Compaction of metal powders

• Compaction is an important step in powder processing as it enables the forming of loose metal powders into required shapes with sufficient strength to withstand till sintering is completed.

• In general, compaction is done without the application of heat. Loose powders are converted into required shape with sufficient strength to withstand ejection from the tools and subsequent sintering process. IN cases like cemented carbide, hot compaction is done followed by sintering. One can not call this as compaction strictly, as sintering is also involved in this.

Powder compaction methods

Powder compaction techniques can be classified as,

1. Methods without application of pressure – i) loose powder sintering in mould, ii) vibratory compaction, iii) slip casting, iv) slurry casting, v) injection moulding

2. Methods with applied pressure – i) cold die compaction (single action pressing, double action pressing, floating die pressing), ii) isostatic pressing, iii) powder rolling, iv) powder extrusion, v) explosive compaction

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Pressureless compaction techniques

-Used for the production of simple and low density parts such as filters, other parts that are porous in nature; these techniques involve no external force and depend upon gravity for powder packing

I) Loose powder sintering: - Also known as loose powder shaping, gravity sintering, pressureless sintering. In this method, the metal powder is vibrated mechanically into the mould, which is the negative impression of the product and heated to sintering temperature. This is the simplest method and involve low cost equipment. The main reasons for not using this method for part production are, difficulty of part removal from the mould after sintering, & considerable shrinkage during sintering.

- **Applications**: Amount of porosity ranges from 40 vol% to as high as 90 vol%; Highly porous filter materials made of bronze, stainless steel, and monel, porous nickel membrane for use as electrodes in alkaline storage batteries and fuel cells are typical examples.

II) Slip casting: - Used for compacting metal and ceramic powders to make large & complex shapes for limited production runs

- A slip is a suspension of metal or ceramic powder (finer than 5 μm) in water or other soluble liquid which is pored into a mould, dried and further sintered.

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- Slip is usually made of, 1) a **dispersion agent** to stabilize the powder against colloidal forces, 2) a **solvent** to control the slip viscosity and facilitate casting, 3) a **binder** for giving green strength to the cast shape, 4) **plasticizer** to modify the properties of the binder

- For successful slip casting, formation of appropriate and a consistent slip is important. This is achieved by proper control of particle size, size distribution, order of component addition, their mixing time, addition of proper **_deflocculant_** - to prevent the settling and aggregation of powders and maintains the desirable viscosity of the slip.

- Mostly water is used as suspending medium, but absolute alcohol or other organic liquids may also be employed. Additives like alginates – ammonium and sodium salts of alginic acids, serve three fold functions of deflocculant, suspension agent & binding agent to improve green strength of the compact.

- The slip to be cast is obtained in a form of suspension of powder in a suspending medium. The slip should have low viscosity & low rate of setting so that it can be readily poured. The slip cast should be readily removable from the mould. Low shrinkage and high strength after drying is expected.

- To obtain these properties, 5 μm powder particles should be used. In the case of fine molybdenum powders, a slip can be prepared by suspending the powder in 5% aqueous polyvinyl alcohol with a minimum viscosity, at a pH value of 7.

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• For coarser, spherical stainless steel powder, a mixer of 80.7% metal powder, 19% water, 0.3% of sodium alginate as deflocculant having a pH value of 10 can be used.

• Steps in slip casting: i) Preparing assembled plaster mould, ii) filling the mould, iii) absorption of water from the slip into the porous mould, iv) removal of part from the mould, v) trimming of finished parts from the mould

• Sometimes mould release agents like oil, graphite can be used.

• Hollow and multiple parts can be produced

• **Advantages of slip casting:** Products that can not be produced by pressing operation can be made, no expensive equipment is required, works best with finest powder particles

• **Disadvantage:** slow process, limited commercial applications

• **Applications:** tubes, boats, crucibles, cones, turbine blades, rocket guidance fins; Also products with excellent surface finish like basins, water closets.

Assembled mould   **Filling mould**   **Absorption of water from slip**   **Part removal**
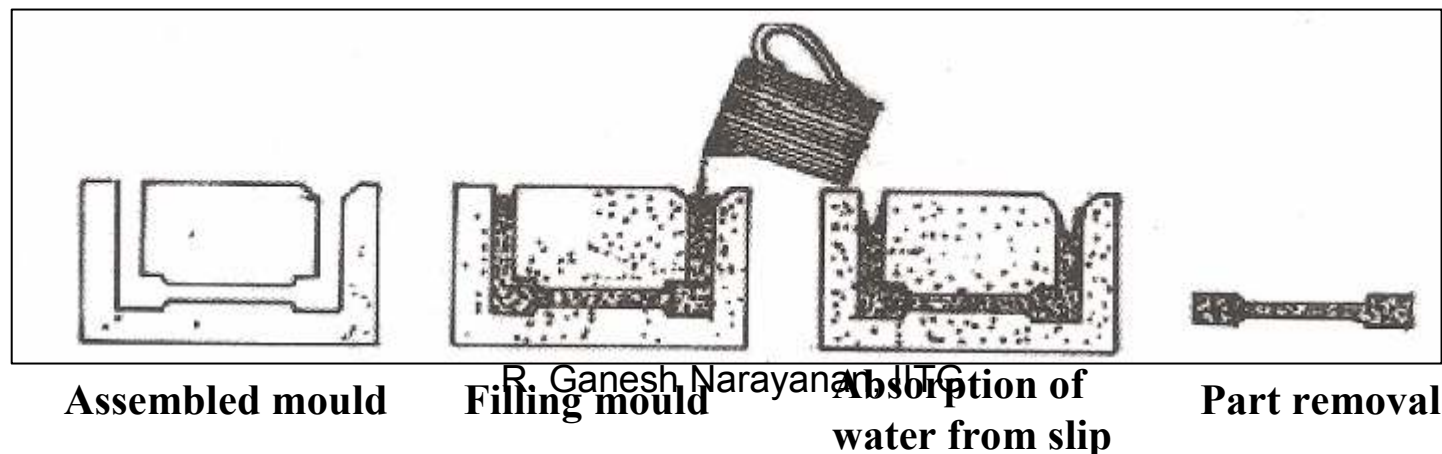
III) Slurry casting: This process is similar to slip casting except that a slurry of metal powders with suitable liquids, various additives, and binders is poured into a mould and dried. The solvent is removed either by absorption into the POP or by evaporation. Very high porous sheet for use as electrodes in fuel cells and nickel-cadmium rechargeable batteries are produced by this method.

IV) Tape casting (doctor blade casting): - This is a variation of slurry casting process and is used to produce thin flat sheets.

-This process involves preparing a dispersion of metal or ceramic powder in a suitable solvent with the addition of dispersion agent (to improve the dispersion of the particles). Then a binder is added and fed to a reservoir. Whole mixture is fed on to a moving carrier film from the bottom of the reservoir.

-This slurry layer is deposited on the film by the shearing action of a blade. The slurry should be free of air bubbles, otherwise result in porosity. During sintering, the binder is burnt off first and densification of material occurs.

- In present days, endless stainless steel belt is used instead of carrier tape. This process can be used for making very thin tapes between 50 to 1000 μm thickness. This method is used for making electronic substrates, dielectrics for capacitors and piezoelectric actuators.
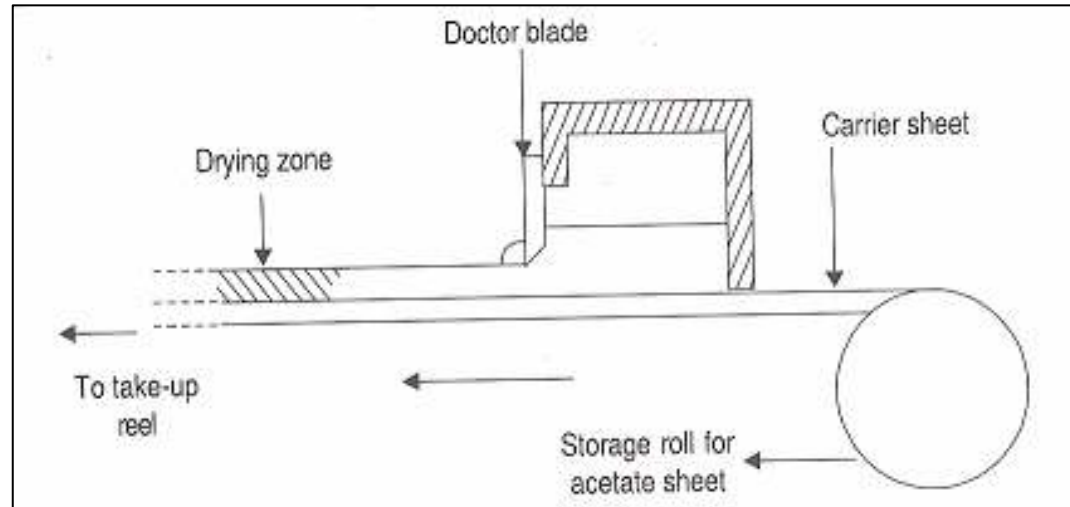
Schematic of tape casting
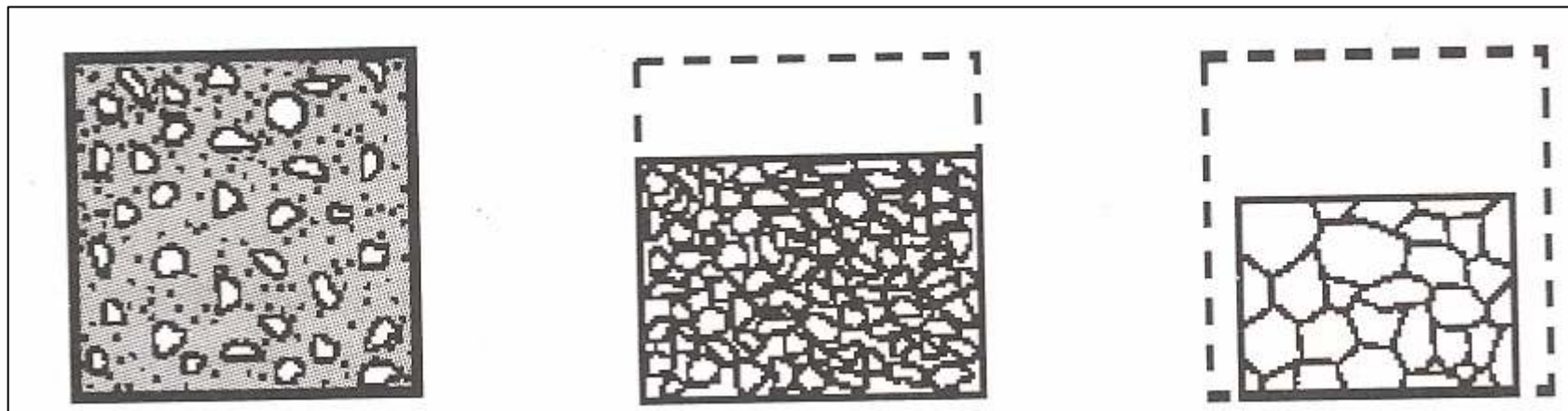
Slip   Green tape   Sintered tape

Stages in tape casting

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<u>V) Vibratory compaction</u>: - Vibratory compaction uses vibration energy to compact the powder mass. During this process, smaller voids can be filled with particles of still smaller size and this sequence is carried out till a high packing density of powder is achieved even before consolidation. Mechanical vibration facilitates the formation of nearly closed packed powder by settling particles in the voids present in the powder agglomerate. During vibration, small pneumatic pressure is usually superimposed on the powder mass.

- Brittle powders can be compacted by this method as they develop crack if done by pressure compaction

- This method is generally used when, 1) powders have irregular shape, 2) use of plasticizers for forming is not desirable, 3) sintered density is required to be very close theoretical density

- Important variables in vibratory compaction:

  1. <u>inertia of system:</u> larger the system, more the energy required for packing

  2. <u>friction force between particles:</u> more friction results in need of more KE for compaction

  3. <u>particle size distribution:</u> more frequency required if more large particles are present. Vibration cycle is important and not period of vibration.

<u>Pressure compaction techniques</u>

• These techniques involve application of external pressure to compact the loose powder particles; Pressure applied can be unidirectional, bidirectional or hydrostatic in nature.

• **<u>Die compaction:</u>** In this process, loose powder is shaped in a die using a mechanical or hydraulic press giving rise to densification. The mechanisms of densification depend on the material and structural characteristics of powder particles.

• Unidirectional and bidirectional compaction involves same number of stages and are described in this figure. They are, i) charging the powder mix, ii) applying load using a punch (uni-) or double punch (bi-) to compact powders, iii) removal of load by retracting the punch, iv) ejection of green compact. The table gives compaction pressure ranges for metals and ceramics.

Material type	**Compaction pressure range (MPa)**
Metals	
Aluminium	70–275
Brass	400–700
Bronze	200–275
Iron	350–800
Iron-copper (2%) premix	600–720
Tungsten	70–140
Ceramics	
Alumina	100–140
Carbon	140–160
Hard metals	150–400
Magnetic ceramics (ferrites)	110–165

Effect of powder characteristics

For a good compaction, 1) irregular shaped particles are preferred as they give better interlocking and hence high green strength, 2) apparent density of powders decides the die fill during compaction. Hence powder size, shape & density affect the apparent density, 3) flow rate affects the die fill time, and once again powder size, shape & density affect the flow rate.
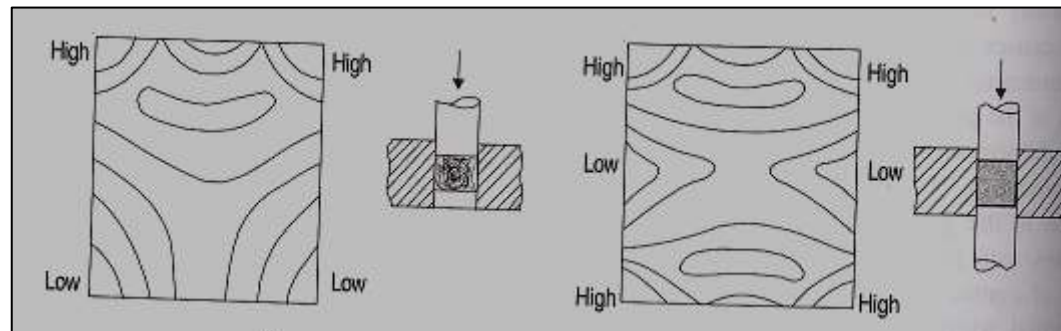
Powder behavior during compaction

- Compaction involves, 1) flow of powder particles past one another interacting with each other and with die-punch, 2) deformation of particles. In the case of homogeneous compaction, two stages are observed. **First stage** => rapid densification occurs when pressure is applied due to particle movement and rearrangement resulting in improved packing; **Second stage** => increase in applied pressure leads to elastic and plastic deformation resulting in locking and cold welding of particles. In the second stage, large increments in pressures are seen to effect a small increase in density.
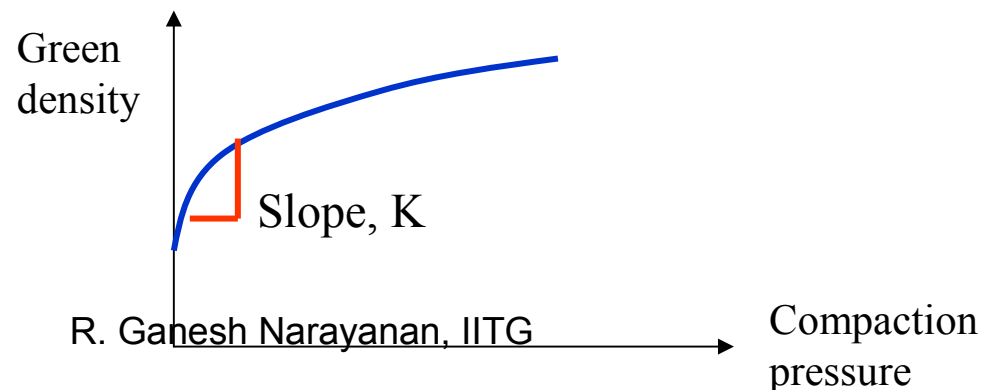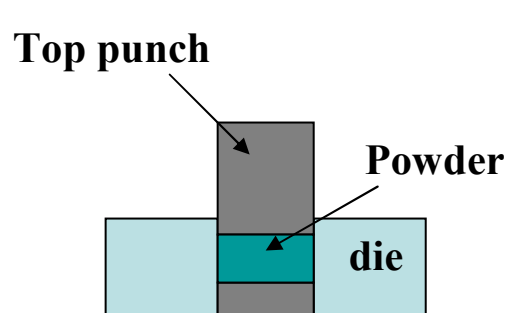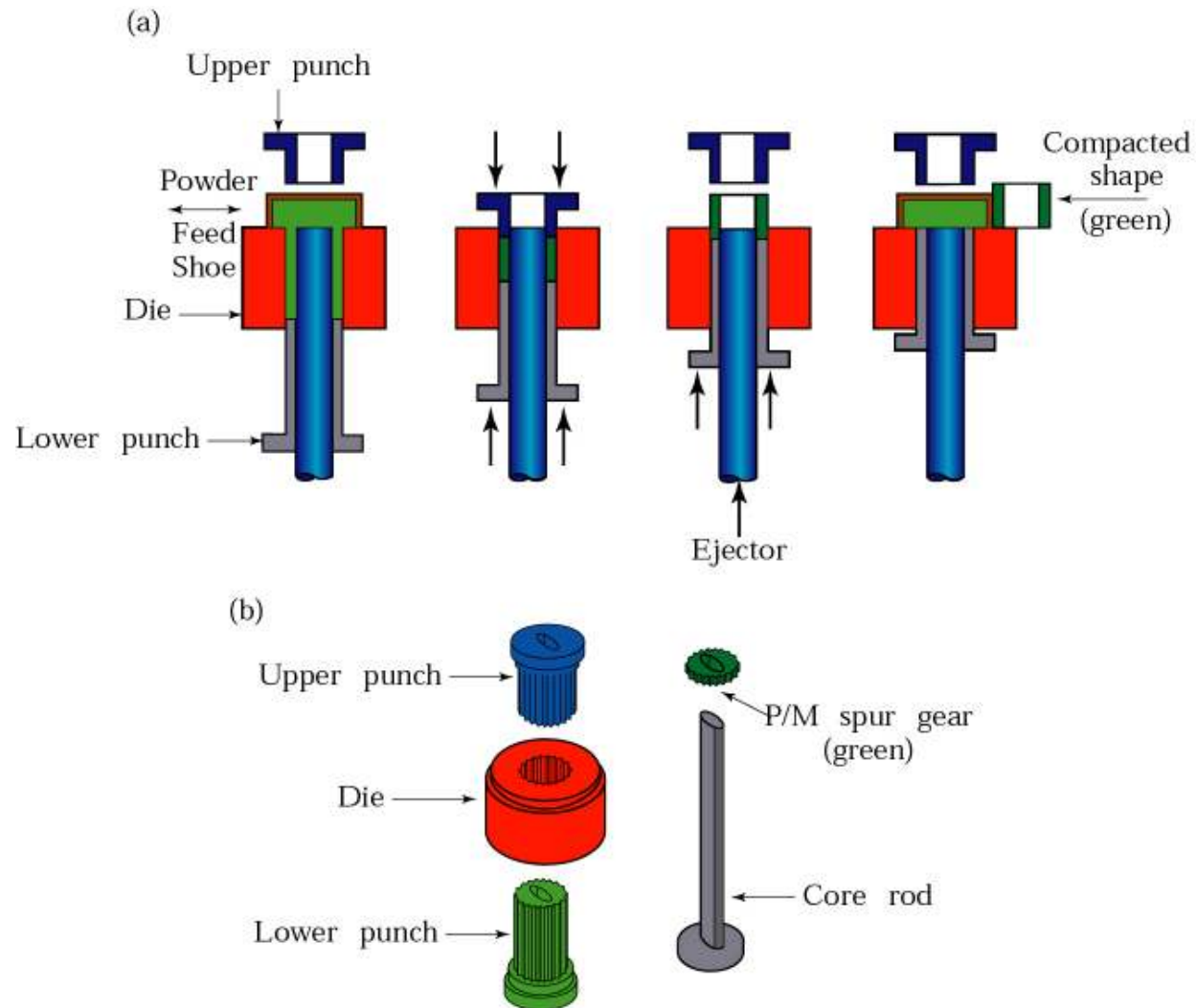
• The green compact produced can be considered as a two-phase aggregate consisting of powder particles and porosity each having own shape and size.

• Compaction can be done at low and high temperatures. Room temperature compaction employs pressures in the range of 100-700 MPa and produce density in the range of 60-90% of the theoretical density. At higher temperatures, pressures are kept low within the limits for preventing die damage.

• In **single die compaction**, powders close to the punch and die walls experience much better force than in center. This results in green density variation across the sample length. Longer the sample more the density difference. This non-uniformity can result in non-uniformity in properties of sintered part.

• This density variation and hence final property variation can be greatly reduced by having **double ended die compaction**. In this case, powder experiences more uniform pressure from both top and bottom, resulting in minimization of density variation. But this variation will still be considerable if the components have high aspect ratio (length to diameter ratio). This means that long rods and tubes cannot be produced by die compaction. In this case, isostatic pressing can be used.

Single ended compaction Double ended compaction

Schematic of powder compaction

(a)

Upper punch

Powder

Feed Shoe

Die

Lower punch

Ejector

Compacted shape (green)

(b)

Upper punch

Die

Lower punch

P/M spur gear (green)

Core rod

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Die compaction lubricants

- It is known that presence of frictional forces limits the degree of densification.

- Usage of lubricants either mixed or applied to contact surfaces can be done to minimize friction

- **Lubricants** => organic compounds such as waxes or metallic stearates or salts and they generally have low boiling points; Amount of lubricant added can be 0.5 to 2 % by weight of charge

- **Mixed lubrication** => Reduce the interparticle friction and aid better packing. But they may affect the densification property depending on their volume and density. The mixed lubricants should be removed before sintering to avoid distortion of compact.

- Even 1 wt% of lubricant can occupy large volume of app. 5% and maximum attainable density will be 95% (assuming zero porosity) only.

- **Die wall lubrication** => Graphite & MoS_2 can be applied physically on the die, punch surfaces; They can be easily removed, but takes longer production times.

- **Commonly used lubricants in P/M** => Paraffin wax, Aluminium stearate, Lithium stearate, Zinc stearate, Magnesium stearate, stearic acid, Oleic acid, Talc, Graphite, boron nitride, Mos_2

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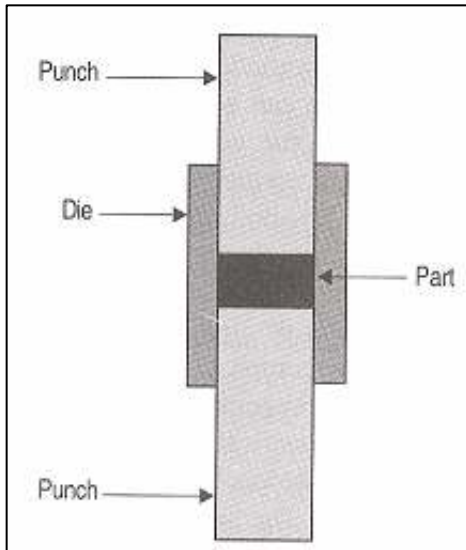
Tooling for die compaction

P/M part classification

Class I P/M part => simple, thin sections, uni-directionally pressed with single level compaction; class II P/M Part => Simple, but thick sections requiring pressing from two direction; class III => Two different thickness levels requiring two direction pressing; class IV => Multiple levels of thickness, requiring pressing from both the directions

Tooling: Single action tooling: pressure is applied by lower punch, while the die cavity and upper punch remain stationary. After compaction, the upper punch moves away and compact is ejected by movement of lower punch. Class I parts can be made by this tooling.

Double action tooling: IN this, Simultaneous movement of top and bottom punches are seen, while die and core rod remain stationary. Class II, III, IV type parts are made by this tooling.

Powder characteristics that affect the tooling design include, 1) Flow of powders – powder particles should flow freely to fill the die. By using lubricants, flow can be made smooth and improved; 2) die fill – this is the amount of powder in the cavity before compaction. This depends on shape and geometry of part, free flow of powders, complexity of part like thin sections and protrusions.

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Double action tooling
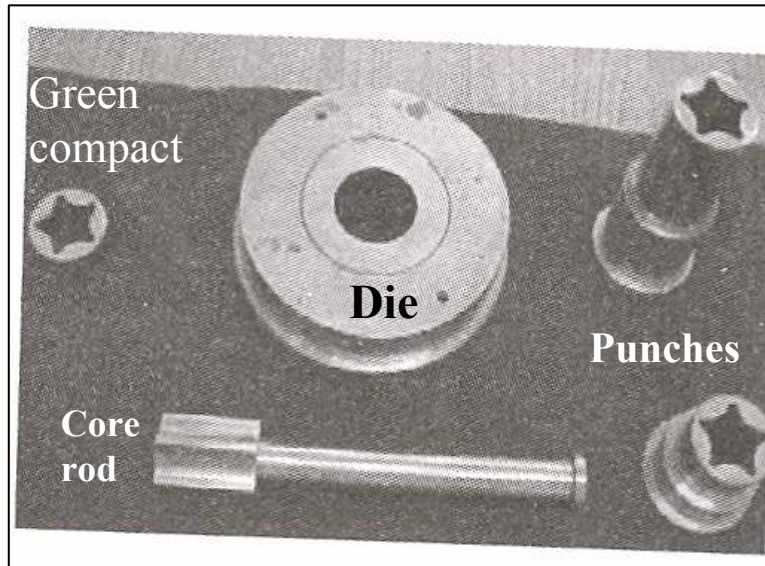
Tooling for double action die compaction

- Green compact
- Die
- Punches
- Core rod

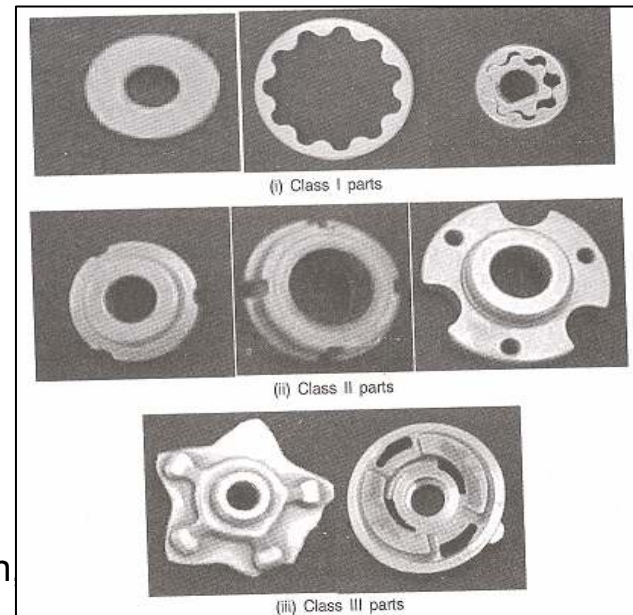Hydraulic press used for die compaction
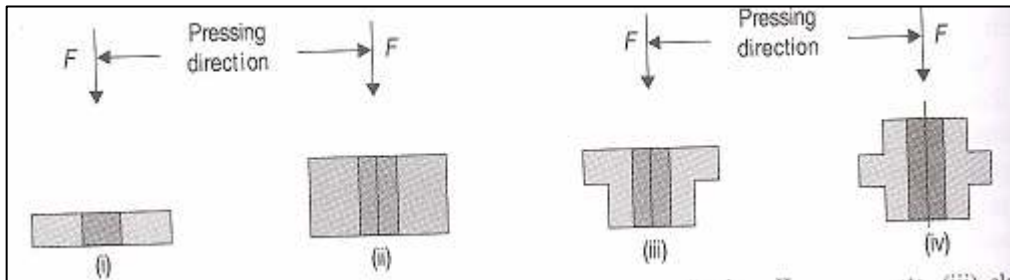
Class I part   Class II part   Class III part   Class IV part

Class I
Class II
Class III

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Soft powders like aluminium, copper, lead => abrasion resistant steel such as air-hardened steels, die steels are used for making die

Relatively hard powders => dies made of tool steel are used

More hard & abrasive powders like steel => tungsten carbide dies are used. But carbide dies are costly & high hardness (difficult to machine)

Coated dies with hard & wear resistant coating material like titanium nitride or titanium carbide can be used

Defects occurring in die pressing of powders:

1) lamination cracking – this is caused by trapped air in compact sample. This cracking occurs perpendicular to load direction. This trapped air prevents the interlocking of particles.

2) Blowout – occurs when all the entrapped air tries to escape at the interface between the die and punch

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Cold isostatic compaction (CIP)

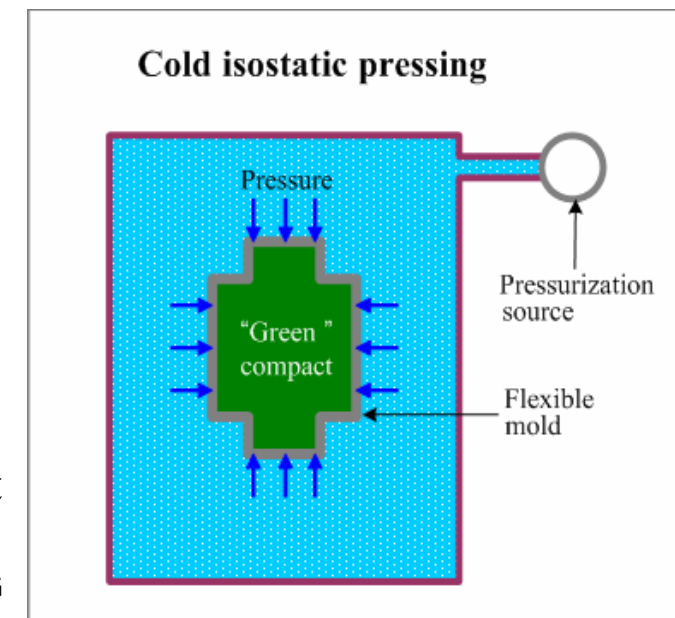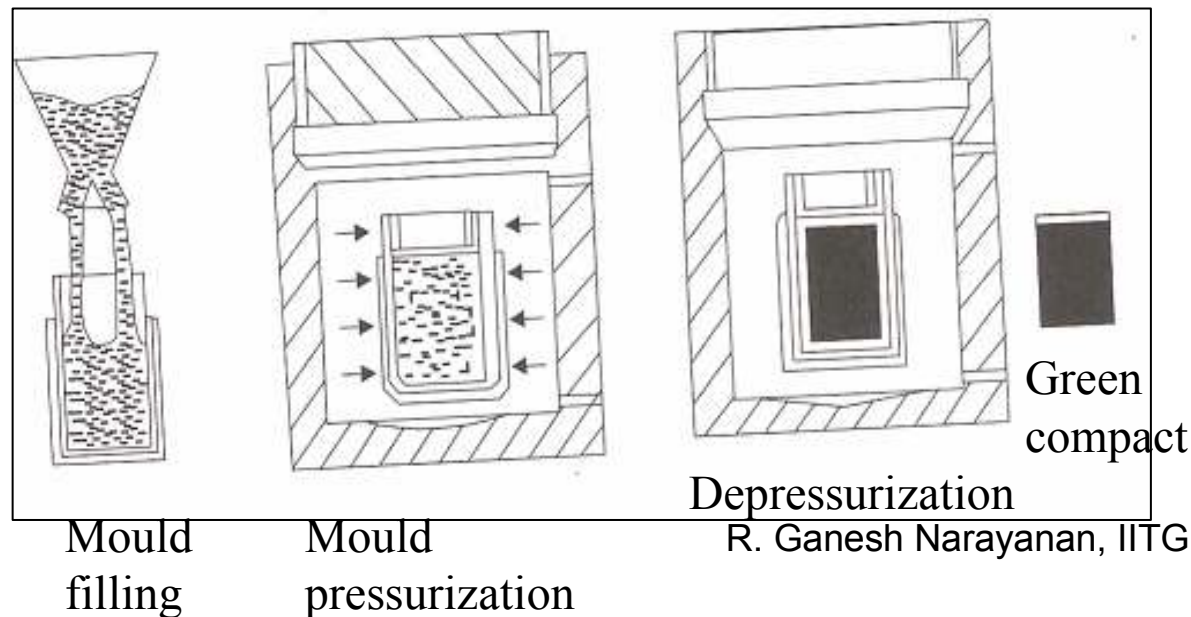• CIP is a compaction process in which isostatic fluid pressure is applied to a powder mass at room temperature to compact it into desired shape. The powder parts can be compacted up to 80-90 % of their theoretical densities. Water or oil can be used as pressuring medium.

• Process details: High density near-net shape green parts, long thin walled cylinders, parts with undercuts can be readily fabricated. In this process, pressure is applied simultaneously and equally in all directions using a fluid to an elastomeric fluid with powder at room temperature. Sintered CIP component can reach up to 97 % of theoretical density. Steps in this process is shown in flowchart.

Select elemental or pre-alloyed powders → Fill mould with powder → Load mould into press → Pressurise & hold

Remove compact sample & sinter ← De-pressurise & remove mould ← Pressurise & hold
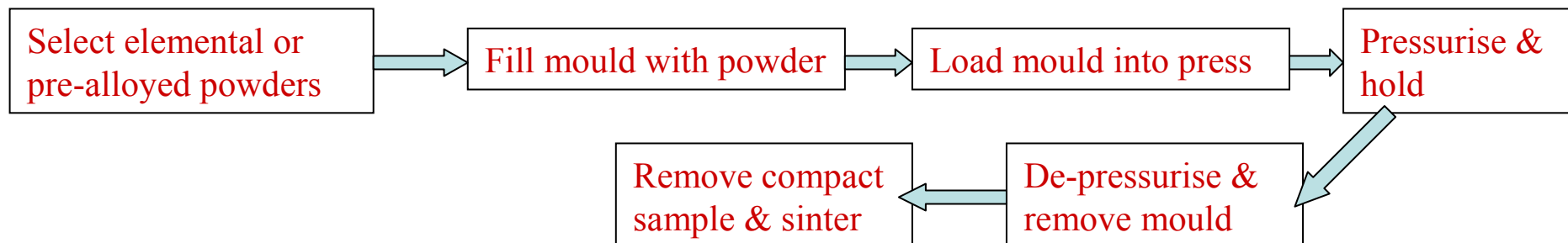
Good mould filling is required in CIP because the initial powder distribution and density affect the preform shape. Powder size, shape, density and mechanical properties affect the flowability of powder into the mould and the packing density. Optimum pressing is obtained by using a free-flowing powder along with controlled vibration or mould tapping. **Materials used for flexible moulds are natural, synthetic rubber like neoprene, urethane, nitrile, silicones.**

• During pressing, high density is achieved at a low pressure, while the green strength of the compact rises linearly with pressure. The pressure applied can range from 100-400 MPa. Initially the applied stress (exactly shear stress) serves to improve the density of the compact by particle sliding and rotation. In the next stage, deformation of powder particles occur and particle characteristics like shape play vital role in deciding this stage.

• Irregular particles which interlock with one another and also deform during both the stages, tend to densify much easily than spherical powders. In the case of spherical powders, in spite of their higher initial packing densities, particles do not mechanically interlock with one another and hence do not easily deform. Hence high pressures are required for their compaction.

Mould filling   Mould pressurization   Depressurization   Green compact

Cold isostatic pressing

Pressure

"Green" compact

Pressurization source

Flexible mold

Types of cold isostatic pressing:

Wet bag process: IN this, the mould is directly in contact with the fluid. This reduces the productivity, since the bag has to be removed every time before refilling. Tooling costs are reduced in this.

Fixed mould process: the mould is fixed in the pressure vessel and powders are filled in situ. The tooling has internal channel into which fluid is pumped. This is an automated process in which the powder filling, compaction, depressurization and removal of green parts are done continuously. This involves higher tooling cost, but has higher production rate.

Advantages of CIP:

Uniform, controlled, reproducible densification of powder; long, slender parts can be pressed; neat net shape forming; short production times; economy of operation for complex and large parts.

Applications:

Metallic filters made from bronze, brass, stainless steel, Inconel, Monel, Titanium, high speed tools, carbide tools. Also ceramic parts such as sparks plugs and insulators are made by this method.

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Powder rolling

This process involves feeding of powders between rolls to produce a coherent and brittle green strip. This green strip is then sintered & re-rolled to obtain a dense, finished product.
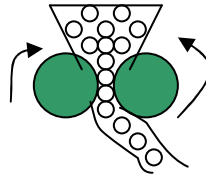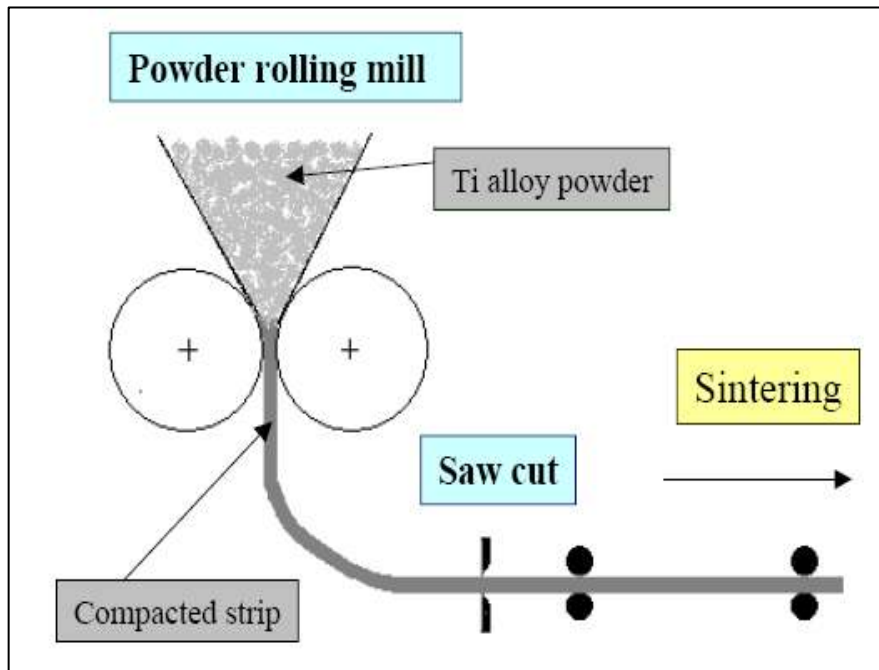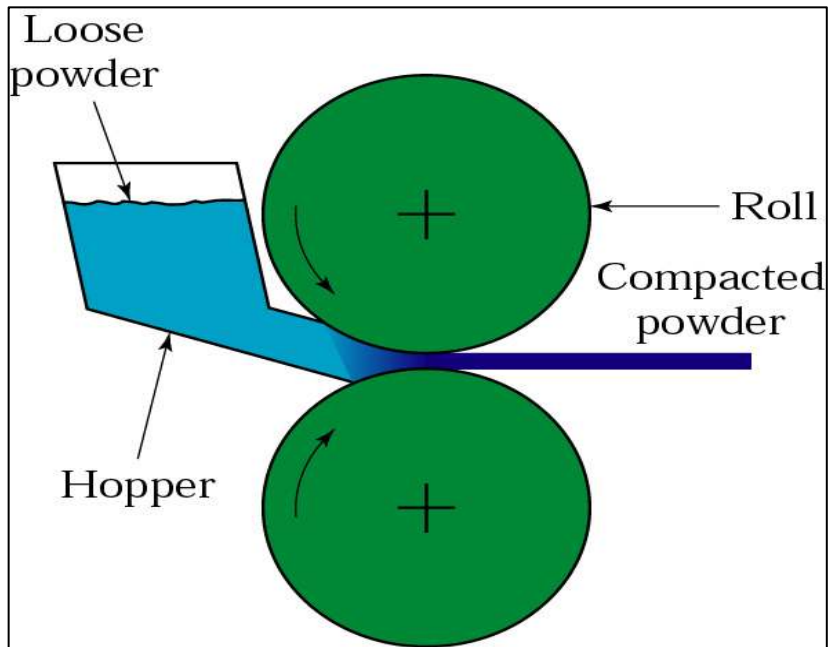

Steps: 1) preparation of green strip, 2) sintering, 3) densification of sintered strip, 4) final cold rolling and annealing

Parameters affecting powder rolling are roll gap, roll diameter, roll speed, powder characteristics; **Roll gap** => large roll gap leads to decrease in green density; very small roll gap leads to edge cracking; **roll diameter** => increase in density and strength with increase in roll dia. for a given strip thickness; **roll speed** => Kept low, 0.3-0.5 m/s; **Powder** => irregular powder with rough surfaces provide better strip density

In densification stage, either **repeated cold rolling followed by annealing** or **hot rolling of strip** can be followed

Applications: nickel strips for coinage, nickel-iron strips for controlled expansion properties, Cu-Ni-Sn alloys for electronic applications, porous nickel strip for alkaline batteries and fuel cell applications.
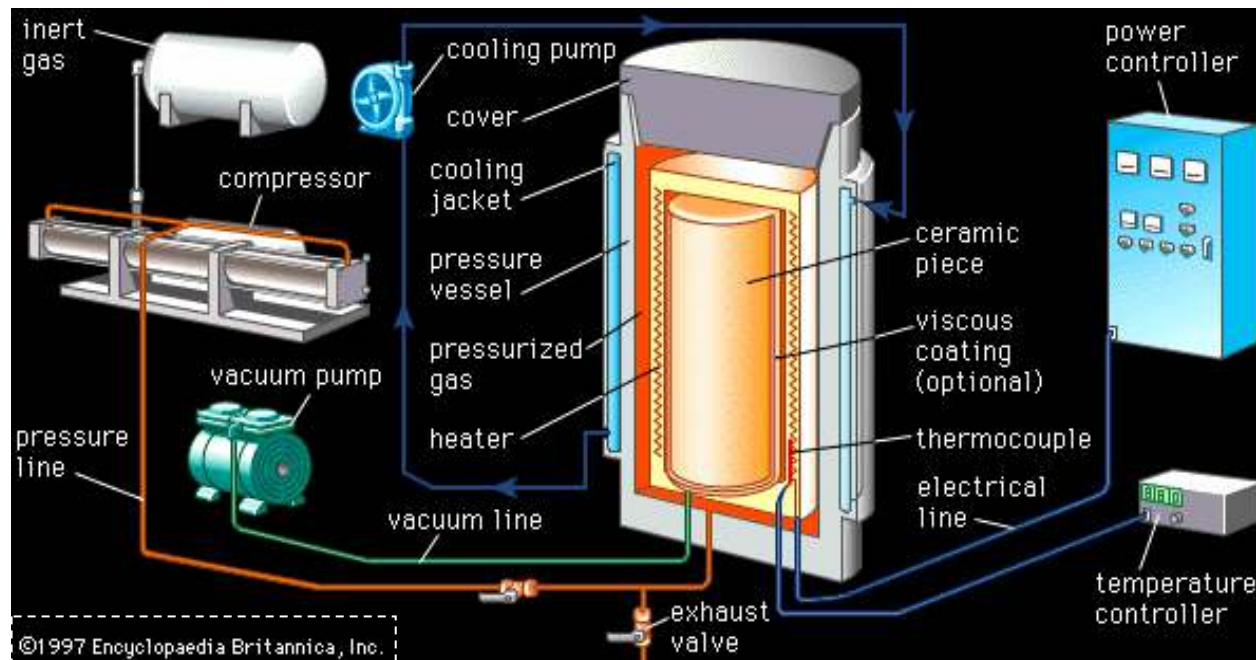
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Loose powder

Roll

Compacted powder

Hopper

Powder rolling mill

Ti alloy powder

Sintering

Saw cut

Compacted strip

12" wide Ti-6Al-4V strip

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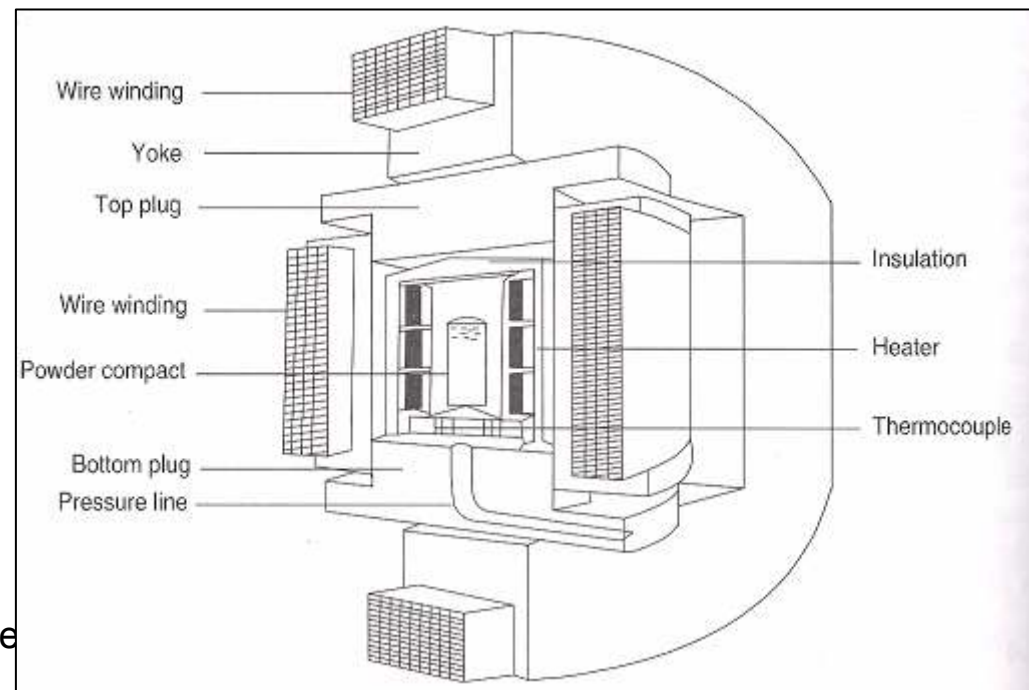
Hot isostatic pressing

- Ideal method for consolidation of powders of nickel and cobalt base super alloys, tool steels, maraging steels, titanium alloys, refractory metal powders, cermets. It has got variety of applications including bonding of dissimilar materials, consolidation of plasma coatings, processing hard and soft magnetic materials etc.

- HIP is the application of pressure at elevated temperatures to obtain net or near net shape parts from metal, ceramic, cermet powders.

- HIP unit consists of a pressure vessel, high temperature furnace, pressurizing system, controls and auxiliary systems (material handling, vacuum pumps, metering pumps).

- The pressure vessel is made of low alloy steel. Its function is to heat the powders while applying uniform gas pressure on all the sides. Furnaces are of radiation or convection type heating furnaces with graphite or molybdenum heating elements. Nichrome is also used. The furnace heats the powder part, while pressurizing medium (a gas) is used to apply a high pressure during the process. Generally, argon, nitrogen, helium or even air is used as pressurizing medium.

- The pressurizing gas, usually argon, is let into the vessel and then a compressor is used to increase the pressure to the desired level. The furnace is then started and both temperature and pressure are increased to a required value.

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HIP UNIT– used for ceramic material (photo from public domain)

inert gas
cooling pump
cover
cooling jacket
pressure vessel
pressurized gas
heater
vacuum line
vacuum pump
pressure line
compressor
exhaust valve
ceramic piece
viscous coating (optional)
thermocouple
electrical line
power controller
temperature controller
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Schematic of HIP UNIT (cross-section)

R. Gane

Wire winding
Yoke
Top plug
Wire winding
Powder compact
Bottom plug
Pressure line
Insulation
Heater
Thermocouple

- HIP presses are available in diameters up to 2m with pressures ranges from 40 to 300 MPa with temperature range from 500 to 2200 °C. The processing time can last up to 4 hours depending on the material and size of the part.

- during HIP, the pores are closed by flow of matter by diffusion and creep, but also bonded across the interface to form a continuous material.

- <u>Commonly used heating elements:</u> Kanthal heating element – up to 1200 °C; Molybdenum heating element – 1200 to 1700 °C; Graphite heating element – 2000 to 2600 °C

- Typical range of temperature & pressures used in HIP is given in table

Material	HIP temperature range (°C)	Applied pressure (MPa)
Al alloy	350–500	100
Cu alloy	500–900	100
High-speed steel	1,000–1,200	100
Ni base superalloy	1,170–1,280	100–150
Ti alloy (Ti-6Al-4V)	880–960	100
Al$_2$O$_3$	1,350–1,450	100
Ba Ti O$_3$	100–1,200	100
Partially stabilized zirconia	1,350–1,500	100
SiAlON	1,700–1,800	100
WC-Co	1,300–1,350	30–100

Sintering

• It is the process of consolidating either loose aggregate of powder or a green compact of the desired composition under controlled conditions of temperature and time.

• Types of sintering: a) solid state sintering – This is the commonly occurring consolidation of metal and alloy powders. In this, densification occurs mainly because of atomic diffusion in solid state.

b) Liquid phase sintering – The densification in improved by employing a small amount of liquid phase (1-10% vol). The liquid phase existing within the powders at the sintering temperature has some solubility for the solid. Sufficient amount of liquid is formed between the solid particles of the compact sample. During sintering, the liquid phase crystallizes at the grain boundaries binding the grains. During this stage, there is a rapid rearrangement of solid particles leading to density increase. In later stage, solid phase sintering occurs resulting in grain coarsening and densification rate slows down. Used for sintering of systems like tungsten-copper and copper-tin. Also covalent compounds like silicon nitride, silicon carbide can be made, that are difficult to sinter.

c) Activated sintering – IN this, an alloying element called 'doping' is added in small amount improves the densification by as much as 100 times than undoped compact samples. Example is the doping of nickel in tungsten compacts

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d) Reaction sintering – IN this process, high temperature materials resulting from chemical reaction between the individual constituents, giving very good bonding. Reaction sintering occurs when two or more components reacts chemically during sintering to create final part. A typical example is the reaction between alumina and titania to form aluminium titanate at 1553 K which then sinters to form a densified product.

Other than mentioned above, rate controlled sintering, microwave sintering, gas plasma sintering, spark plasma sintering are also developed and practiced.

Sintering theory

- Sintering may involve, 1) single component system – here self-diffusion is the major material transport mechanism and the driving force resulting from a chemical potential gradient due to surface tension and capillary forces between particles, 2) multi-component system (involve more than one phase) – inter-diffusion occurs with the concentration gradient being the major driving force for sintering in addition to self-diffusion caused by surface tension and capillary forces. IN this sintering, liquid phase formation and solid solution formation also occurs with densification.

- First theory was proposed by Sauerwald in 1922. This theory says that two stages are involved in sintering namely *adhesion* and *recrystallisation*. Adhesion occurs during heating due to atomic attraction and recrystallisation occurs at recrystallisation temperature (above $0.5 \, T_m$). In recrystallisation, microstructure changes, phase changes, grain growth, shrinkage occurs.

Solid state sintering process

Condition for sintering: 1) densification occurs during sintering and solid state sintering is carried out at temperatures where material transport due to diffusion is appreciable. Surface diffusion is not sufficient, atomic diffusion is required.

2) This occurs by replacing high energy solid-vapour interfaces (with free energy γ_{SV}) with the low energy solid-solid interface (particle-particle) of free energy γ_{SS}. This reduction in surface energy causes densification.

3) Initially free energy of solid-solid interface must be lower than free energy of solid-vapour interface. The process of sintering will stop if the overall change in free energy of the system (dE) becomes zero, i.e., $dE = \gamma_{SS} dA_{SS} + \gamma_{SV} dA_{SV} \leq 0$

Where dA_{SS} & dA_{SV} are the interfacial area of solid-solid and solid-vapour interfaces.

4) Initially, the surface area of compact represent the free surface area, since no grain boundaries have developed and hence $A_{SV} = A_{SV0}$ & $A_{SS} = 0$. As sintering proceeds, A_{SV} decreases and A_{SS} increases. The sintering process will stop when $dE = 0$,

i.e., $\gamma_{SS} dA_{SS} + \gamma_{SV} dA_{SV} = 0 \Rightarrow \gamma_{SS} / \gamma_{SV} = - dA_{SV} / dA_{SS}$

5) Densification stops when $- dA_{SV} / dA_{SS}$ is close to zero. To achieve densification without grain growth, the solid-solid interface must be maximized. Such conditions can be achieved by doping or by using suitable sintering conditions for surface free energy maximization.
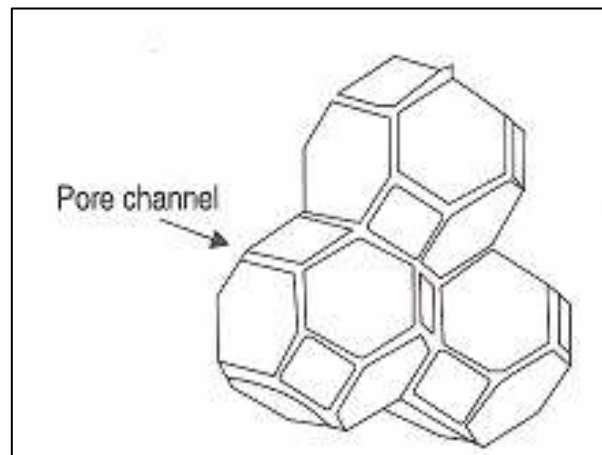
Stages in solid state sintering

• In general, solid state sintering can be divided into three stages – 1st stage: *Necks are formed at the contact points between the particles*, which continue to grow. During this rapid neck growth takes place. Also the pores are interconnected and the pore shapes are irregular.

• 2nd stage: In this stage, with sufficient neck growth, the pore channels become more cylindrical in nature. The curvature gradient is high for small neck size leading to faster sintering. With sufficient time at the sintering temperature, the pore eventually becomes rounded. As the neck grows, the curvature gradient decreases and sintering also decreases. This means there is no change in pore volume but with change in pore shape => pores may become spherical and isolated. *With continued sintering, a network of pores and a skeleton of solid particle is formed*. The pores continue to form a connected phase throughout the compact.

• 3rd or final stage: In this stage, *pore channel closure occurs and the pores become isolated and no longer interconnected*. Porosity does not change and small pores remain even after long sintering times.

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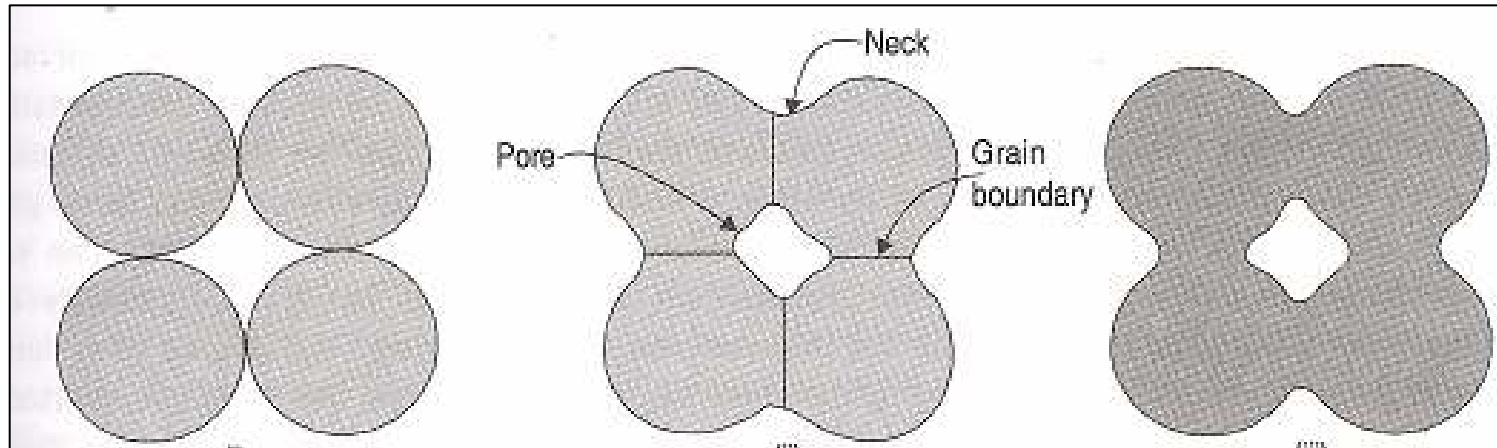
Particles in contact   Formation of necks, grain boundaries, pores   Final sintered geometry

Pore channel formation

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Driving force for sintering

• *The main driving force is excess surface free energy in solid state sintering*. The surface energy can be reduced by transporting material from different areas by various material transport mechanisms so as to eliminate pores.

• material transport during solid state sintering occurs mainly by surface transport, grain boundary transportation. This surface transport can be through adhesion, surface diffusion. Many models available to describe sintering process – like viscous flow, plastic flow, grain boundary and volume diffusion models. These models will be briefly described here.

Mechanism in solid state sintering

As discussed earlier, material or atom transport forms the basic mechanism for sintering process. A number of mechanisms have been proposed for sintering operation. These are,

1. Evaporation condensation, 2. diffusion (can be volume diffusion, grain boundary diffusion, surface diffusion), 3. viscous flow, 4. plastic flow

1. Evaporation and condensation mechanism
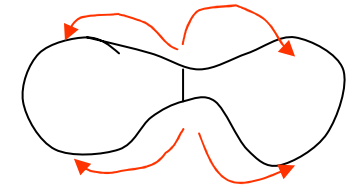
The basic principle of the mechanism is that the equilibrium vapor pressure over a concave surface (like neck) is lower compared to a convex surface (like particle surface). This creates the vapor pressure gradient between the neck region and particle surface. Hence mass transport occurs because of vapor pressure gradient from neck (concave surface) to particle surface (convex surface). The driving force of this is based on Gibbs-Thomson equation, $\mu - \mu_0 = RT \ln(p/p_0) = (-\gamma)(\Omega)/r$ where μ and μ_0 are chemical potentials of initial and final surfaces, R is universal gas constant, T is temperature in K, p and p_0 are partial pressures over the curved and flat surface respectively, γ is the surface free energy, Ω is the atomic volume

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2. Diffusion mechanism

- Diffusion occurs because of vacancy concentration gradient. In the case of two spheres in contact with each other, a vacancy gradient is generated between the two surfaces. This condition can be given by, $\mu-\mu_0 = RT\ ln(C/C_0) = (-\gamma)(\Omega)/r$ Where C and C_0 are the vacancy concentration gradient around the curved and flat surface.

- Kuczynski has derived empirical relation for neck growth rate for the following two cases, i) a sphere in contact with flat surface – the rate of neck growth is proportional to seventh root of time ($t^{1/7}$), ii) when two spheres are in contact – the neck growth rate is, $x^5/a^2 = 40\ \gamma\ \Omega D.t/RT$ where a – radius of sphere, D – volume diffusivity of material, Ω – atomic or molecular volume.

- Neck growth due to surface diffusion, lattice diffusion, vapour transport, grain boundary transport from GB source, lattice diffusion from sources on GB, lattice diffusion from dislocation sources

3. Viscous flow mechanism

According to this concept, sintering occurs due to the presence of lattice vacancies. This is important in sintering of glass. Frenkel developed the equation, $(x^2/a) = 3/2\ (\gamma/\eta).t$ where x is the neck radius & a is the radius of particle. Increasing the temperature results in increased plasticity of metal powders. Balshin proposed the following mechanisms to happen during sintering.

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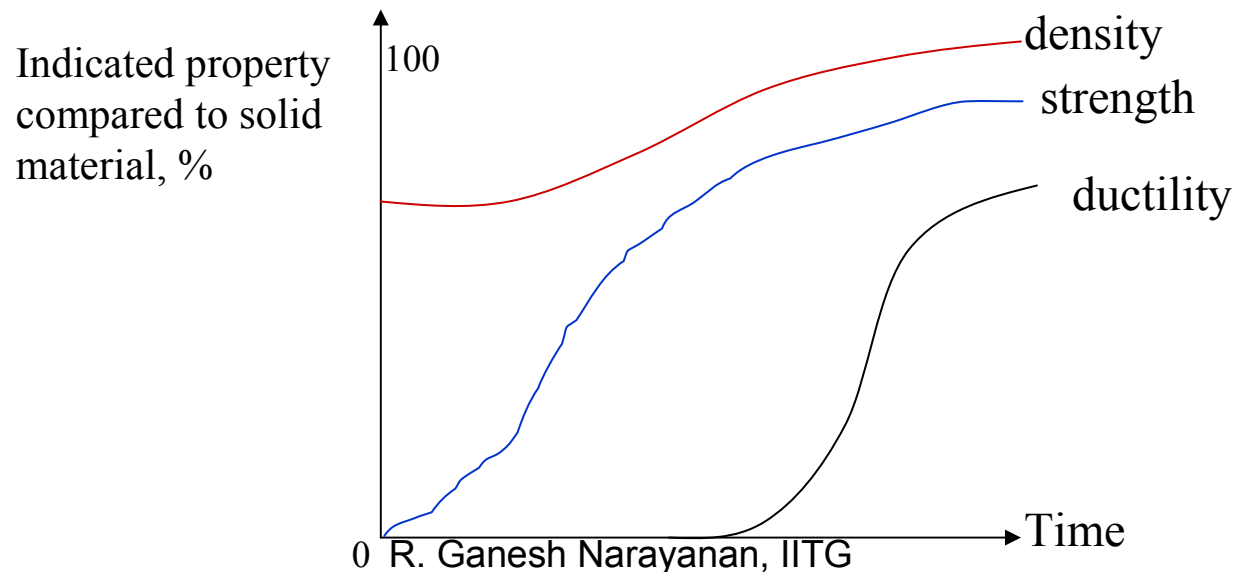1. Particle rearrangement, 2. particle shape change, 3. grain growth.

Frenkel suggested that surface tension lead to sintering and solids could behave like newtonian liquids at high temperatures i.e., sintering occurs by viscous flow. He derived an equation for the viscosity coefficient, $\eta = kT/D\Omega$ where k is the Boltszman's constant, T is the absolute temperature, D is the self-diffusion coefficient, Ω is the atomic volume. He derived an expression on neck growth during sintering of two spherical particles of radius a with time t as, $x^2 = 3a\gamma/2\eta$ where x is the neck radius and γ is the surface energy.

4. Plastic flow mechanism

Bulk flow of material by movement of dislocations has been proposed as possible mechanism for densification during sintering. Importance was given to identify dislocation sources during the sintering process. Even if frank read sources are present in the neck region, the stress available for dislocation generation is very small, indicating that the generation of dislocation must come from free surfaces. Only if the surface is very small of the order of 40 nm, the stress required for dislocation generation will be sufficient. But experimental results have shown the absence of applied stress and plastic flow is expected to occur during early stages of sintering. Plastic flow mechanism is predominant during hot pressing.

Property changes during sintering

• Densification is proportional to the shrinkage or the amount of pores removed in the case of single component system

• IN multicomponent system, expansion rather than shrinkage will result in densification and hence densification can not be treated as equal to the amount of porosity removed.

• densification results in mechanical property change like hardness, strength, toughness, physical properties like electrical, thermal conductivity, magnetic properties etc. Also change in composition is expected due to the formation of solid solution.

Indicated property compared to solid material, %

100

density

strength

ductility

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Time

Mechanism during liquid phase sintering

In the sintering of multi-component systems, the material transport mechanisms involve self diffusion and interdiffusion of components to one another through vacancy movement. **Sintering of such systems may also involve liquid phase formation, if the powder aggregate consists of a low melting component whose melting point is below the sintering temperature**

Liquid phase sintering: In this, the liquid phase formed during sintering aids in densification of the compacts. **Liquid phase sintering employs a small amount of a second constituent having relatively low melting point. This liquid phase helps to bind the solid particles together and also aids in densification of the compact.** This process is widely used for ceramics – porcelain, refractories.

Three main considerations are necessary for this process to occurs, 1. presence of appreciable amount of liquid phase, 2. appreciable solubility of solid in liquid, 3. complete wetting of the solid by liquid.

Three main stages are observed in liquid phase sintering, 1. initial particle rearrangement occurs once the liquid phase is formed. The solid particles flow under the influence of surface tension forces, 2. solution & reprecipitation process: in this stage, smaller particles dissolve from areas where they are in contact. This causes the particle centers to come closer causing densification. The dissolved material is carried away from the contact area and reprecipitate on larger particles, 3. solid state sintering

This form of liquid phase sintering has been used for W-Ni-Fe, W-Mo-Ni-Fe, W-Cu systems. The three stage densification is schematically shown in figure.
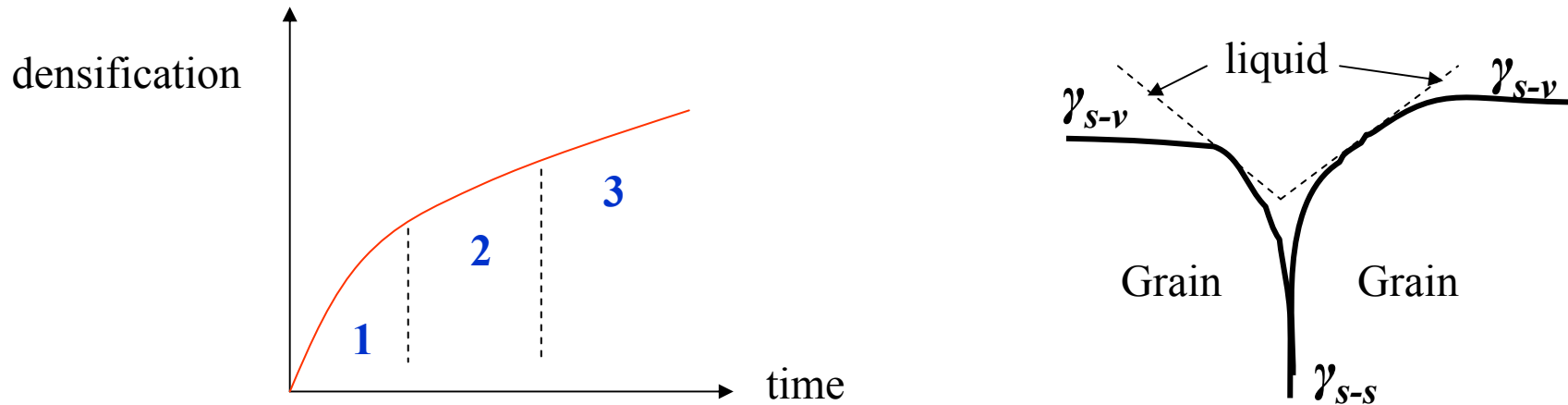
IN solid phase sintering, the solid particles are coated by the liquid in the initial stage. In liquid phase sintering, the grains are separated by a liquid film. The dihedral angle (θ) is important. For the figure shown here, the surface energy for the solid-liquid-vapour system is, $\theta = \gamma_{s-s}/2\gamma_{l-s}$ where γ_{s-s} & γ_{l-s} are the interfacial energies between two solid particles and liquid-solid interfaces respectively.

For complete wetting θ should be zero. This means that two liquid-solid interface can be maintained at low energy than a single solid-solid interface. This pressure gradient will make the particles to come closer. If θ is positive, grain boundaries may appear between the particles and an aggregate of two or more grains will be established. This creates formation of rigid skeleton and will hinder with densification.

Sintering atmosphere

Functions of sintering atmosphere: 1. preventing undesirable reactions during sintering, 2. facilitate reduction of surface oxides, 3. facilitating the addition of other sintering and alloying elements which enhance the sintering rate and promote densification, 4. aiding the removal of lubricants, 5. composition control and adjusting the impurity levels.

Eg. for sintering atmosphere: pure hydrogen, ammonia, reformed hydrocarbon gases, inert gases, vacuum, nitrogen based mixtures without carburizing addition, nitrogen based mixtures with carburizing addition

Type of transport	Material transport mechanism	Driving force
Vapour phase	Evaporation-condensation	Vapour pressure gradient between convex and concave regions
Sold state	Diffusion – surface diffusion Grain boundary diffusion, volume diffusion, viscous flow, plastic flow	Chemical potential Chemical potential Chemical potential
Liquid phase	Viscous flow Solution-precipitation	Surface tension Surface tension

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Selected application of powder metallurgy

<u>P/M porous filters:</u> porous filters made by P/M route can be classified into four types based on their applications like filtration, flow control, distribution, porosity. Filtration is the separation process involving the removal of gas, liquid or solid from another gas or liquid. Flow control involves regulation of fluid flow in a system with controlled pressure drop. Distribution involves providing a uniform flow over a wide area.

<u>Production of porous metal filters:</u> Typical filter shapes that can be produced from the powder include discs, cups, bushings, sheets, tubes. The major advantages of porous filters include high temperature resistance, good mechanical strength, corrosion, long service life.

<u>Made by Gravity sintering:</u> - Bronze filters are produced by this method. This sintering, as discussed earlier, involves pouring of graded powders in to a mould prior to sintering operation. Then sintering is performed and metallurgical bonding is achieved by diffusion.

- <u>Bronze filters</u> are made by gravity sintering using either atomized spherical bronze powder or from spherical Cu powder coated with Sn layer. The powders are sintered in graphite or stainless steel moulds at temperatures near the solidus temperature of the bronze composition. Porosities of the range 40 to 50 % can be formed.

- Porous nickel filters are made in the same fashion. Hollow, cylindrical stainless steel filters with thin wall thickness can be fabricated by cold extrusion of the plasticized mixture. These products are available in corrosion resistant alloys like stainless steel, Ti, Ni, and nickel base alloys. Desired porosity is obtained by using specific particles size and shape. Compaction and sintering is performed under controlled atmosphere to obtain good green compact part.

Made by powder rolling: porous strips of Ni, Ti, Cu, bronze and Ti alloys are prepared by powder rolling. Strips having thickness from 0.25 to 3 mm and length of several meters can be successfully made by this technique.

Made by die compaction & sintering: porous filter parts can also be made by die compaction, but with only low compaction pressures. Once achieving the green compact, the parts are heated to the desired temperature under protective atmosphere to promote bonding between atoms. Porous parts from bronze, nickel, stainless steel, titanium powders can be produced by this method.

Made by powder spraying: spraying of metal powders on a substrate under controlled conditions can be used to produce porous material. It is also possible to co-spray the material along with a second material and removing the latter to obtain the porous part.

Secondary operations on P/M part: Machining – In general, machining is not necessary for porous parts. But it can be done to produce specific shape and size in which case a very sharp tooling with a slight rake is employed. The machined surface is then treated to remove the cutting fluids. EDM and laser cutting are also performed to obtain specific shape and size.

Joining – Joining of porous parts can be done with one another or with solid part mainly in the case of stainless steel porous components. TIG, LASER or electron beam welding are recommended for satisfactory joining of porous parts. Soldering and brazing are not used. Epoxy resins are also used for bonding of porous parts.

Insert moulding, sinter bonding, press fitting are other secondary operations.

Applications of porous parts: porous metallic filters – porous filters remove solid particles from streams of liquid such as oil, gasoline, refrigerants, polymer melts and from air or other gases. The important characteristics of filter materials are, adequate mechanical strength, retention of solid particles up to a specified size, fluid permeability, adequate resistance to atmosphere attack.

Typical pore sizes are 0.2, 0.5, 1, 2, 5, 10, 20, 40, 60 and 100 microns. The most widely used metallic filter materials are porous copper-tin bronze and porous stainless steel. For filtering highly corrosive fluids, filters made form monel, inconel, Ti can be used.

They are also used in flow control devices, distribution applications etc.