Ceramics Materials Manufacturing

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2017

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

a-SINTERING WITH LIQUID PHASE

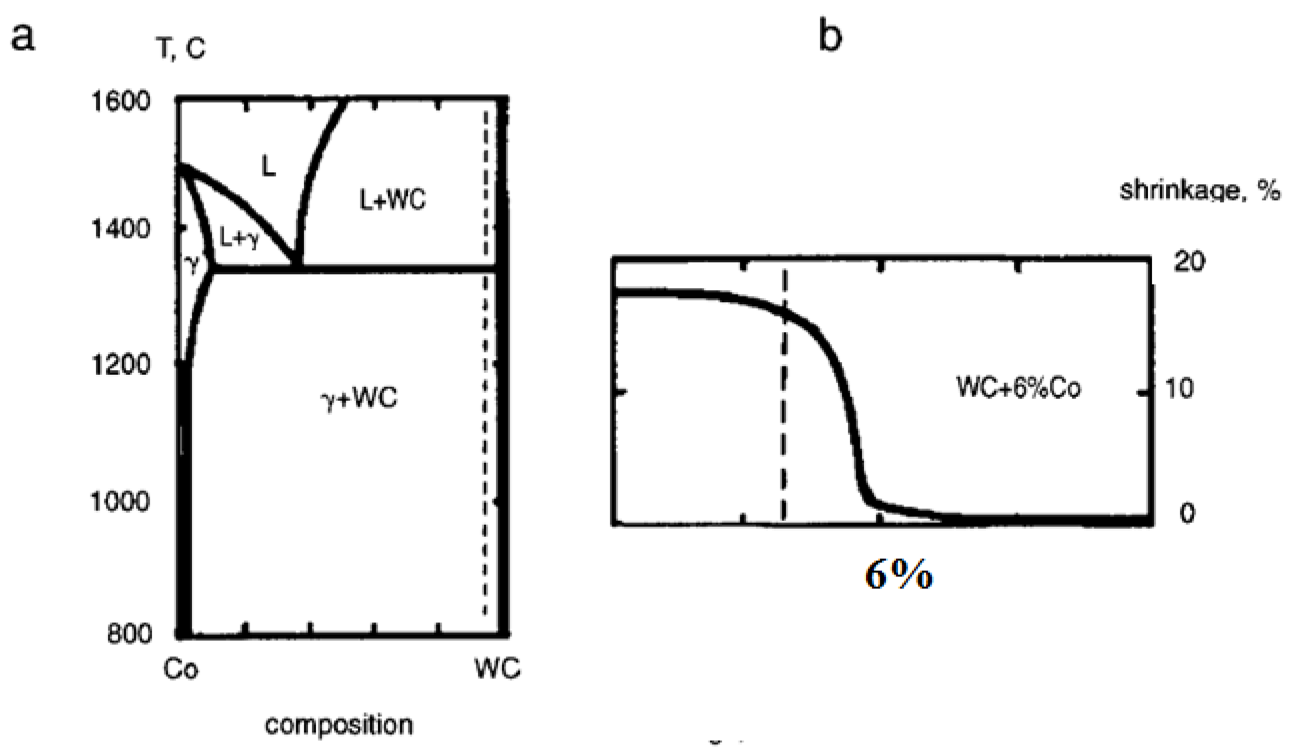
Liquid phase sintering is frequently used in ceramics processing to lower the sintering temperature of the ceramic.

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:

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

$$\begin{gathered} NiO(s) + Al_2O_3(s) \rightarrow NiAl_2O_4(s) \\ MgO(s) + Cr_2O_3(s) \rightarrow MgCr_2O_4(s) \\ ZrO_2(s) + CaO(s) \rightarrow ZrCaO_3(s) \end{gathered}$$

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:

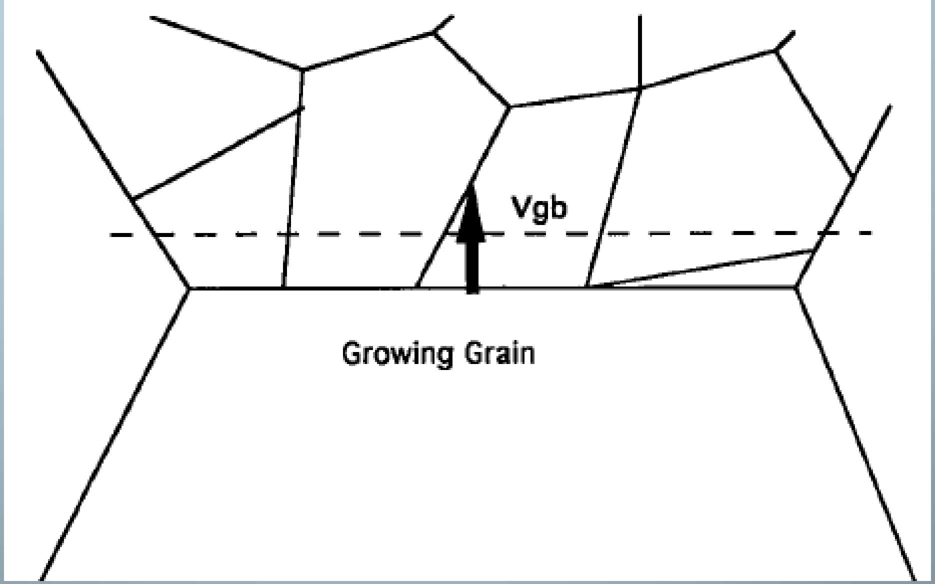
$$3\ \mathrm{Si(s)} + 2\ \mathrm{N_2(g)} \rightarrow \mathrm{Si_3N_4(s)} + \Delta H = -724\ \mathrm{kJ/mole}$$

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).

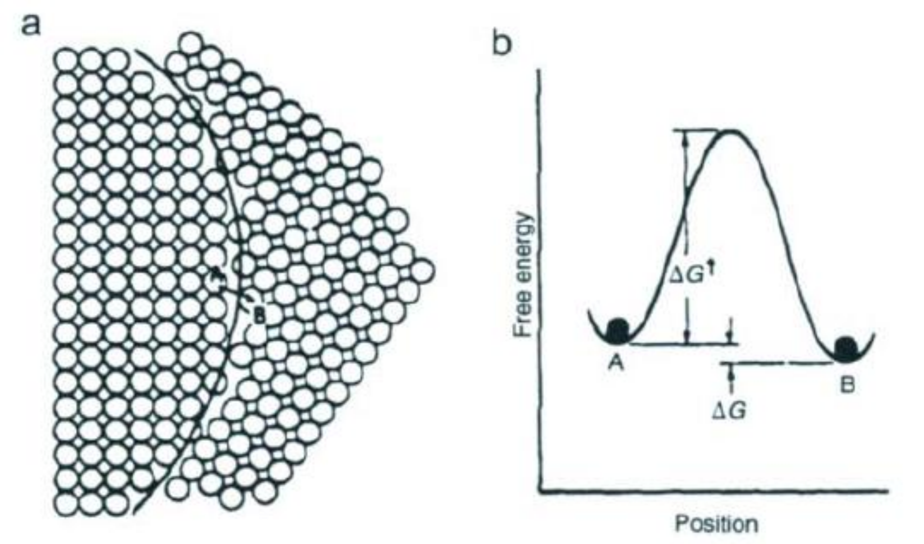


FIGURE 32 The movement of an atom from one side of the grain boundary to the other involves a change of Gibbs free energy.

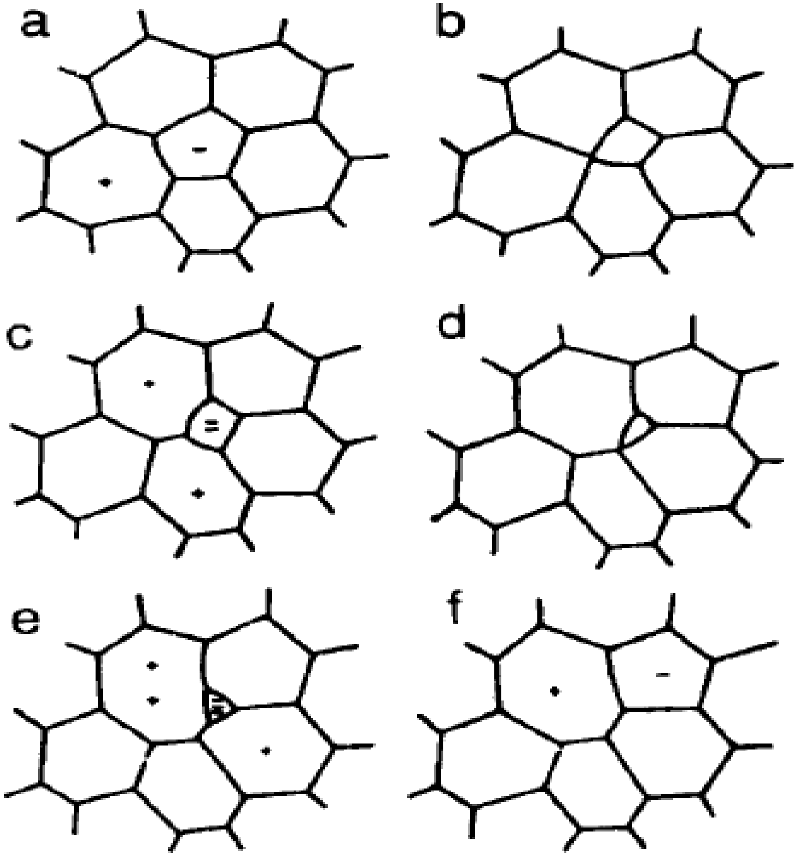


***FIGURE* 34** Unstable grain structure during normal grain growth.

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.

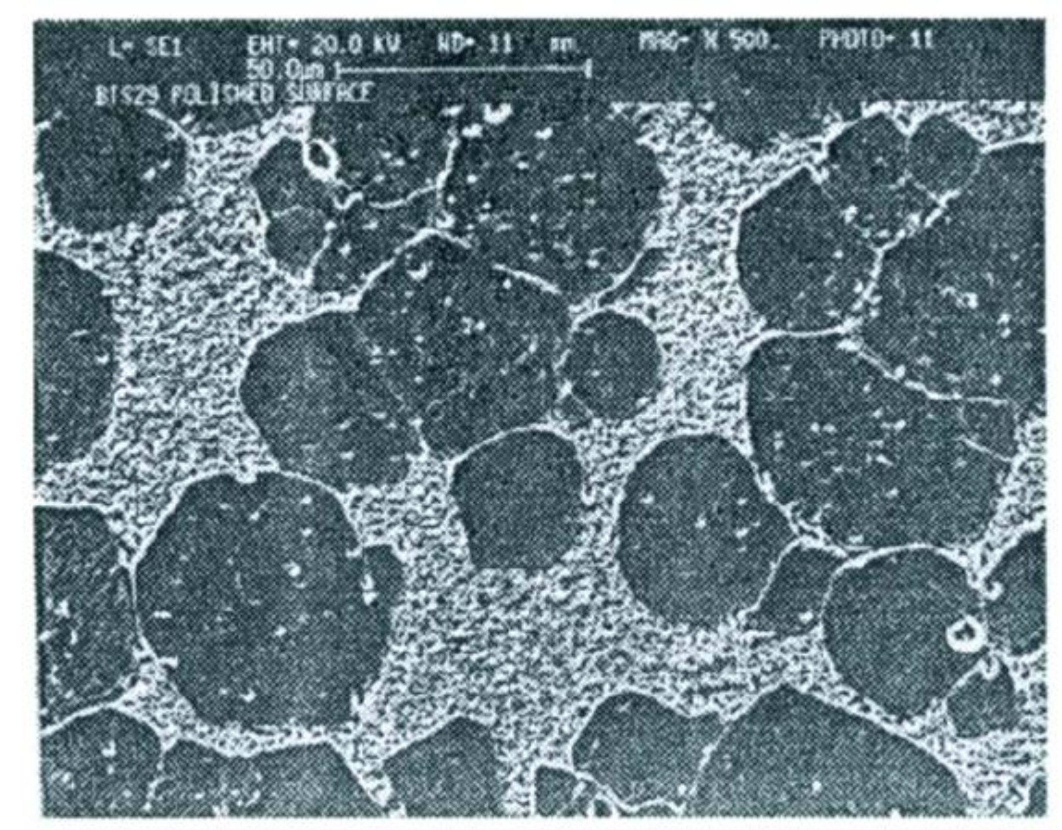


FIGURE .36 SEM BaTiO3 sintered. Abnormal grain growth is prevalent, giving large grains 50 μm in diameter in addition to small grains near 1 μm in diameter.

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.

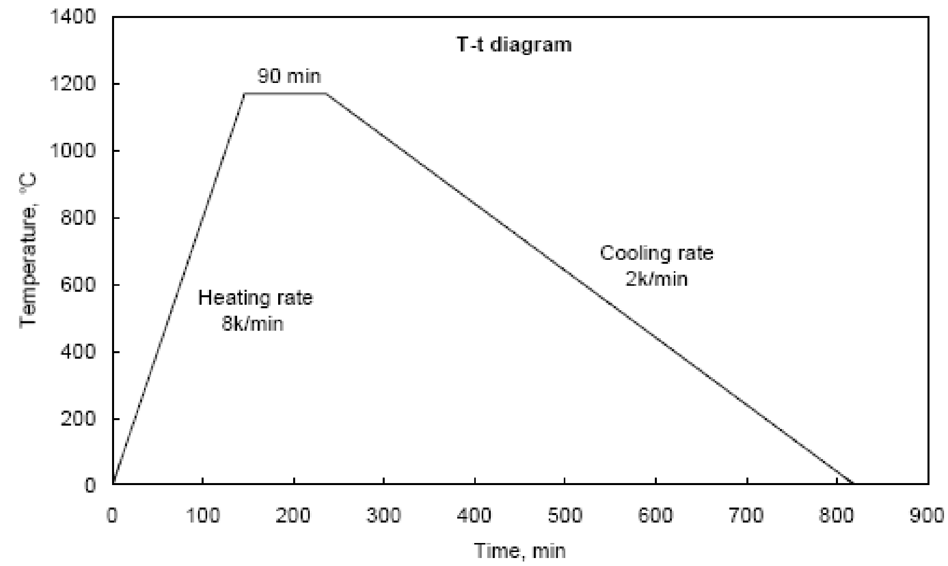
This phenomena is called polymorphism.

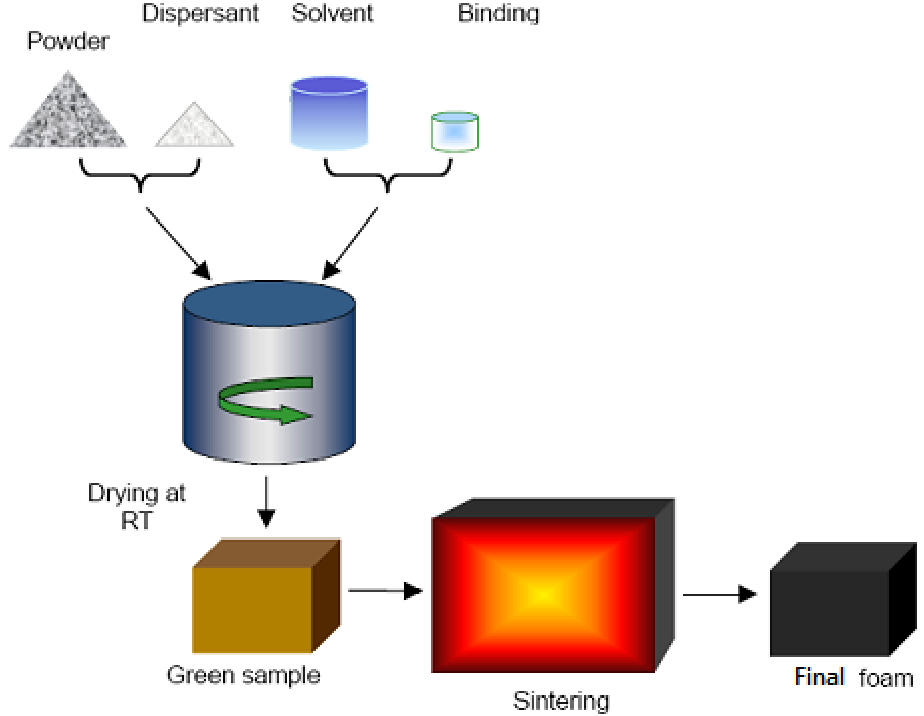
Polymorphic transformations occur during heating and cooling of a material.

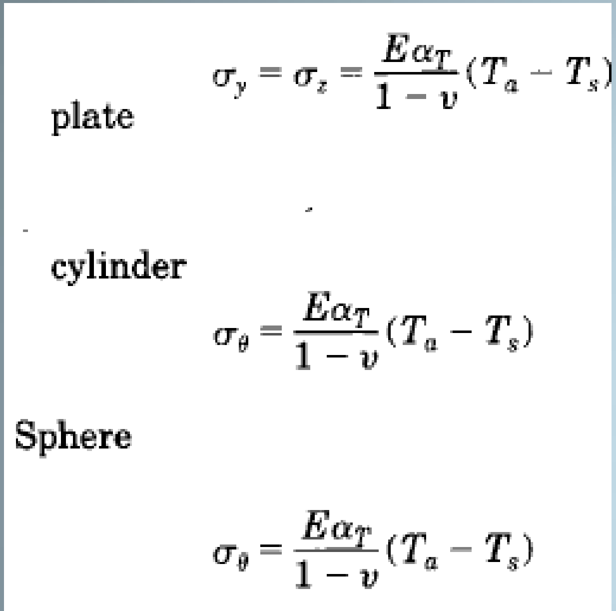
During heating, the different crystal structures increase in molar volume abruptly at particular transformation temperatures.

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
Time, min
0
200
400
600
800
1000
1200
1400
0
100
200
300
400
500
600
700
800
900


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



plate

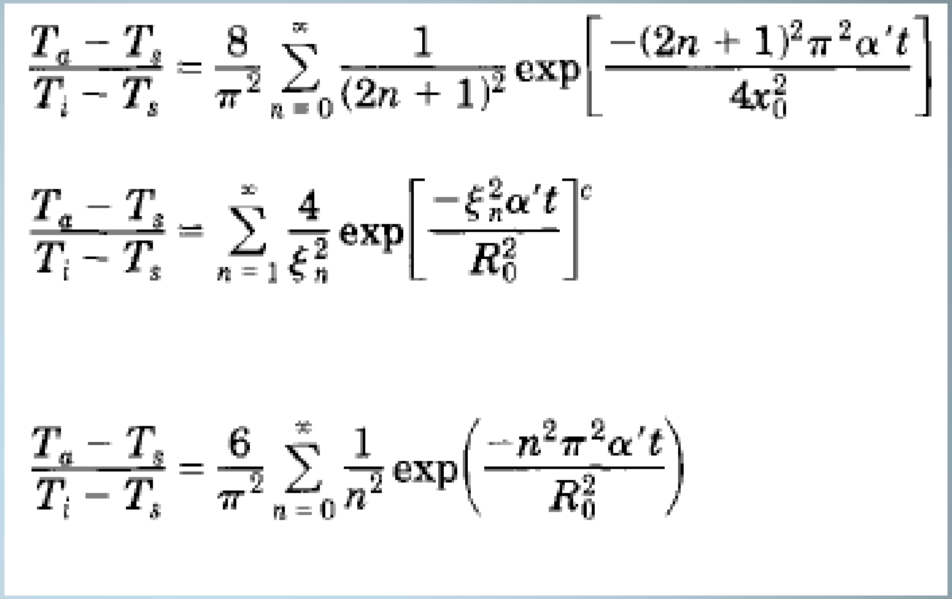
$$\sigma_y = \sigma_z = \frac{E\alpha_T}{1-\nu}(T_a - T_s)$$

cylinder

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

Sphere

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



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

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

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

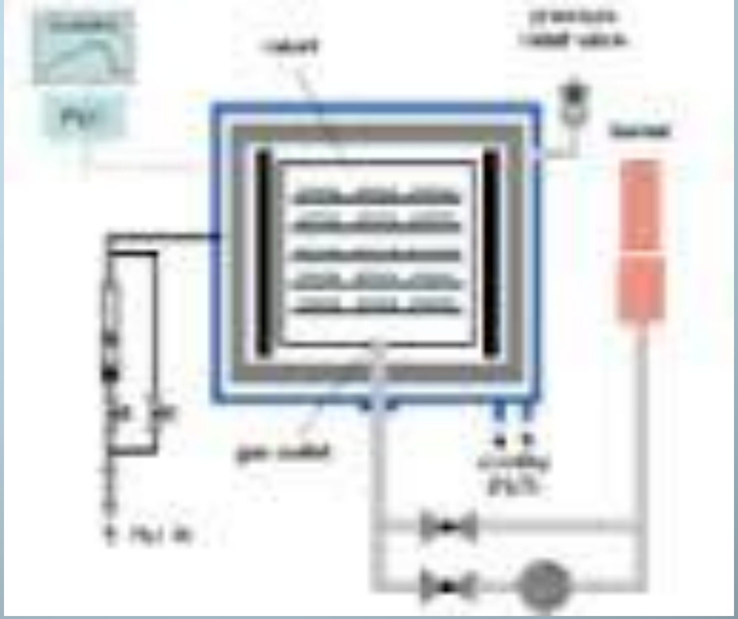
SINTERING ACHIEVEMENT

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.

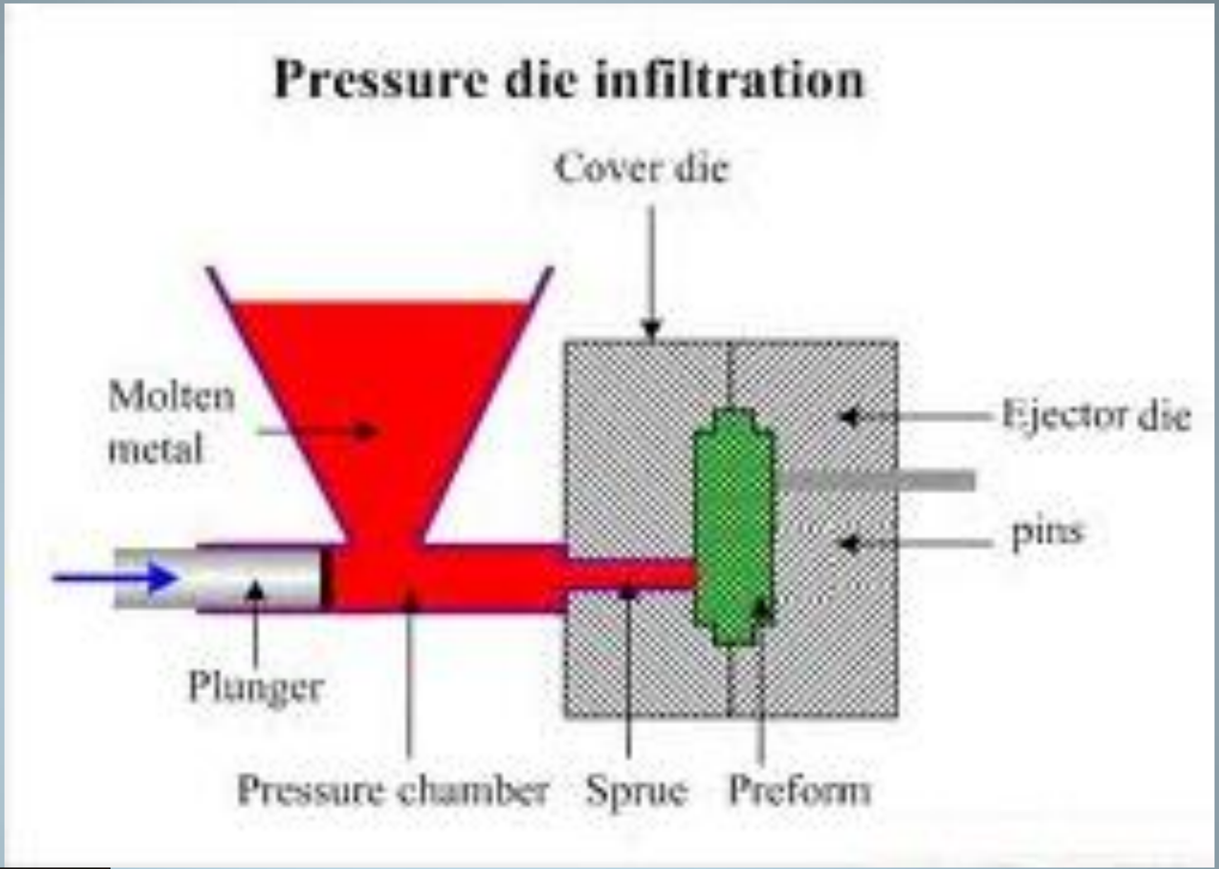
This composite was applied to automobile engine piston.

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
Cover die
Molten metal
Ejector die
pins
Plunger
Pressure chamber
Sprue
Preform


10
20
30
40
No.101C

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.

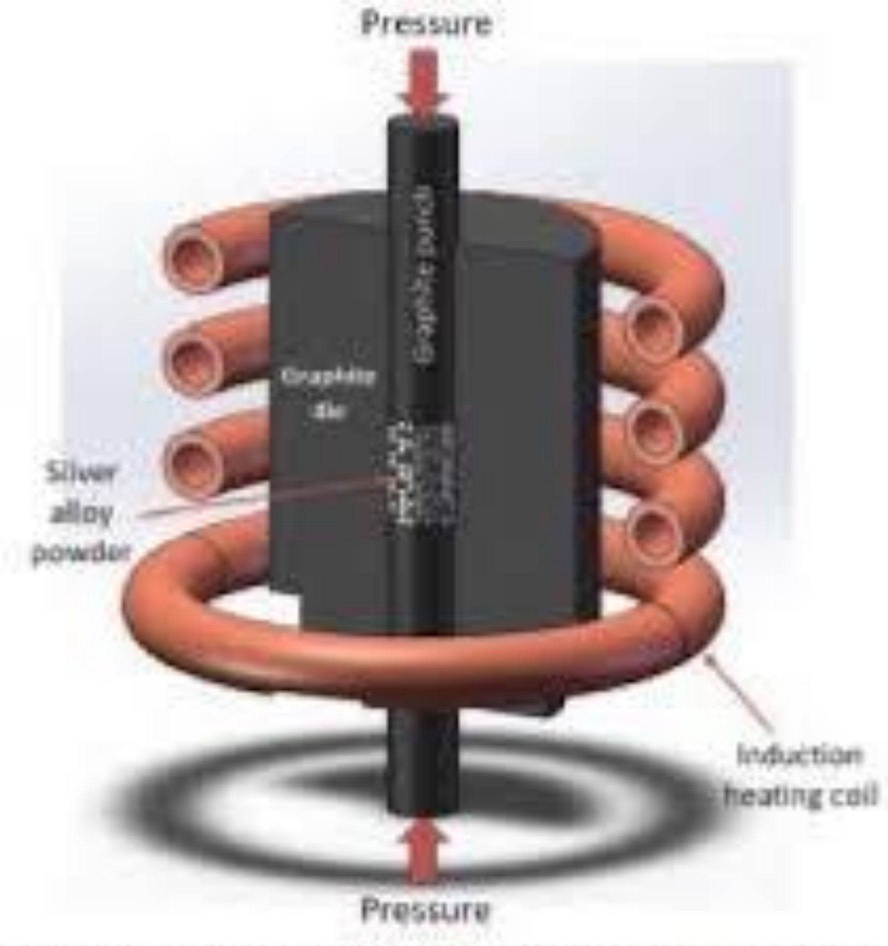
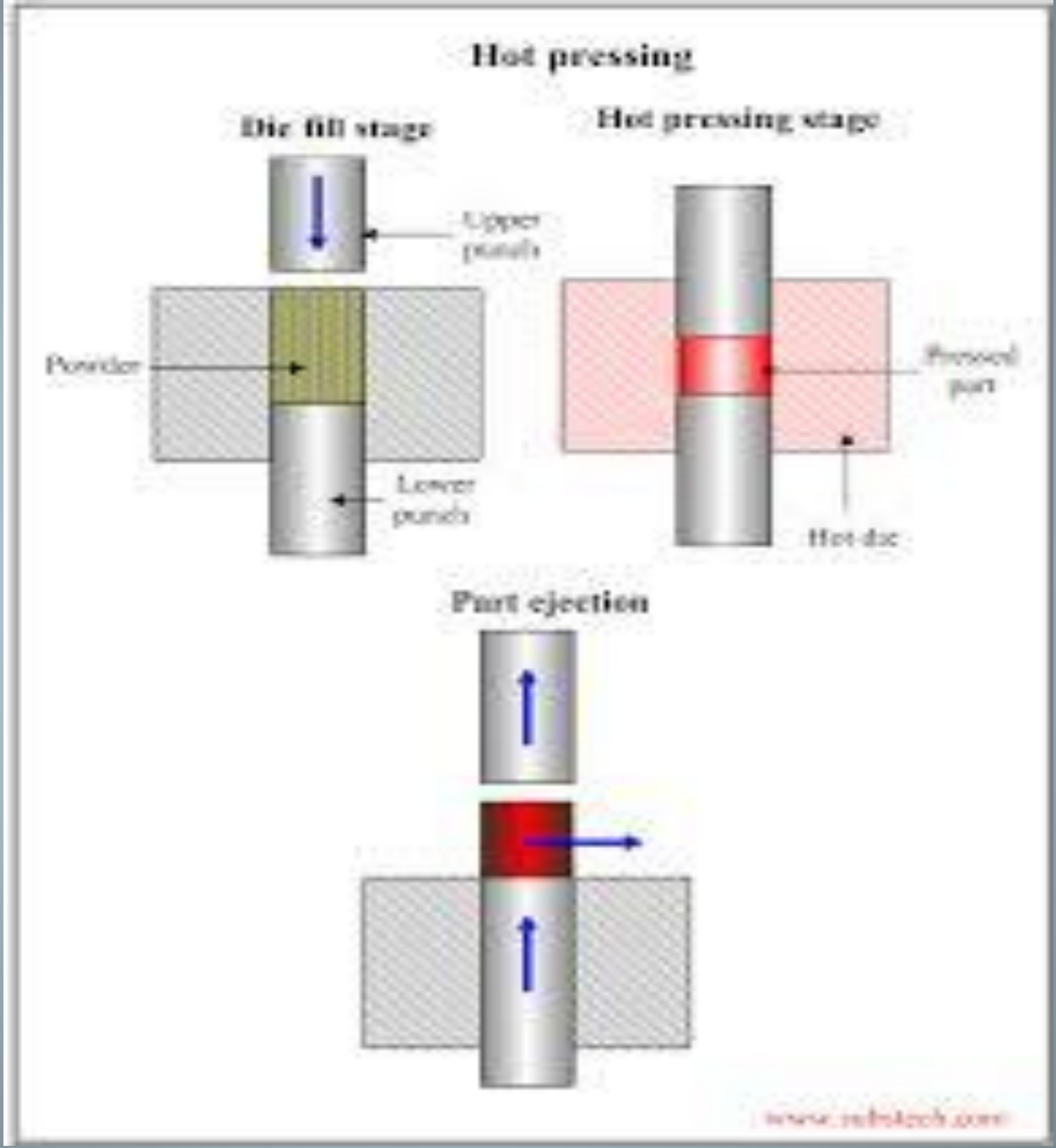


Figure 3. The hot pressing process: schematic of the apparatus.



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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.

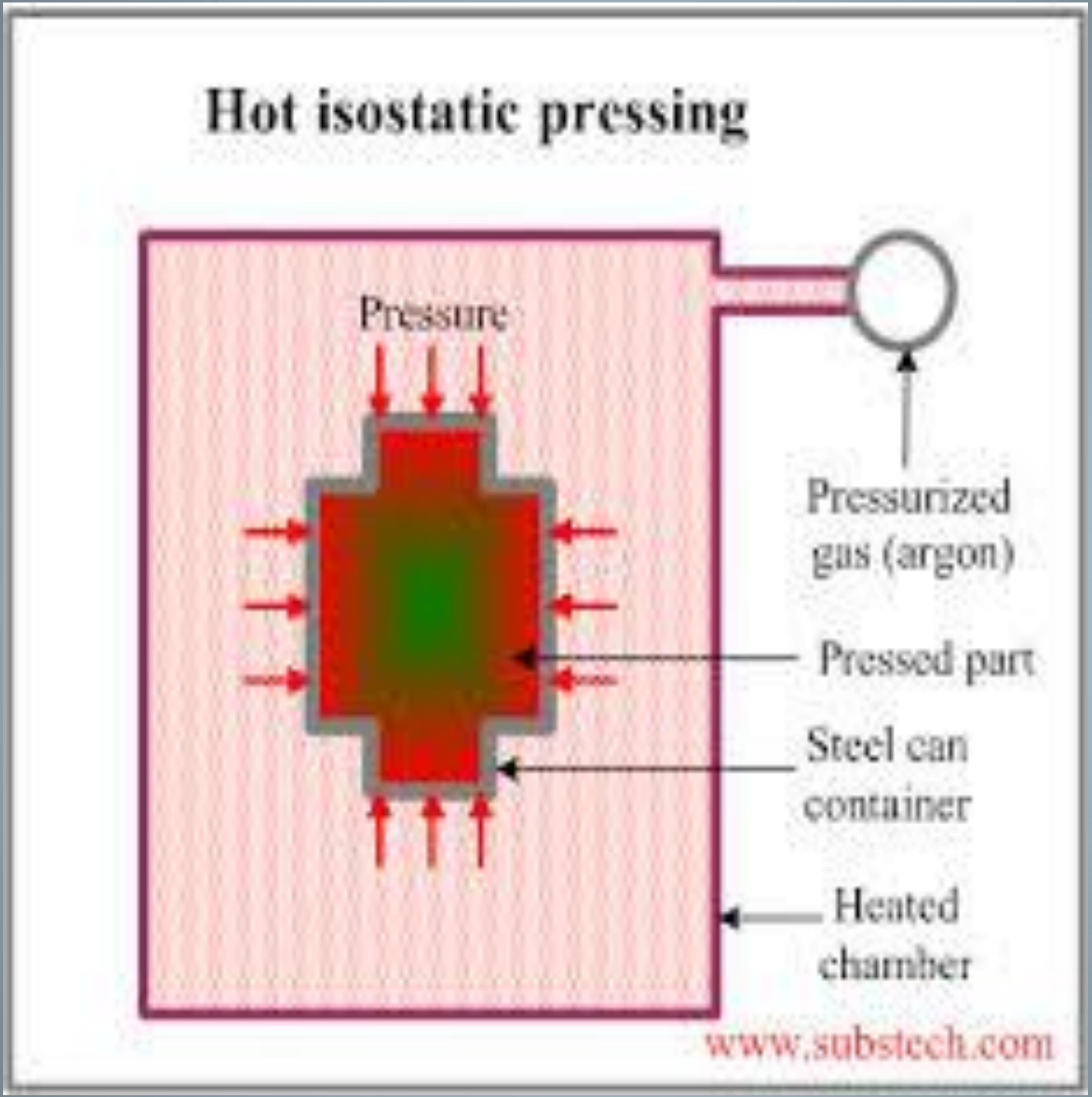
To achieve densification of a ceramic green body, the body must be evacuated and sealed in a gas-impermeable vessel.

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.

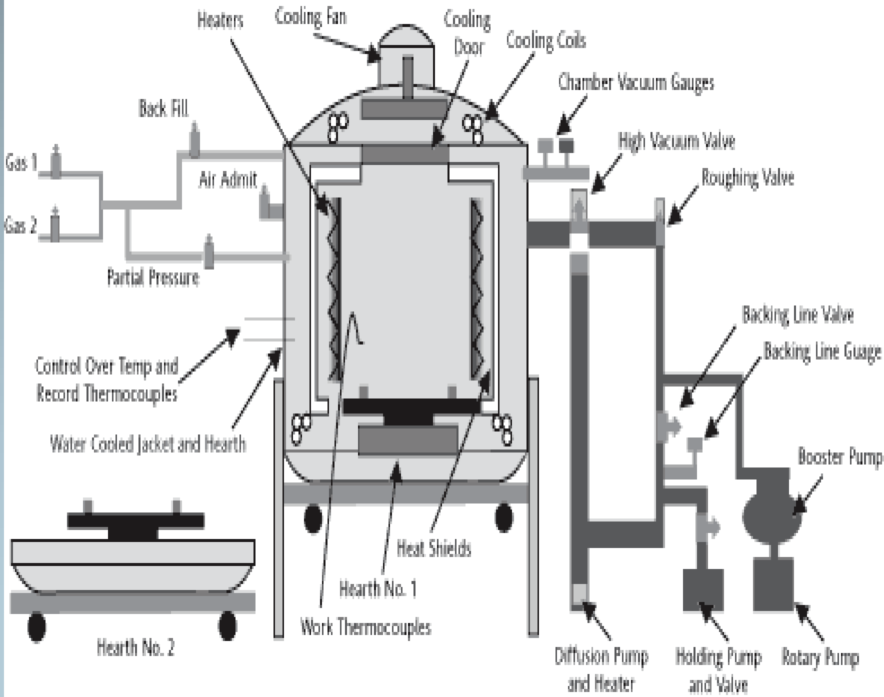
The temperature and pressure are then increased to densify the ceramic body.

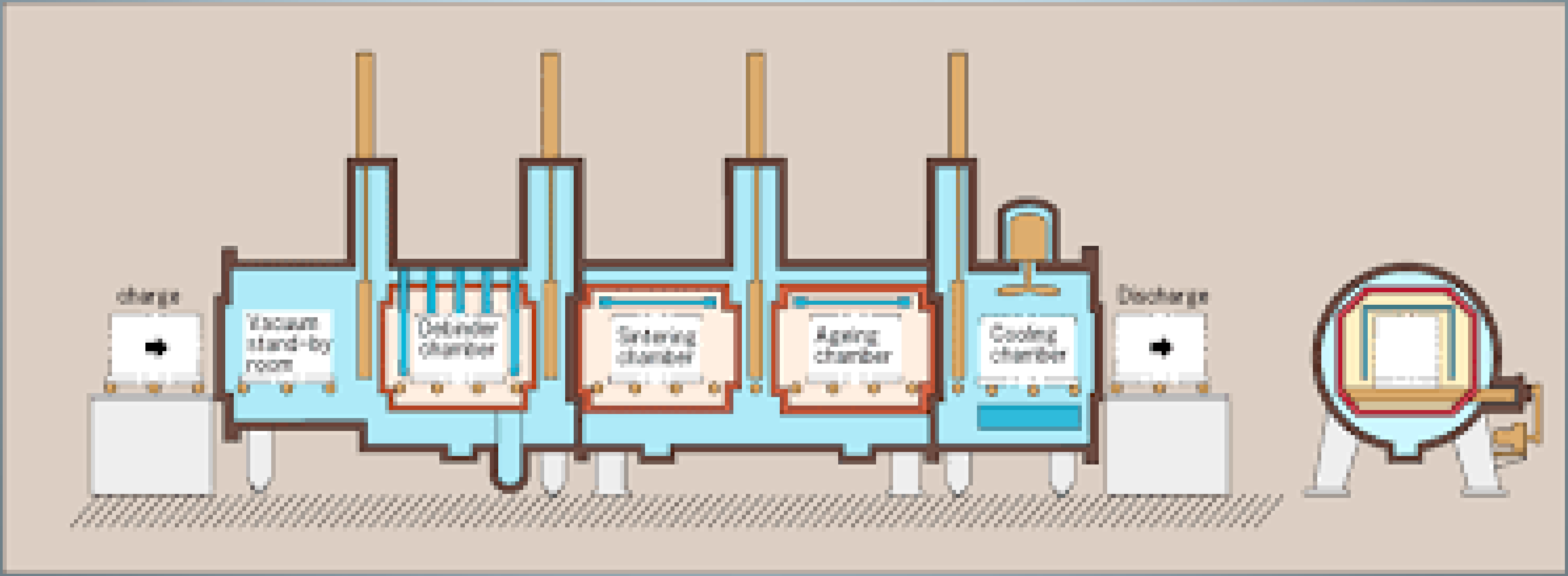
VACUUM SINTERING

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
Roughing Valve
Gas 1
Air Admit
Gas 2
Partial Pressure
Control Over Temp and Record Thermocouples
Water Cooled Jacket and Hearth
Backing Line Valve
Backing Line Guage
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

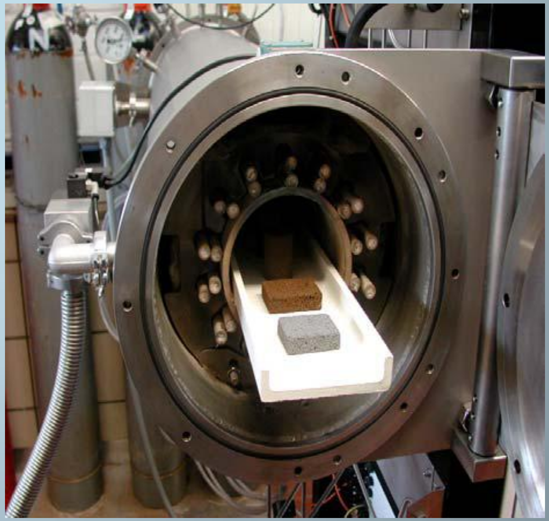
Sintering indirect heating :.
It means the body heat conduction by Convection or radiation with the help of another is heating medium .
1 – sintering by Dipped in a liquid medium, which includes : -
A - sintering in liquid salt B - sintering in liquid metal .C - sintering in an inert powder
2 - sintering 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