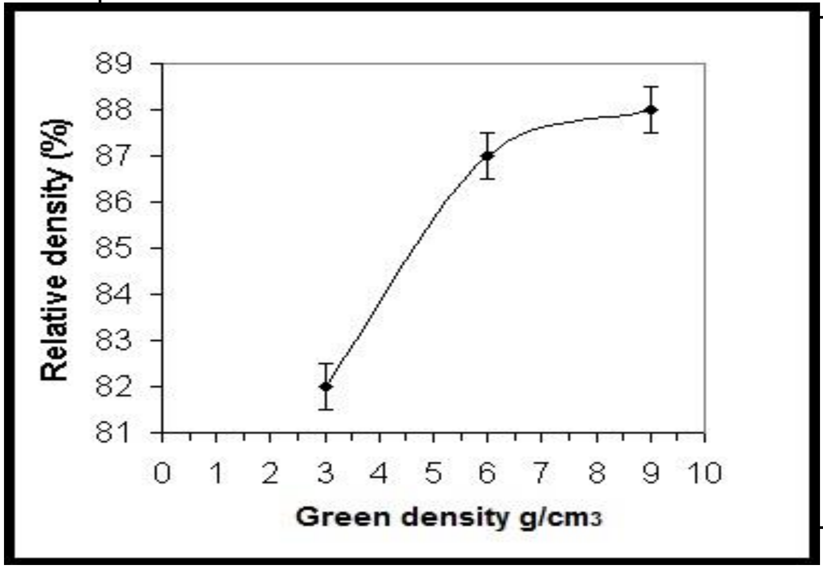
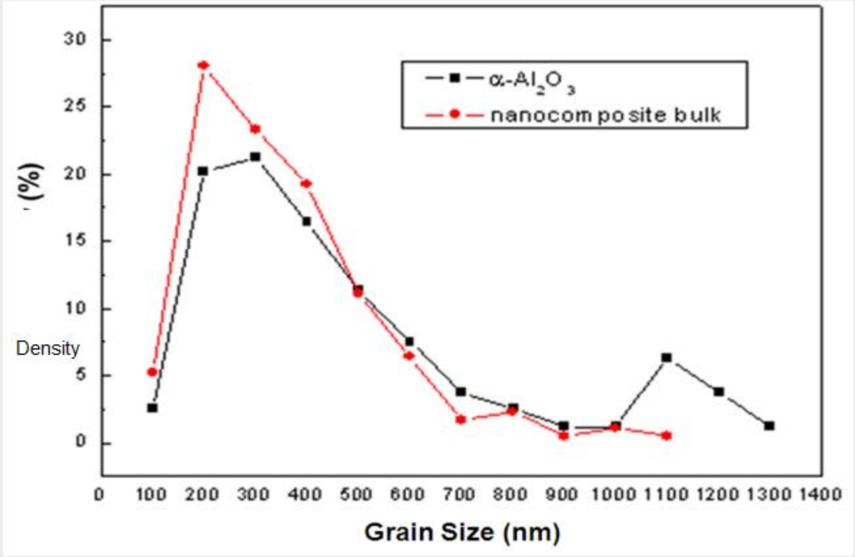


FIGURE .2 The differences between coarsening and sintering


Relative density (%)
89
88
87
86
85
84
83
82
81
0
1
2
3
4
5
6
7
8
9
10
Green density g/cm3


(%)
Density
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
Grain Size (nm)
α-Al2O3
nanocomposite bulk

MECHANISM OF SINTERING

The various stages of sintering are described next

Initial Stage:

The initial stage of sintering is frequently referred to as the neck formation stage, as is shown in Figure 1.

The sintering driving force for the initial powder compact is due to the curvature difference between particle surface and that of the neck, see Figure 5.

MECHANISM OF SINTERING

Initial Stage:

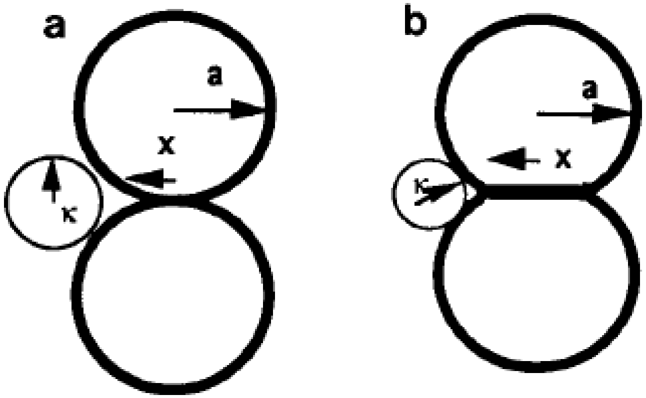


FIGURE 5 shows the contact area between two partically sintered spheres: (a) center-to-center distance is constant, (b) decreasing center-to-center distance.

MECHANISM OF SINTERING

Initial Stage:

The six distinguishable diffusion-controlled paths of material transport **(vacancies diffuse normally),** considered to be the most probable sintering mechanisms, are shown in Figure .3. Any one of these pathways increases the neck size, but not all time.

To clearly see this distinction, transport mechanisms :

(1) vapor transport

(2) bulk diffusion

MECHANISM OF SINTERING

Initial Stage:

- Particle surface smoothing and rounding of pores
- Grain boundaries form
- Neck formation and growth
- Homogenization of segregated material by diffusion
- Open pores
- Small porosity decreases <12%

MECHANISM OF SINTERING

Intermediate Stage:

The intermediate stage of sintering begins after grain and pore shape changes caused during the initial stage produce a pore and grain-boundary matrix consisting of equilibrium dihedral angles formed on the solid-vapor (pore) surface at the intersections with the solid-solid (grain-boundary) interfaces. At this stage, the pore shape approximates a continuous cylindrical channel coincident with three grain edges throughout the matrix as shown in Figure .9. During this intermediate stage of sintering, the cylindrical pore simply shrinks.

MECHANISM OF SINTERING

Intermediate Stage:

Assuming all grains have the same size and shape (cube, dodecahedron،or tetrakaidecahedron) and all pores are cylindric and of the same size، the porosity function.

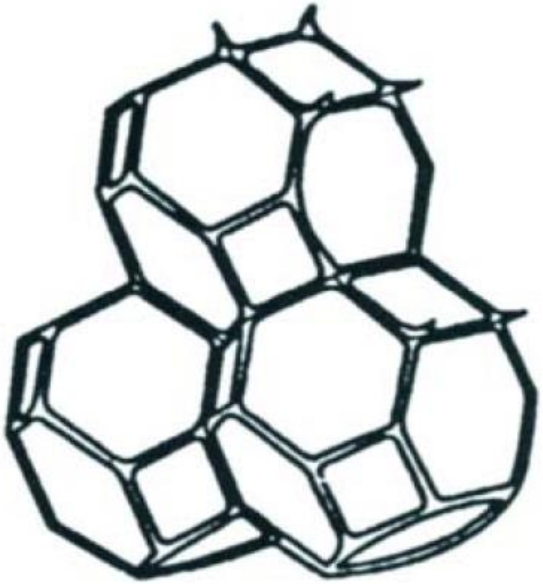


FIGURE .9 The microstructure model used for intermediate stage sintering. This model consists of tetrakaidecahedra

MECHANISM OF SINTERING

Intermediate Stage:

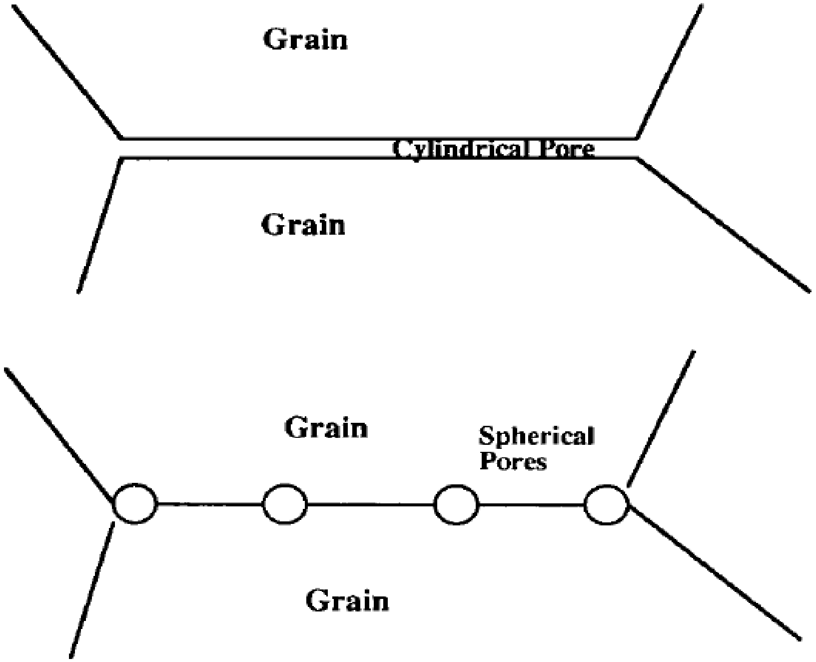


FIGURE 16.10 Breakup of a cylindrical pore into a string of spherical pores.

MECHANISM OF SINTERING

Intermediate Stage:

- Intersection of grain boundaries
- Shrinkage of open pores
- Porosity decreases substantially
- Slow grain growth
- Differential pore shrinkage and grain growth in heterogeneous material

MECHANISM OF SINTERING

Final Stage:

During the final stage the removal of these closed pores takes place. The final stage densification is dependent on the association of pores with grain boundaries and the rate of grain growth. The string of pores at the grain boundary will migrate to the point of lowest energy.

The energetically favored pore location is at the intersection of three grains in two dimensions, four grains in three dimensions. As shown in Figure 12, the movement of the string of pores to a single pore at the four grain intersection is a complicated process. In some cases ‹it occurs but in others it is prevented from occuring by the movement of grain boundaries caused by discontinuous (or abnormal) grain growth.

MECHANISM OF SINTERING

Final Stage

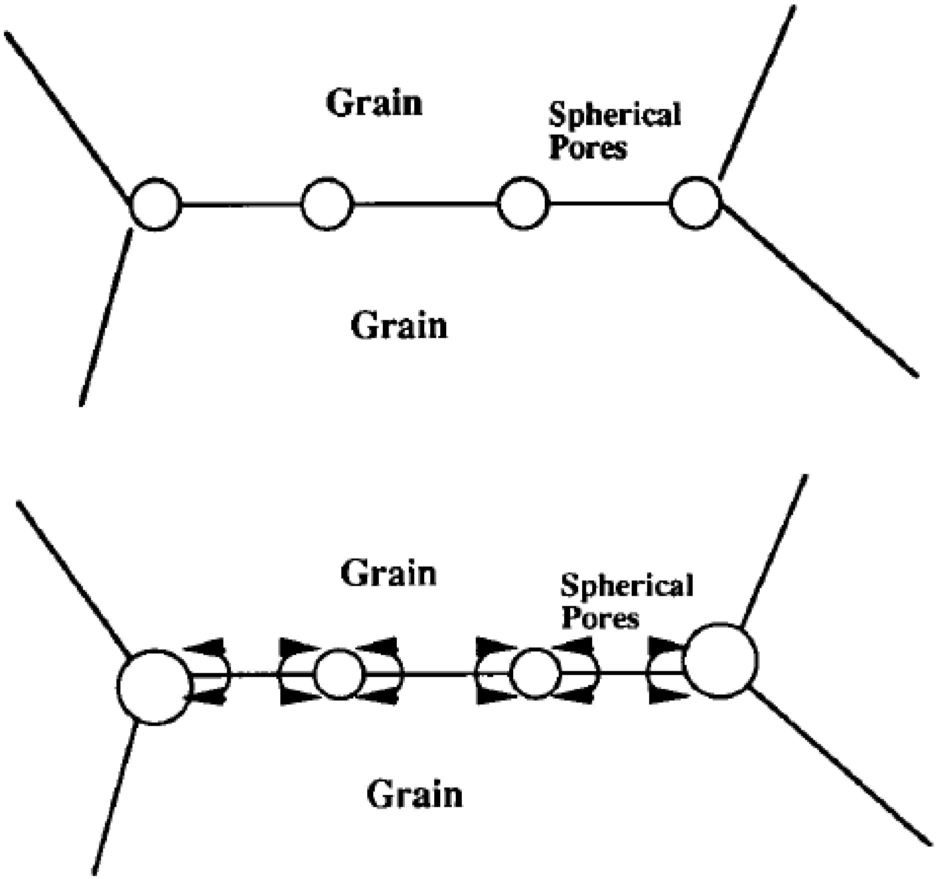
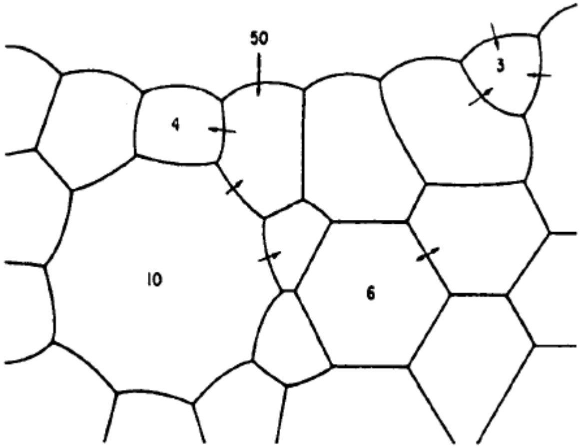
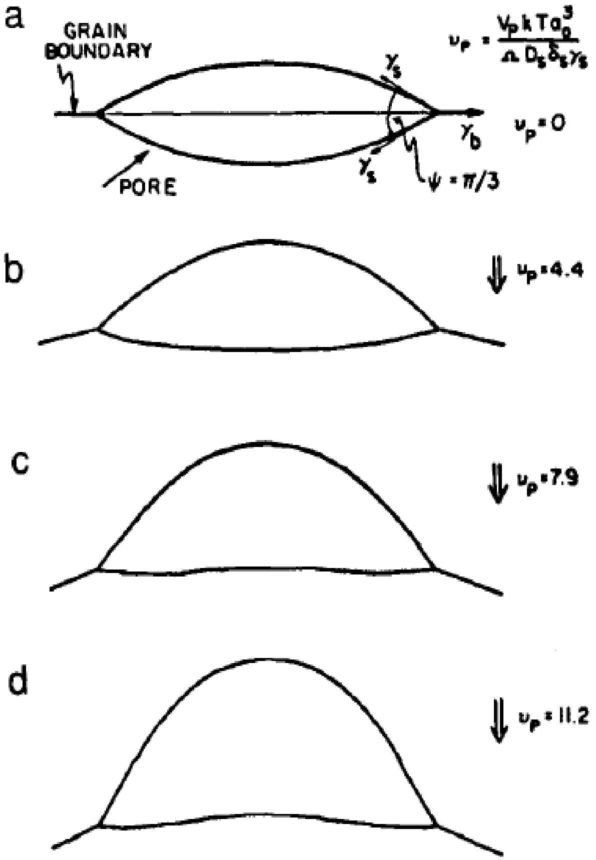


FIGURE .12 The mean diffusion distance for material transport is smaller when there are more of the same size of pores on the grain boundary

Final Stage





- •Closed pores--density >92%
- •Closed pores intersect grain boundaries
- •Pores shrink to a limiting size or disappear
- •Pores larger than the grains shrink very slowly

TYPES OF SINTERING PROCESSES

Solid state sintering,

After composed of ceramic particles in contact as shown in Figure .2. As the temperature is increased, material flows come from various sources within the ceramic green body to the neck at the intersection between particles, as shown in Figure 3 .

This neck has a negative curvature, compared to the positive curvature of the spherical ceramic particle.

TYPES OF SINTERING PROCESSES

Solid state sintering,

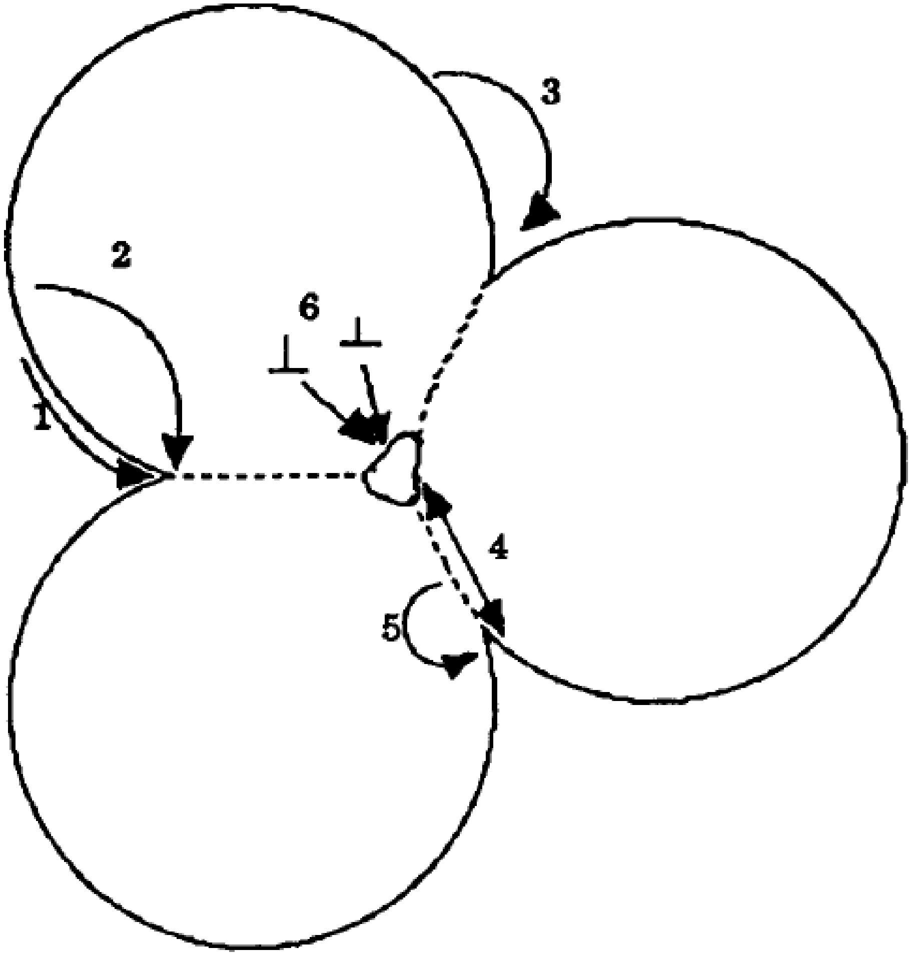
A tabulation of the possible sources of material is given in Table 1 with the transport pathway used to transport the material from the source to the neck.

These pathways are drawn on Figure 3 and consist of *surface, lattice, and grain boundary diffusion*, as well as vapor phase diffusion.

These pathways give rise to different mechanisms of sintering.

Each of these mechanisms is used to establish the kinetics of sintering.

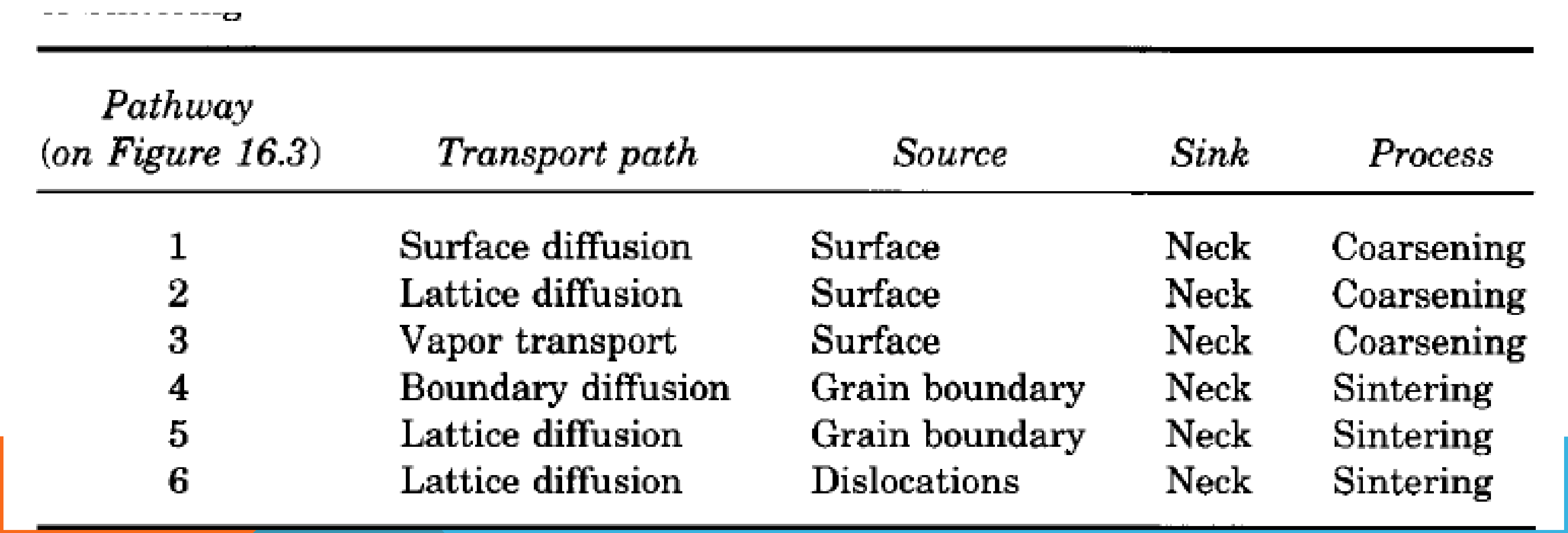
TYPES OF SINTERING PROCESSES



{*FIGURE 3* Pathways for the transport of material during the initial stage of sintering}

TYPES OF SINTERING PROCESSES

TABLE1 Pathways for the Transport of Material during the Initial Stage of Sintering



Pathway (on Figure 16.3)	*Transport path*	*Source*	*Sink*	*Process*
1	Surface diffusion	Surface	Neck	Coarsening
2	Lattice diffusion	Surface	Neck	Coarsening
3	Vapor transport	Surface	Neck	Coarsening
4	Boundary diffusion	Grain boundary	Neck	Sintering
5	Lattice diffusion	Grain boundary	Neck	Sintering
6	Lattice diffusion	Dislocations	Neck	Sintering

TYPES OF SINTERING PROCESSES

REACTIVE SINTERING

Sintering in composite systems which include phase transformation or chemical reaction takes place in the same time .

TYPES OF SINTERING PROCESSES

REACTIVE SINTERING

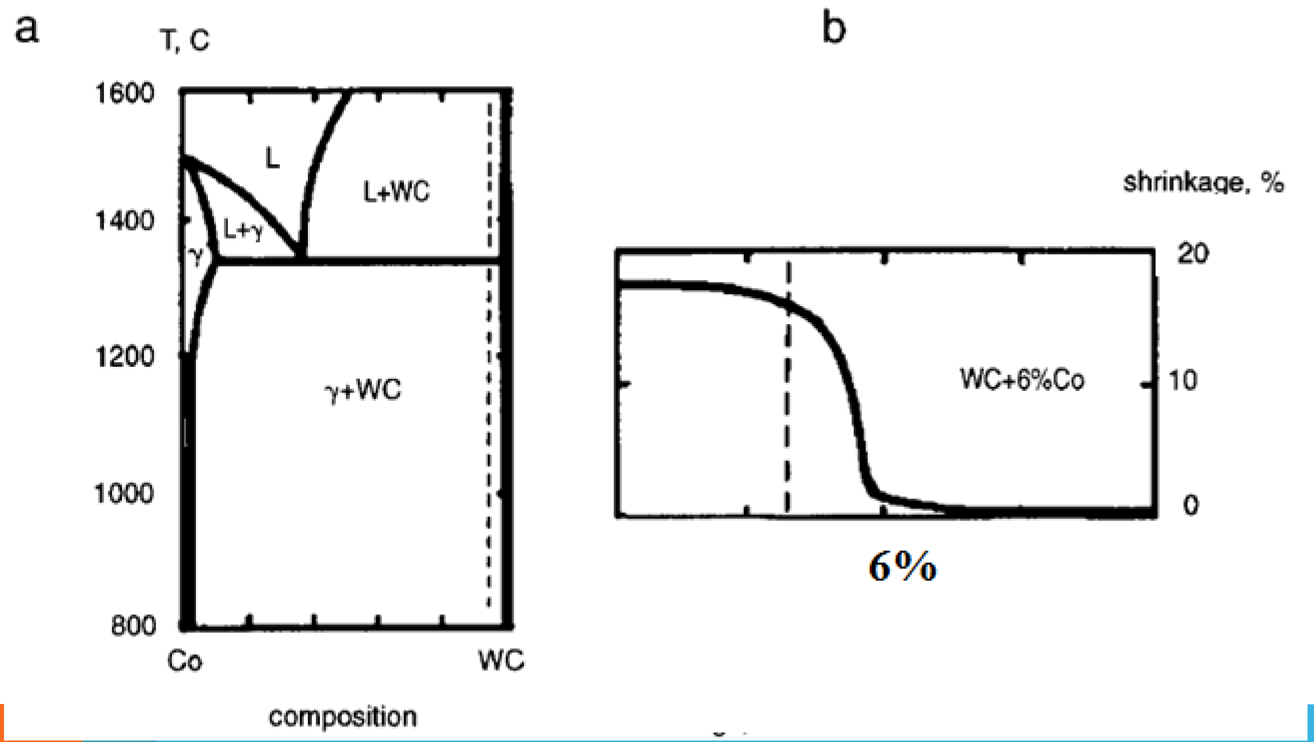
Liquid phase sintering is frequently used in ceramics processing to lower the sintering temperature of the ceramic.

For ceramics with melting temperature near 3000~ or higher, the sintering temperatures are very high, nearly 90% of the melting temperature expressed in degrees Kelvin.

To produce these materials at lower temperatures, additives are used to aid in their sintering. Such sintering aids usually melt at much lower temperatures and form a liquid phase. This liquid phase provides a vehicle for fast diffusion of a solid which, often has a small solubility in the liquid phase.

In fabrication of these: Ceramic matrix composites،
Metal and ceramic matrix composites (mixed) ،
Metal matrix composites.

TYPES OF SINTERING PROCESSES



{FIGURE 4 (a) The WC-Co phase diagram.
(b) The liquid phase, WC + 6% Co, sintering shrinkage versus temperature for WC + 6% Co}.

TYPES OF SINTERING PROCESSES

b-SINTERING WITHOUT LIQUID PHASE

During sintering of multi component green bodies, solid state reactions can take place. Examples of solid state reactive sintering are:

$$3\,TiO_2(s) + 4\,A1N(s) \rightarrow 3\,TiN(s) + 2\,Al_2O_3(s) + \frac{1}{2}N_2(g)$$

$$NiO(s) + Al_2O_3(s) \rightarrow NiAl_2O_4(s)$$
$$MgO(s) + Cr_2O_3(s) \rightarrow MgCr_2O_4(s)$$
$$ZrO_2(s) + CaO(s) \rightarrow ZrCaO_3(s)$$

TYPES OF SINTERING PROCESSES

In each case, inter diffusion of the two solids gives an **intermediate compound** found on the phase diagram .

This type of sintering takes place at temperatures below the lowest melting point in the phase diagram, typically one of the two eutectics associated with the to disagree melting intermediate compound .
This type of sintering is very complex.
In principle, the reaction is taking place by **interdiffusion**, and simultaneously each of the **individual types of reactant particles** as well as the **product of the reaction are sintering**.
The slow steps in sintering are therefore **limited** to the solid state reaction and the sintering of the intermediate compound, assuming that no liquid phase sintering can take place due to the temperature of the system.

The intermediate compound often has a **higher diffusion coefficient** than either reactant material in solid state reactive sintering, due to a *larger number of defects in its structure than the original materials.*

TYPES OF SINTERING PROCESSES

c-GAS-SOLID SINTERING

In some cases, the reaction between a gas and a solid gives a ceramic of interest, and this reaction can be used to densify the green body.

The classic example is reaction sintered Si3N4, also called reaction bonded Si3N4. The gas-solid reaction used to make reaction bonded silicon nitride is between silicon metal powder and nitrogen:

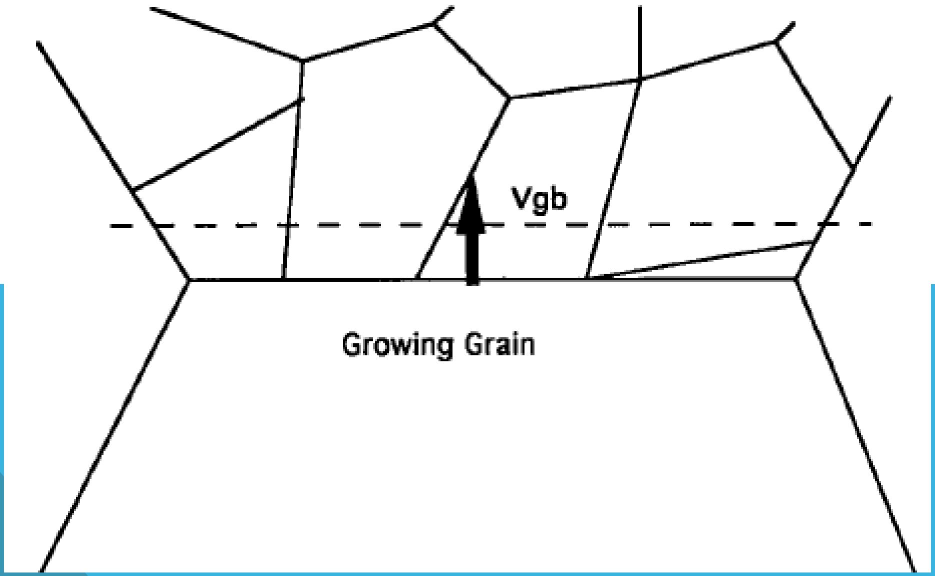
$$3\ \mathrm{Si(s)} + 2\ \mathrm{N_2(g)} \rightarrow \mathrm{Si_3N_4(s)} + \Delta H = -724\ \mathrm{kJ/mole}$$

Grain Growth

Grain growth is an integral part of sintering during the final stage because the movement of the grain boundary can be looked upon as that of a remove out micro-structural marks such as pores and inclusions.

There are two types of grain growth: normal and discontinuous or abnormal, also called secondary recrystallization (grain growth).

In abnormal grain growth, a few large grains develop and eventually consume all the smaller grains, see Figure .29



Grain Growth

1 Normal Grain Growth

In a classic model of a grain boundary growth due to atom transport under a driving force caused by the difference in surface curvature.

of the change in free energy related with the diffusion of an atom from one grain to the next is shown in Figure .32.

Due to the pressure of the surface curvature, the boundary tends to moved toward its center of curvature, as this reduces the grain boundary area (energy).

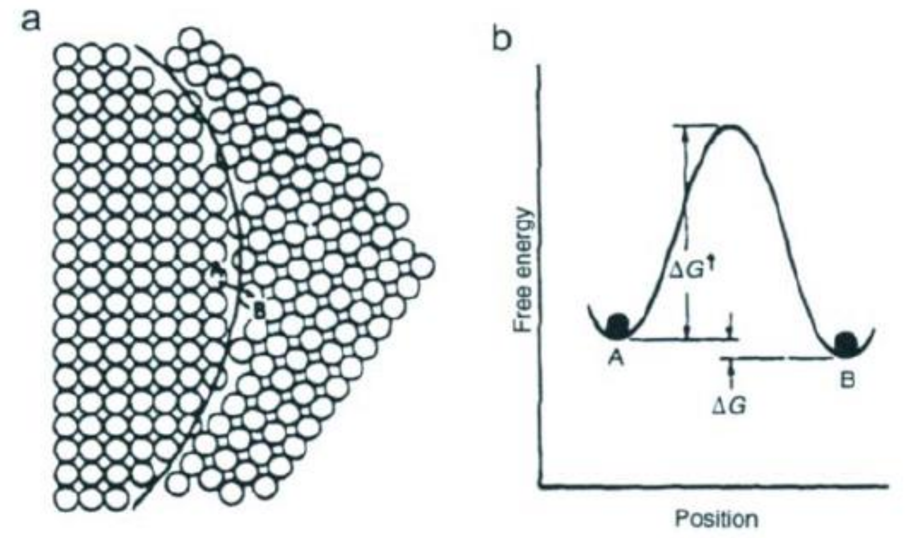


FIGURE 32 The movement of an atom from one side of the grain boundary to the other involves a change of Gibbs free energy.

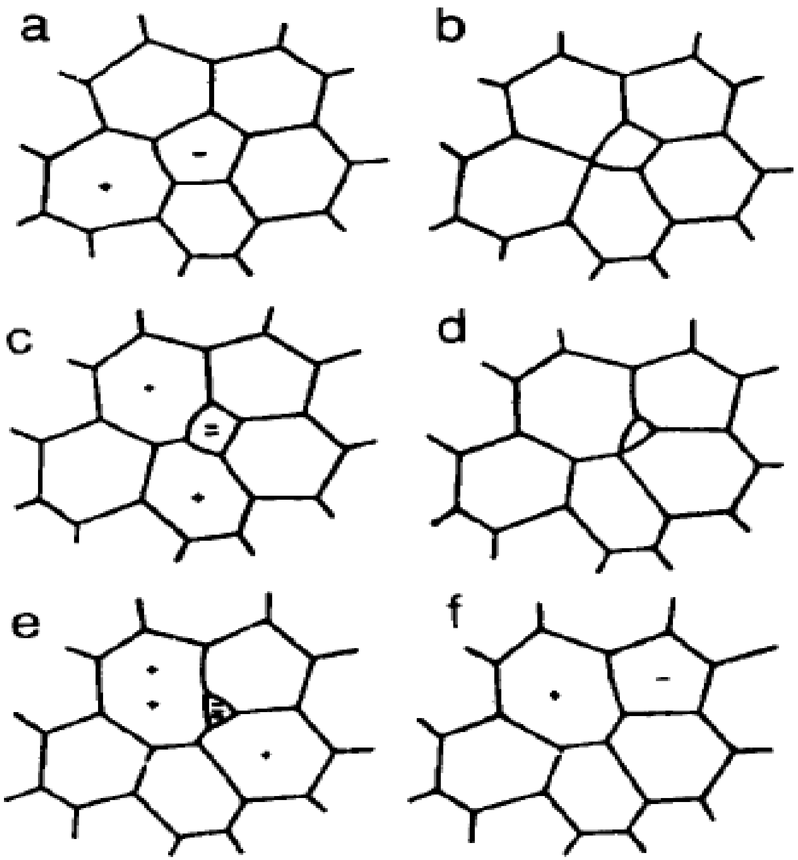


FIGURE ***34*** Unstable grain structure during normal grain growth.

2 Abnormal Grain Growth

In abnormal grain growth, a small number of grains in the population grow rapidly to a very large size, typically several orders of magnitude larger than the average in the population at the expense of the smallest particles in the distribution.

The populations that result for normal and abnormal grain growth are shown in Figure .30.

Abnormal grain growth is important because it leads to extremely large grains.

The grain boundary velocity is so large that the grain boundaries can pull away for any restraining second phase (i.e., pores or precipitates) leaving these second phases inside the large grains. Pores that are left inside large grains are trapped, and densification is essentially limited. Once abnormal grain growth starts, the grain boundary velocity different.

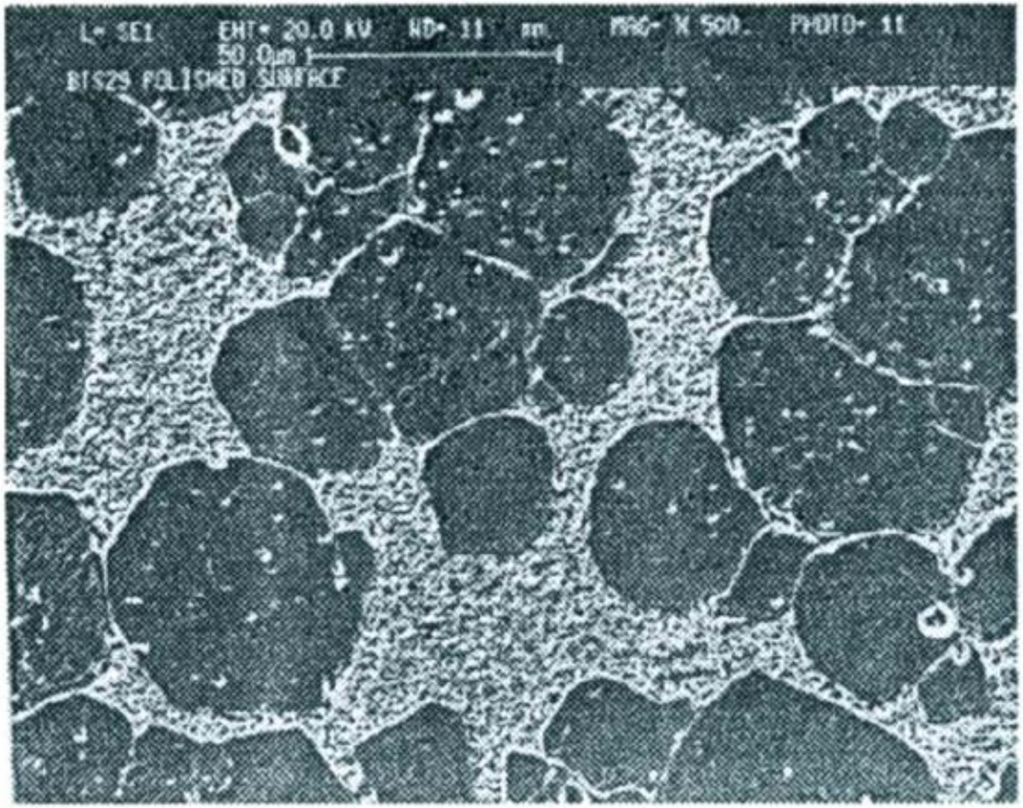


FIGURE .36 SEM BaTiO3 sintered. Abnormal grain growth is prevalent, giving large grains 50 µm in diameter in addition to small grains near 1 µm in diameter.

Cool Down after Sintering

After sintering the ceramic is cooled. The tensile stress at the surface during cooling is the most severe because ceramics are weakest in tension.

The stress at the surface are various with shapes.

Such surface stress is tensile and can lead to fracture of the sintered body if cooling is too abrupt.

The cooling rate that gives a particular surface tensile stress can be calculated from these formulas with material properties and initial and average ceramic temperatures.

If the surface stress is greater than the strength of the ceramic, cracking will result; if it is less than the strength of the ceramic, warping will result.

Even after the complete system is solid, further crystal transformations can take place as the solid is cooled to room temperature.

A material will have different crystal structures which are stable at different temperatures.

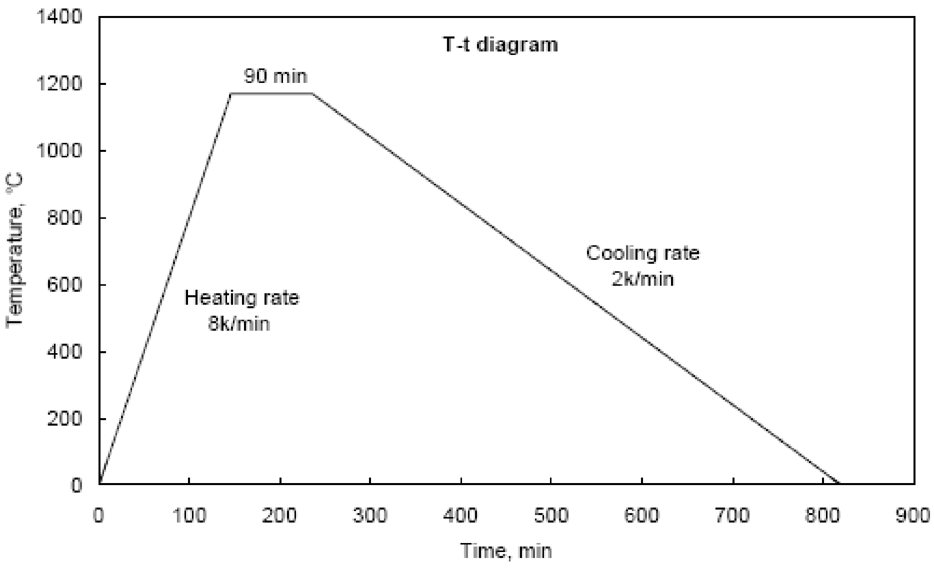
This phenomena is called polymorphism.

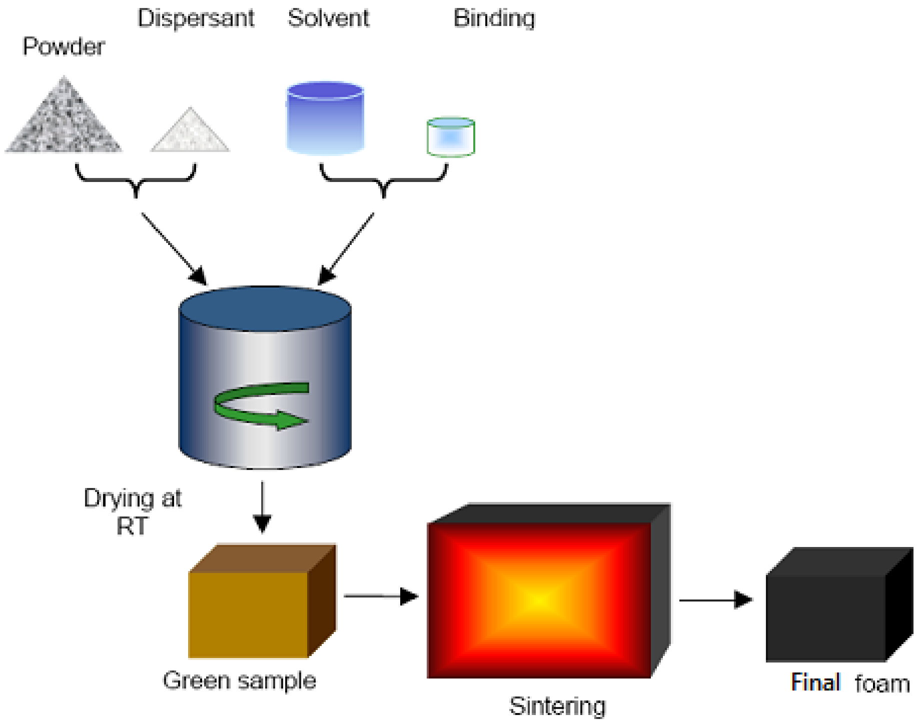
Polymorphic transformations occur during heating and cooling of a material.

During heating, the different crystal structures increase in molar volume abruptly at particular transformation temperatures.

This is generally not a problem, as the individual grains are not constrained.

But on cooling after sintering, the sudden decrease in volume of either one component of a multicomponent polycrystalline ceramic or one grain of a polycrystalline ceramic with random grain orientations can cause high internal stresses which may cause cracking.


T-t diagram
90 min
Heating rate
8k/min
Cooling rate
2k/min
Temperature, °C
1400
1200
1000
800
600
400
200
0
0
100
200
300
400
500
600
700
800
900
Time, min


Powder
Dispersant
Solvent
Binding
Drying at
RT
Green sample
Sintering
Final foam

plate

$$\sigma_y = \sigma_z = \frac{E\alpha_T}{1-\nu}(T_a - T_s) \qquad \frac{T_a - T_s}{T_i - T_s} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2\alpha' t}{4x_0^2}\right]$$

cylinder

$$\frac{T_a - T_s}{T_i - T_s} = \sum_{n=1}^{\infty}\frac{4}{\xi_n^2}\exp\left[\frac{-\xi_n^2\alpha' t}{R_0^2}\right]^c$$

$$\sigma_\theta = \frac{E\alpha_T}{1-\nu}(T_a - T_s)$$

Sphere

$$\frac{T_a - T_s}{T_i - T_s} = \frac{6}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{n^2}\exp\left(\frac{-n^2\pi^2\alpha' t}{R_0^2}\right)$$

$$\sigma_\theta = \frac{E\alpha_T}{1-\nu}(T_a - T_s)$$

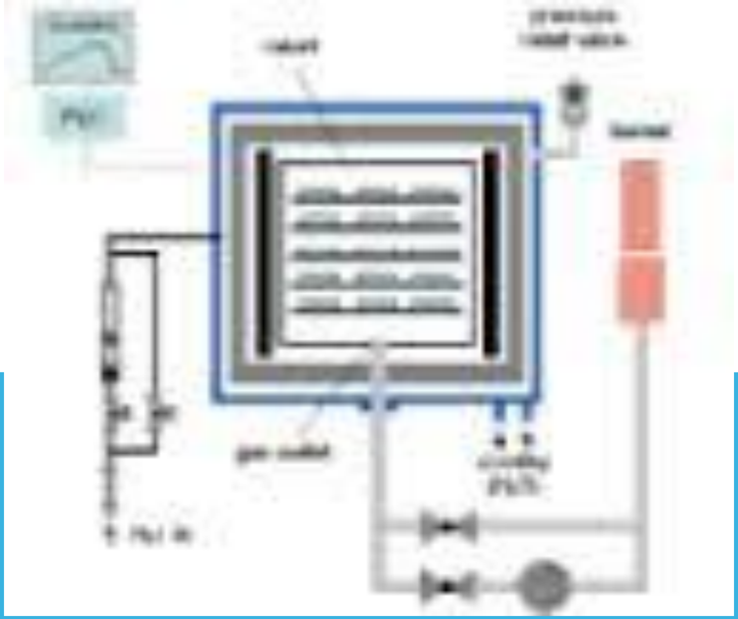
SINTERING ACHIEVEMENT

There are two methods to accomplish different sintering process:

1) sintering heat only.
2) sintering using concurrent pressure and heat.

SINTARING

In this type sintering traditionally occur as a direct effect of heat previously mentioned



INFILTRATION

Sintering and then infiltration a liquid material:

Infiltration and low-pressure infiltration techniques

In order to develop these processes the good wetability is important ,and good flow and pressure distribution of molten in perform.

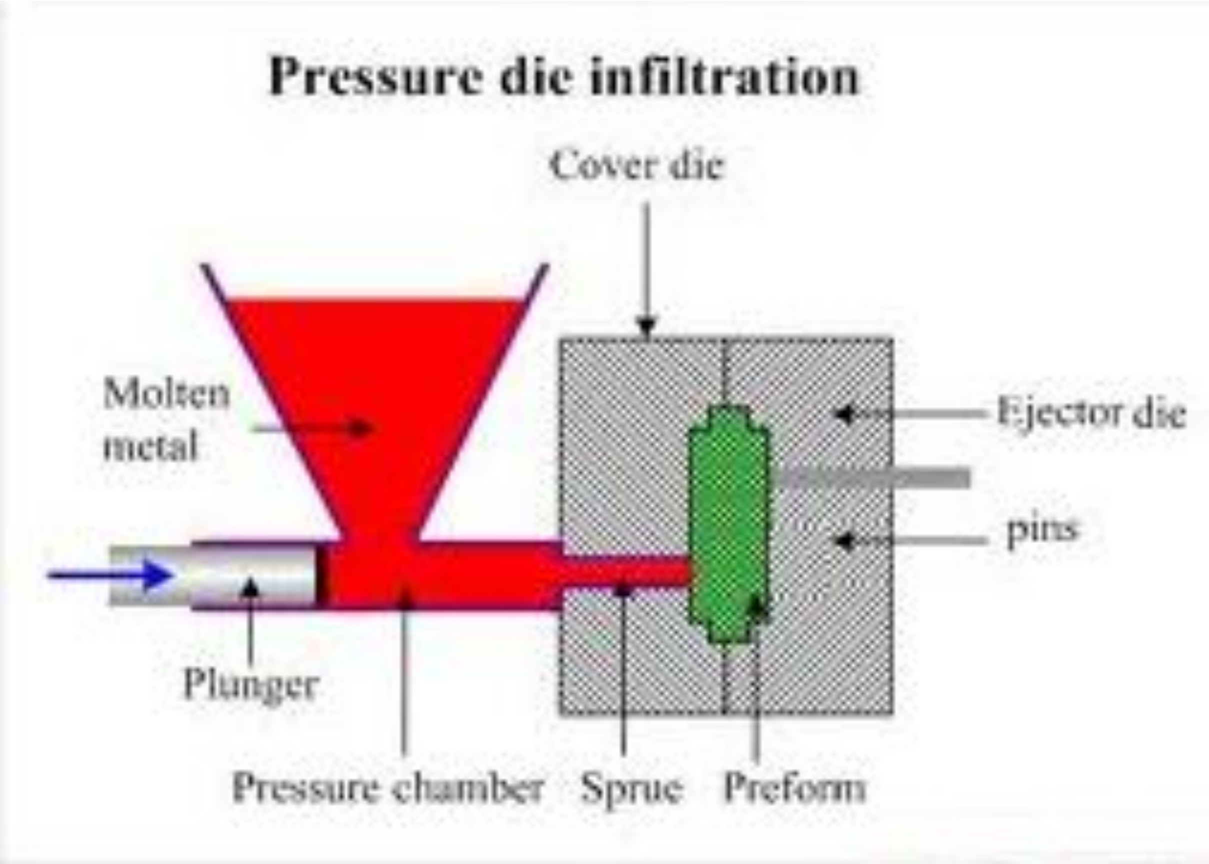
This composite was applied to automobile engine piston.

DURING INFILTRATION, a liquid, metal mass or front moves through or penetrates the pore system of a solid-phase powder compact.

This process is similar to liquid-phase sintering, in which one of the constituent powders of a compact melts and disperses throughout the compact in situ.

Voids are filled by shrinkage and particle rearrangement.

During infiltration, liquid externally contacts the porous solid, and capillary forces draw it inward.



Pressure die infiltration

HOT PRESSING

Hot pressing is similar to cold pressing of ceramic powders, where a die is used, but the die is heated to temperatures approximately half the absolute melting temperature of the material.

Hot pressing is one of the methods used to obtain densification without the abnormal grain growth seen in solid state sintering.

This is because other densification mechanisms, like aggregate fragmentation, particle rearrangement, plastic flow, and diffusion creep, are important in hot pressing.

Pressure sintering is usually not used when a liquid phase is present because the liquid is squeezed out of the ceramic.

Dies of graphite, carbide, boride, and molybdenum are often used, but they are expensive and subject to excessive , wear and oxidation at temperatures greater than 1200- 1500C Hot pressed shapes are limited as a result of die geometry.

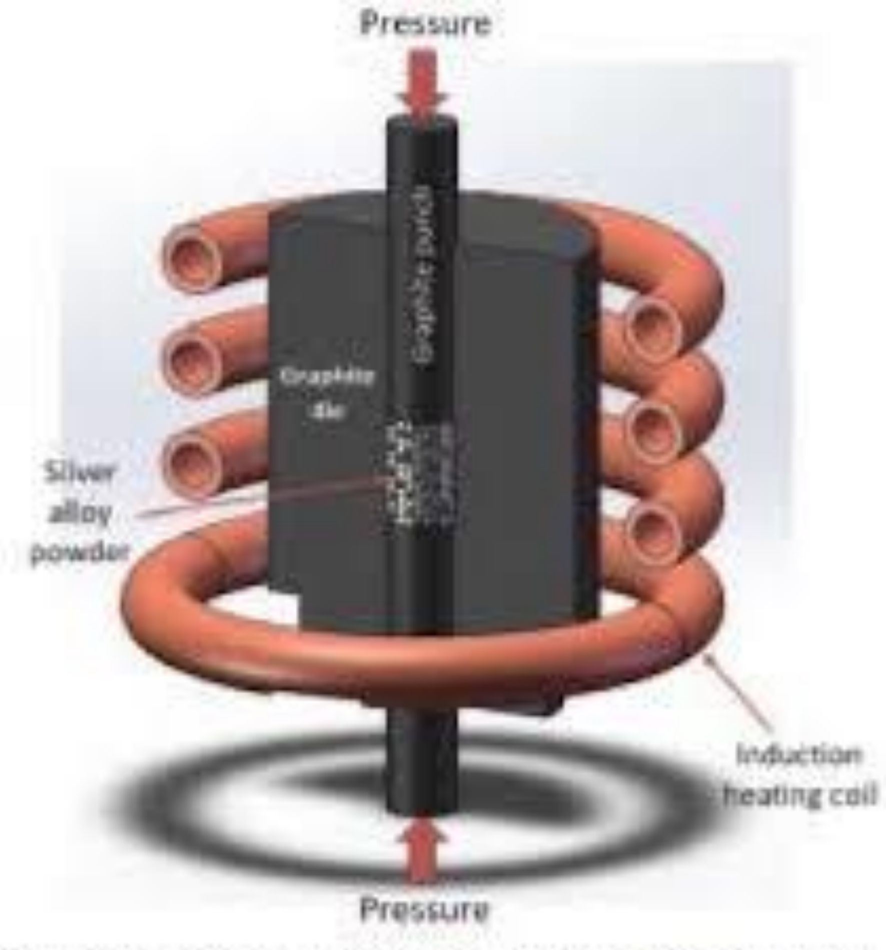
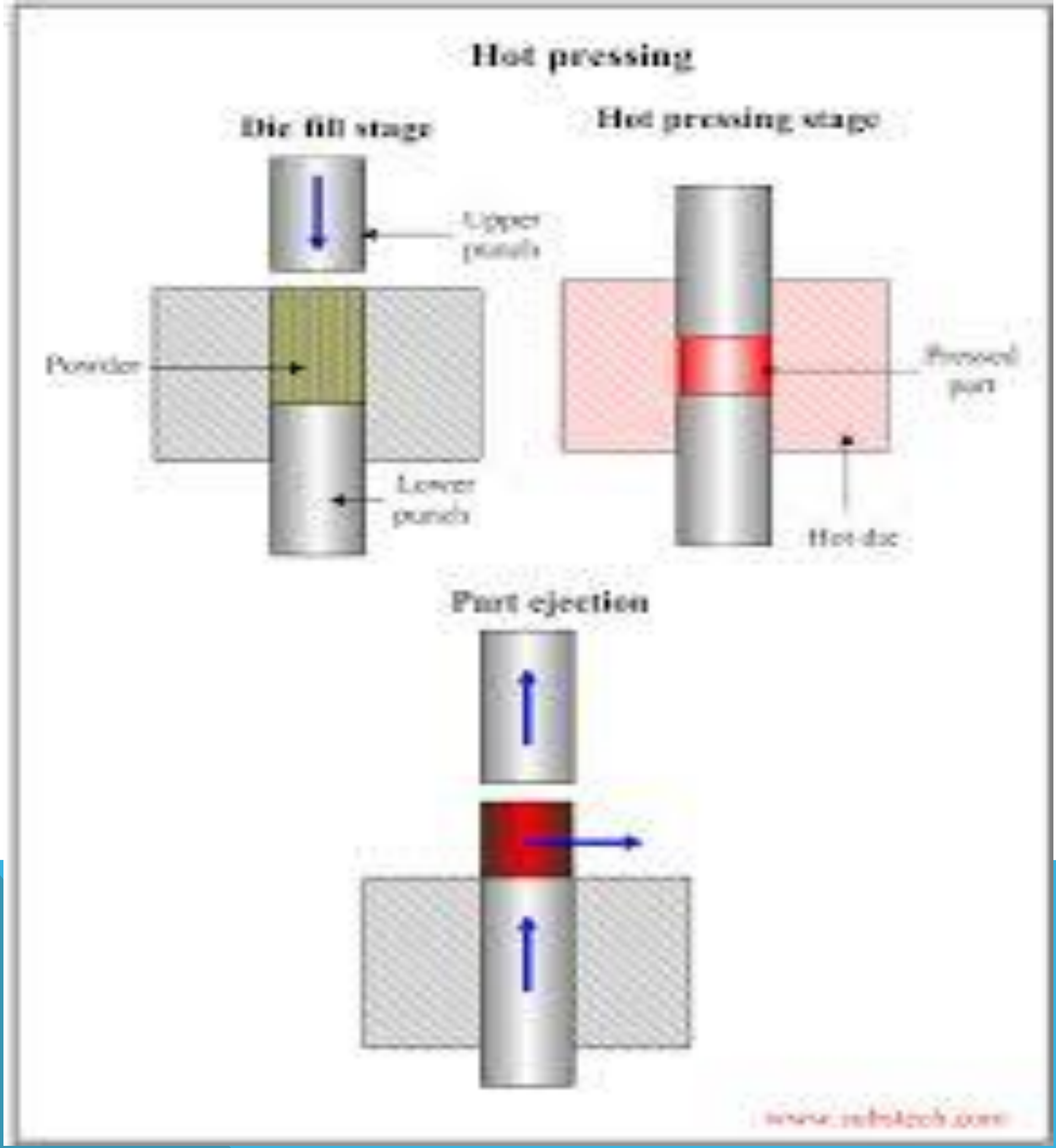


Figure 3. The hot pressing process: schematic of the apparatus.


Hot pressing
Die fill stage
Hot pressing stage
Upper punch
Powder
Lower punch
Pressed part
Hot die
Part ejection
www.substech.com

HOT ISOSTATIC PRESSING HIP

In hot isostatic pressing (HIP), an electric furnace is place inside a pressure vessel.

The pressurizing fluid is a gas like argon or helium.

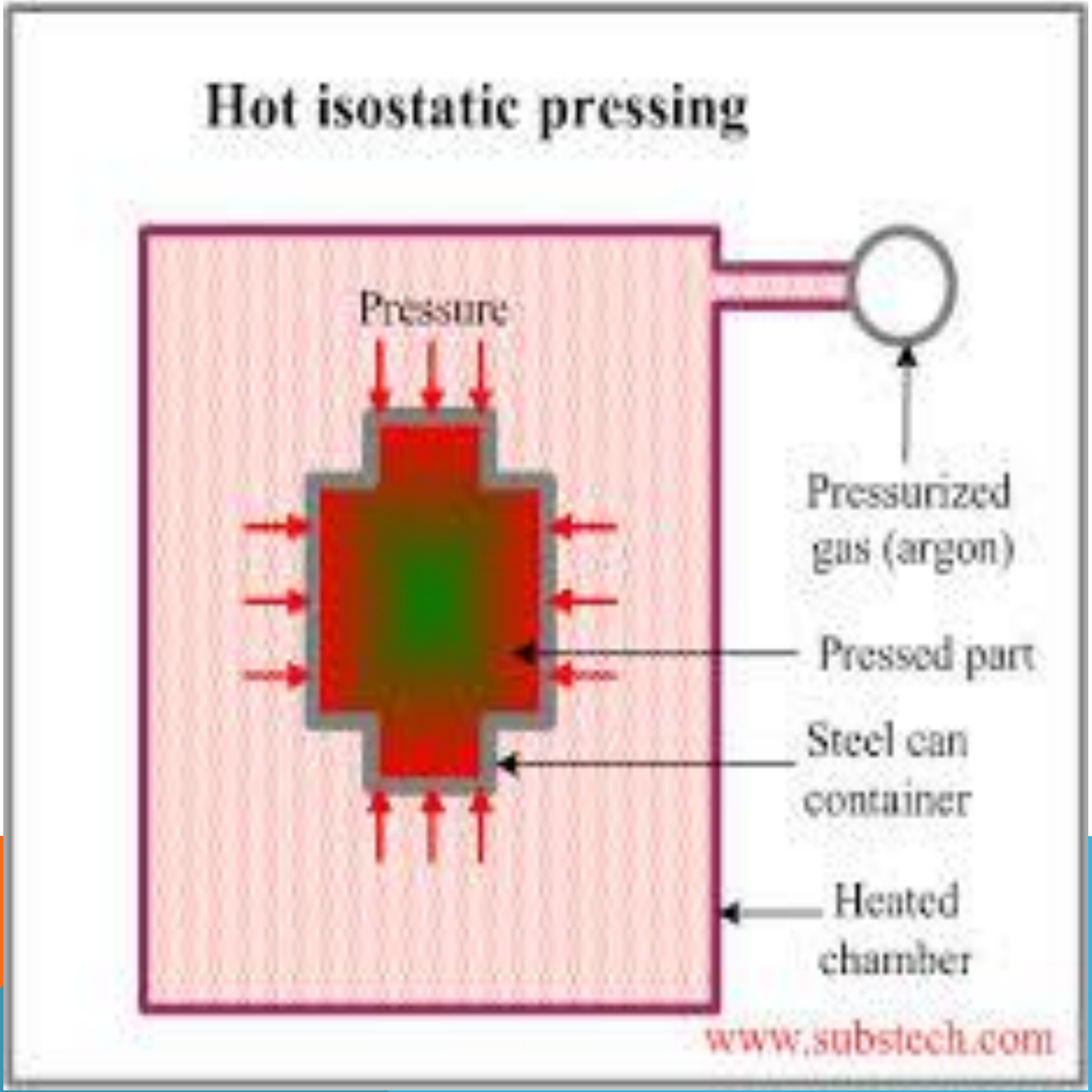
To achieve densification of a ceramic green body, the body must be evacuated and sealed in a gas-impermeable vessel.

If there are any leaks in the seal, the ceramic body cannot be pressure sintered.

Early gas-impermeable vessels were metallic tantalum cans.

Later metal powder or glass encapsulation have been used.

The encapsulation layer is first sintered into a gas-impermeable layer before hot isostatic pressing.


Hot isostatic pressing
Pressure
Pressurized gas (argon)
Pressed part
Steel can container
Heated chamber
www.substech.com

With glass encapsulation, a glass perform is used as a receptacle for the ceramic.

The glass vessel is evacuated and sealed.

It then deforms to the ceramic body's shape during hot isostatic pressing.

Recently, a glass particulate coating has been applied to ceramic bodies to encapsulate them].

In the pressure vessel, evacuation takes place and the temperature is raised to soften the glass until it forms a continuous layer on the ceramic body.

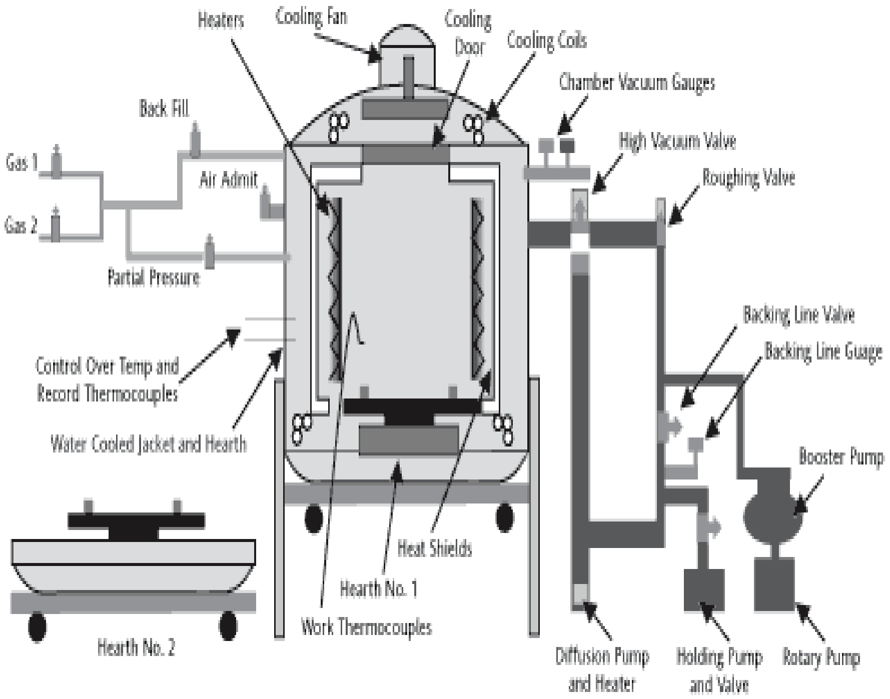
The temperature and pressure are then increased to densify the ceramic body.

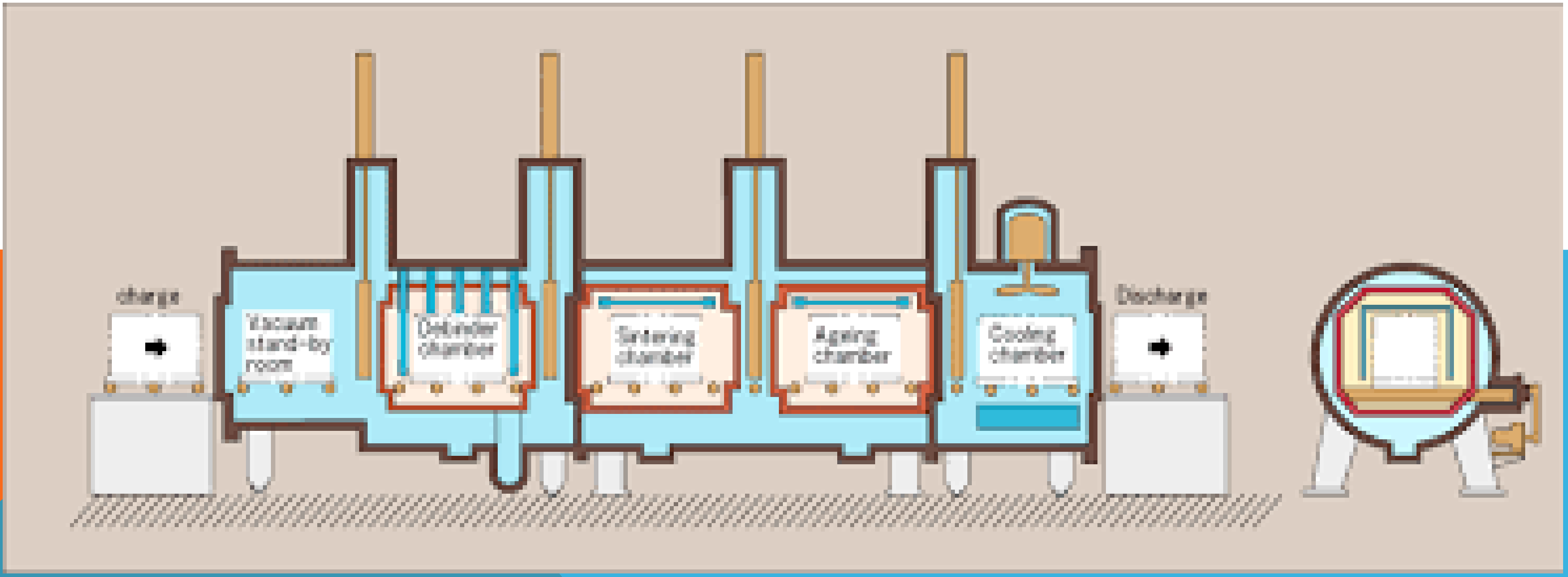
VACUUM SINTERING

Vacuum furnaces are used to high temperatures - treatment processes, and vary in size and capacity.

Equipment has been improved continuously over the past 30 years, so that the application of vacuum treatment is used widely in the aerospace and automotive industries.

When the vacuum pressure is less than atmospheric pressure.


Heaters
Cooling Fan
Cooling Door
Cooling Coils
Chamber Vacuum Gauges
Back Fill
High Vacuum Valve
Gas 1
Air Admit
Roughing Valve
Gas 2
Partial Pressure
Backing Line Valve
Backing Line Guage
Control Over Temp and Record Thermocouples
Water Cooled Jacket and Hearth
Booster Pump
Heat Shields
Hearth No. 1
Work Thermocouples
Hearth No. 2
Diffusion Pump and Heater
Holding Pump and Valve
Rotary Pump


charge
Vacuum stand-by room
Debinder chamber
Sintering chamber
Ageing chamber
Cooling chamber
Discharge

SINTERING FURNACES AND SINTERING ATMOSPHERE

Sintering indirect heating ..

It means the body heat conduction by Convection or radiation with the help of another is heating medium .

1 – sintering by Dipped in a liquid medium, which includes : -

A - sintering in liquid salt B - sintering in liquid metal .C - sintering in an inert powder

2 - sintering direct heating

The advantage of this method of heating comes as compared with the indirect method of heating :

A . Sintering direct heating effect of electrical resistance .

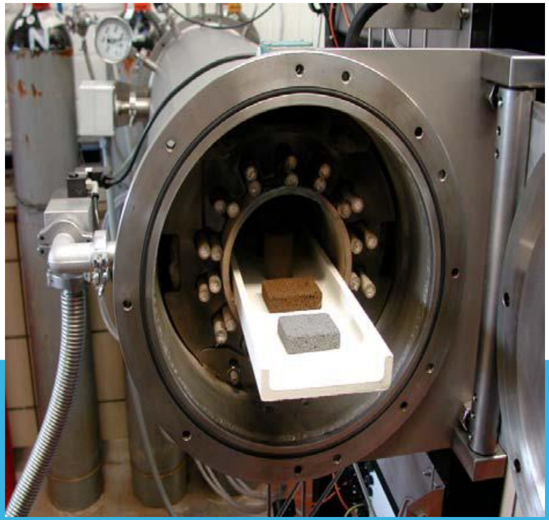
B . Sintering direct heating effect of electric induction .

Section 7

Case of sintering

1- Constant sintering

2 - Continuous sintering



FURNACE ATMOSPHERE

Atmosphere furnace control is enter an inert gas, fillings and absorbent material

inert gas system

Atmosphere furnace inert gas

absorbent material