LECTURE NOTES
4^{th} Semester B. Tech/2020
TH-MATERIALS PROCESSING
BRANCH-METALLURGICAL AND MATERIALS ENGINEERING

DISCLAIMER

MODULE-V

Powder Metallurgy–Engineering and technology of producing metal powders and making finished / semifinished objects from mixed or alloyed powders with or without the addition of nonmetallic constituents

Basic Processes In Powder Metallurgy:

Powder production, Compaction, Sintering, & Secondary operations

Powder production:
Raw materials: Powder
Powders can be pure elements, pre-alloyed powders.
Methods for making powders –

- Atomization: Produces powders of both ferrous and non-ferrous powders like stainless steel, superalloys, Ti alloy powders.
- Reduction of compounds: Production of iron, Cu, tungsten, molybdenum
- Electrolysis: for making Cu, iron, silver powders.

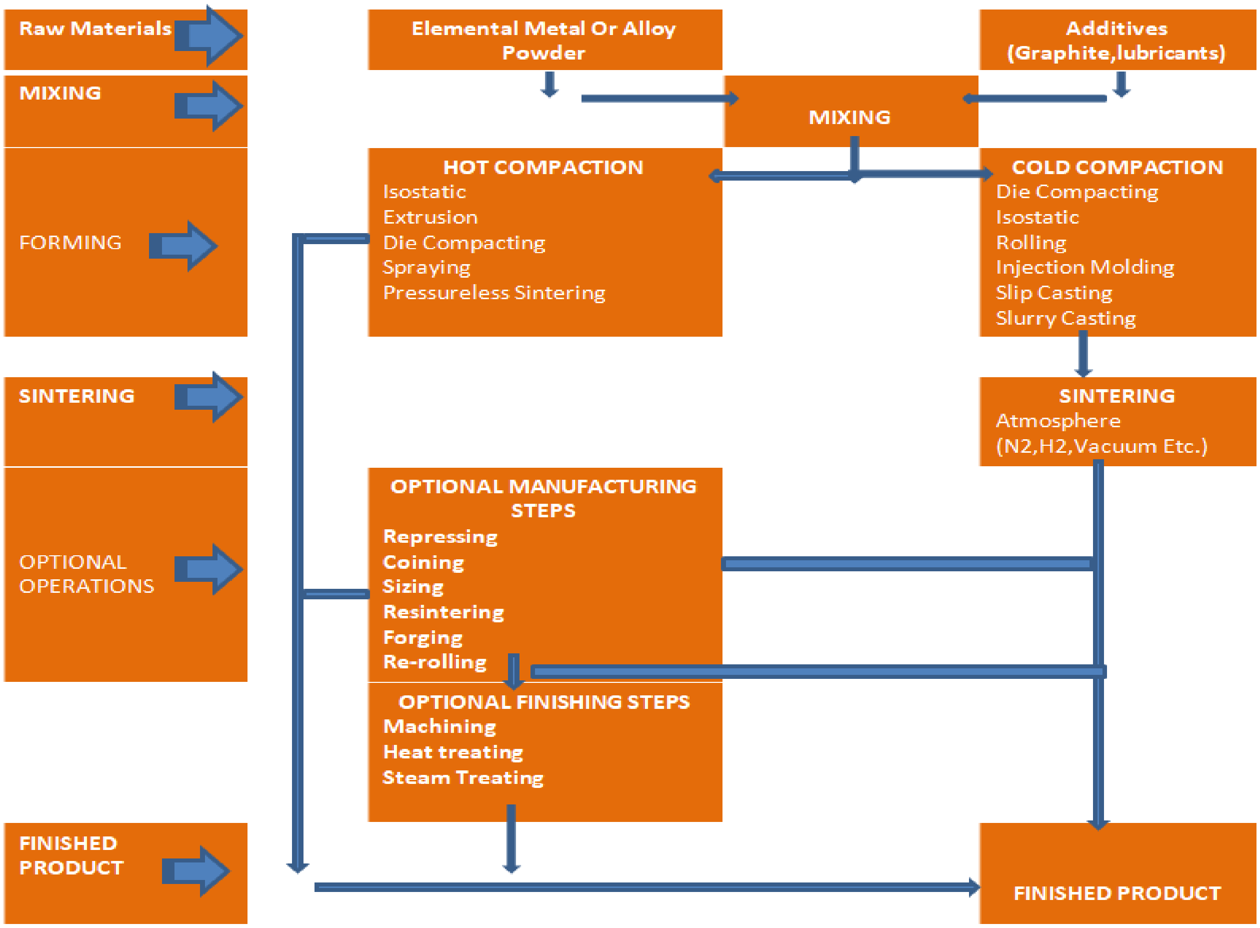
Powders along with additives are mixed using mixers. Lubricants are added prior to mixing to facilitate easy ejection of compact and to minimize wear of tools; Waxes, metallic stearates, graphite etc.
Powder characterization –
size, flow, density, compressibility tests.

Compaction:
compaction is performed using dies machined to close tolerances.Dies are made of cemented carbide, die/tool steel; pressed usinghydraulic or mechanical presses.The basic purpose of compaction is to obtain a green compact with sufficient strength to withstand further handling operations.The green compact is then taken for sintering
Hot extrusion, hot pressing, hot isostaticpressing - consolidation at high temperatures

Sintering:
Performed at controlled atmosphere to bond atoms metallurgically; Bonding occurs by diffusion of atoms; done at 70% of abs. melting point of materials. It serves to consolidate the mechanically bonded powders into a coherent body having desired on service behavior.Densification occurs during the process and improvement in physical and mechanical properties are seen.

Furnaces –mesh belt furnaces (up to 1200C), walking beam, pusher type furnace, batch type furnaces are also used
Protective atmosphere: Nitrogen

Secondary operations:
Operations include repressing, grinding, plating can be done; They are used to ensure close dimensional tolerances, good surface finish, increase density, corrosion resistance etc.



Flow Chart For Making P/M Components

Advantages & Limitations

•Efficient material utilization
•Enables close dimensional tolerances –near net shape possible
•Good surface finish
•Manufacture of complex shapes possible
•Hard materials used to make components that are difficult to machine can be readily made –tungsten wires for incandescent lamps
•Environment friendly, energy efficient
•Suited for moderate to high volume component production
•Powders of uniform chemical composition - reflected in the finished part
•wide variety of materials - miscible, immiscible systems; refractory metals
•Parts with controlled porosity can be made
•High cost of powder material & tooling
•Less strong parts than wrought ones
•Less well known process

Production of powders

•Metal powders - Main constituent of a P/M product; final properties of the finished P/M part depends on size, shape, and surface area of powder particles
•Single powder production method is not sufficient for all applications
Powder production methods: 1. Mechanical methods, 2. Physical methods, 3. Chemical methods
1.Mechanical methods- Cheapest of the powder production methods; These methods involve using mechanical forces such as compressive forces, shear or impact to facilitate particle size reduction of bulk materials;
Eg.:Milling-illing:During milling, impact, attrition, shear and compression forcesare acted upon particles. During impact, striking of one powder particle against another occurs. Attritionrefers to the production of wear debris due to the rubbing action between two particles. Shearrefers to cutting of particles resulting in fracture. The particles are broken into fine particles by squeezing action in compression force type.
Main objective of milling:Particle size reduction (main purpose),Particle size growth, shape change, agglomeration (joining of particles together), solid state alloying, mechanical or solid state mixing, modification of material properties

Mechanism of milling: Changes in the morphology of powder particles during milling results in the following events.
1.Microforging, 2. Fracture, 3. Agglomeration, 4. Deagglomeration
Microforging- Individual particles or group of particles are impacted repeatedly so that they flatten with very less change in mass
Fracture- Individual particles deform and cracks initiate and propagate resulting in fracture
Agglomeration - Mechanical interlocking due to atomic bonding or vandeWaals forces
Deagglomeration- Breaking of agglomerates

The different powder characteristics influenced by milling are shape, size, texture, particle size distribution, crystalline size, chemical composition, hardness, density, flowability, compressibility, sinterability, sintered density

Milling equipment:The equipments are generally classified as crushers & mills
Crushing- for making ceramic materials such as oxides of metals;
Grinding- for reactive metals such as titanium, zirconium, niobium, tantalum

Ball mills:

•This contains cylindrical vessel rotating horizontally along the axis. Length of the cylinder is more or less equal to diameter. The vessel is charged with the grinding media. The grinding media may be made of hardened steel, or tungsten carbide, ceramics like agate, porcelain, alumina, zirconia. During rolling of vessel, the grinding media & powder particles roll from some height. This process grinds the powder materials by impact/collision & attrition.
•Milling can be dry milling or wet milling. In dry milling, about 25 vol% of powder is added along with about 1 wt% of a lubricant such as stearicor oleic acid. For wet milling, 30-40 vol% of powder with 1 wt% of dispersing agent such as water, alcohol or hexane is employed.
•Optimum diameter of the mill for grinding powders is about 250 mm

Vibratory ball mill:

•Finer powder particles need longer periods for grinding
•In this case, vibratory ball mill is better - here high amount of energy is imparted to the particles and milling is accelerated by vibrating the container
•This mill contains an electric motor connected to the shaft of the drum by an elastic coupling. The drum is usually lined with wear resistant material. During operation, 80% of the container is filled with grinding bodies and the starting material. Here vibratory motion is obtained by an eccentric shaft that is mounted on a frame inside the mill. The rotation of eccentric shaft causes the drum of the vibrating mill to oscillate.
•In general, vibration frequency is equal to 1500 to 3000 oscillations/min.The amplitude of oscillations is 2 to 3 mm. The grinding bodies is made of steel or carbide balls, that are 10-20 mm in diameter.The mass of the balls is 8-10 times the charged particles.Final particle size is of the order of 5-100 microns

Attrition mill: In this case, the charge is ground to fine size by the action of a vertical shaft with side arms attached to it. The ball to charge ratio may be 5:1, 10:1, 15:1. This method is more efficient in achieving fine particle size.
Rod mills:Horizontal rods are used instead of balls to grind. Granularityof the discharge material is 40-10 mm. The mill speed

varies from 12 to 30 rpm.

Planetary mill:High energy mill widely used for producing metal, alloy, and composite powders.

Fluid energy grinding or Jet milling:

The basic principle of fluid energy mill is to induce particles to collide against each other at high velocity, causing them to fracture into fine particles

•Multiple collisions enhance the reduction process and therefore, multiple jet arrangements are normally incorporated in the mill design. The fluid used is either air about 0.7 MPa or stream at 2 MPa. In the case of volatile materials, protective atmosphere of nitrogen and carbon-di-oxide is used.

•The pressurized fluid is introduced into the grinding zone through specially designed nozzles which convert the applied pressure to kinetic energy. Also materials to be powdered are introduced simultaneously into the turbulent zone.

•The velocity of fluid coming out from the nozzles is directly proportional to the square root of the absolute temperature of the fluid entering the nozzle. Hence it is preferable to raise the temperature of fluid to the maximum possible level without affecting the feed material.

•If further powdering is required, large size particles are separated from the rest centrifugal forces and re-circulated into the turbulent zone for size reduction. Fine particles are taken to the exit by viscous drag of the exhaust gases to be carried away for collection.

•This Jet millingprocess can create powders of average particle size less than 5 µm

Machining:Mg, Be, Ag, solder, dental alloy are specifically made by machining; Turning and chips thus formed during machining are subsequently crushed or ground into powders

Shotting: Fine stream of molten metal is poured through a vibratory screen into air or protective gas medium. When the molten metals falls through screen, it disintegrates and solidifies as spherical particles. These particles get oxidized. The particles thus obtained depends on pore size of screen, temperature, gas used, frequency of vibration. Metal produced by the method are Cu, Brass, Al, Zn, Sn, Pb, Ni. (this method is like making Boondhi)

Graining: Same as shottingexcept that the falling material through sieve is collected in water; Powders of cadmium, Bismuth, antimony are produced.

2. Physical methods

Electrolytic deposition

•In this method, the processing conditions are so chosen that metals of high purity are precipitated from aqueous solution on the cathode of an electrolytic cell. This method is mainly used for producing copper, iron powders. This method is also used for producing zinc, tin, nickel, cadmium, antimony, silver,lead, beryllium powders.

•Copper powder Solution containing copper sulphateand sulphuricacid; crude copper as anode

•Reaction: at anode: Cu --> Cu++ e-; at cathode: Cu++ e-->Cu

•Iron powder- Anode is low carbon steel; cathode is stainless steel. The iron powder deposits are subsequently pulverized by milling in hammermill. The milled powders are annealed in hydrogen atmosphere to make them soft

•Mg powder-Electrodeposition from a purified magnesium sulphateelectrolyte using insoluble lead anodes and stainless steel cathodes

•Powders of thorium, tantalum, vanadium - fused salt electrolysis is carried out at a temperature below melting point of the metal. Here deposition will occur in the form of small crystals with dendriticshape

Atomization

This uses high pressure fluid jets to break up a molten metal stream into very fine droplets, which then solidify into fine particles

High quality powders of Al, brass, iron, stainless steel, tool steel, superalloysare produced commercially

Types:

water atomization, gas atomization, soluble gas or vacuum atomization, centrifugal atomization, rotating disk atomization, ultrarapidsolidification process, ultrasonic atomization

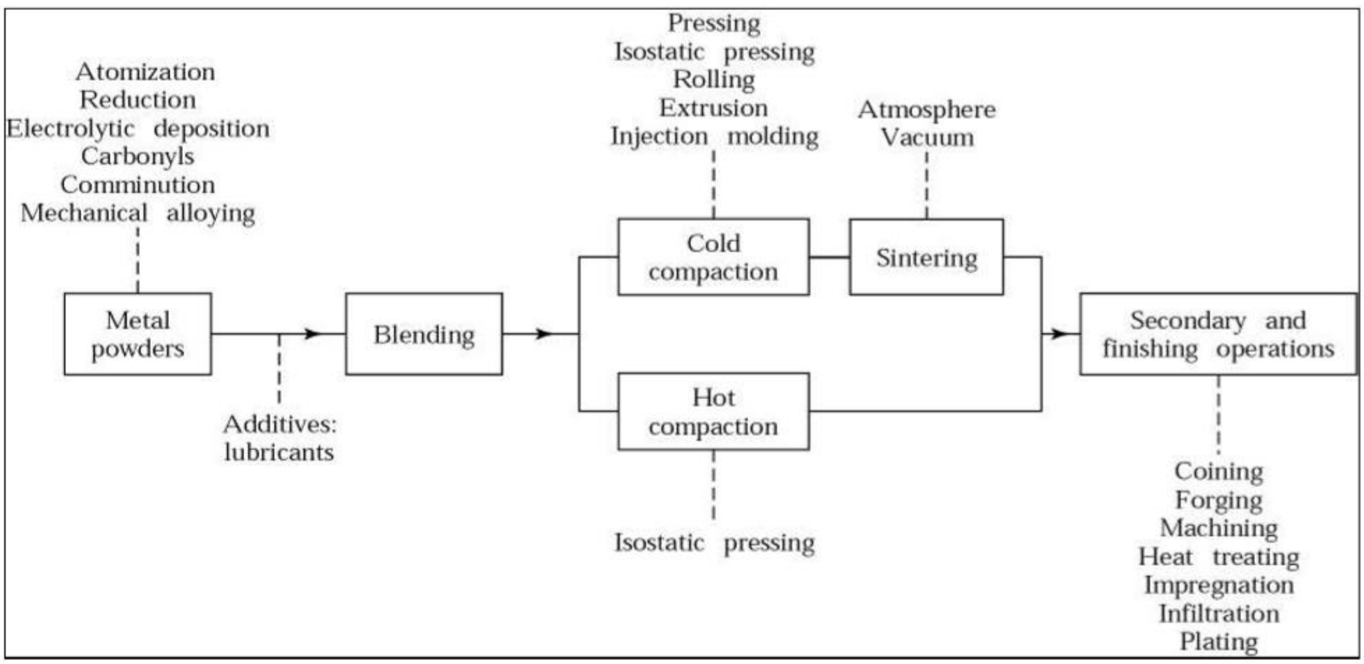
Mechanism of atomization:

In conventional (gas or water) atomization, a liquid metal is produced by pouring molten metal through a tundishwith a nozzle at its base. The stream of liquid is then broken into droplets by the impingement of high pressure gas or water. This disintegration of liquid stream is shown in fig. This has five stages

i)Formation of wavy surface of the liquid due to small disturbances
ii)Wave fragmentation and ligament formation
iii)Disintegration of ligament into fine droplets
iv)Further breakdown of fragments into fine particles
v)Collision and coalescence of particles

•The interaction between jets and liquid metal stream begins with the creation of small disturbances at liquid surfaces, which grow into shearing forces that fragment the liquid into ligaments. The broken ligaments are further madeto fine particles because of high energy in impacting jet.
•Lower surface tension of molten metal, high cooling rate - formation of irregular surface : like in water atomization
•High surface tension, low cooling rates - spherical shape formation : like in inert gas atomization
•The liquid metal stream velocity, $v = A\,[2g\,(P_i - P_g)\rho]^{0.5}$
where P_i–injection pressure of the liquid, P_g –pressure of atomizing medium, ρ–density of the liquid

Making powder & subsequent processing



Powder treatment & Handling

In powder conditioning, the powders prepared by various methodsare subjected to a variety of treatments to improve or modify their physical, chemical characteristics

Powder treatments

Powders manufactured for P/M applications can be classified into–elemental powders, and pre-alloyed powders
Elemental powders- powdersof single metallic element; eg.: iron for magnetic applications
Pre-alloyed powders- more than one element; made by alloying elemental powders during manufacturing process itself; IN this case, all the particles have same nominal composition and each particle is equivalent to small ingot
Majority of powders undergo heat treatmentsprior to compaction like,
i) Drying to remove moisture, ii) grinding/crushing to obtain fine sizes, iii) particle size classification to obtain the desired particle size distribution, iv) annealing, v) mixing and blending of powders, vi) lubricant addition for powder compaction, vii) powder coating

a)Cleaning of Powders:

•Refers to the removal of contaminants, solid or gaseous, from the powder particles
•Solid contaminants- come from several sources like nozzles or crucible linings. They interfere during compaction and sintering preventing propermechanical bonding
•Most of these contaminants are non-reactive, but they act as sites for crack nucleation and reduce the dynamic properties of the sintered part; Non-metallic solid impurities can be removed from superalloypowders by particle separators, electrostatic

separation techniques

•Gaseous impurities like hydrogen and oxygen get into powders during processing, storage or handling if proper care is not taken. Finer the powders, contamination will be more because of large powder surface area.

•These gaseous impurities can form undesirable oxides during processing at relatively high temperatureor gets trapped inside the material as pores, reducing the in situ performance of the P/M part; Degassing techniques like cold, hotstatic or dynamic degassing methods are used to remove adsorbed gases from the powders

•Lubricants added to the powders for better compaction has to be removed for desirable final P/M part

b) Grinding:

Similar to the mechanical methods seen earlier; Milling is widely used for reducing the aggregates of powder; Milling time, speed, type canbe selected for getting required degree of grinding

c) Powder classification & screening:

Powder size and shape, size distribution varied within specified range is required for better behavior of P/M parts; In this method, the desired particle size distributions with particle sizes within specific limits can be obtained; These variation depends on lot also.

d) Blending & mixing:Blending–

Process in which powders of the same nominal composition but having different particle sizes are intermingled. This is done to (i) obtain a uniform distribution of particle sizes, i.e. powders consisting of different particle sizes are often blended to reduce porosity, (ii) for intermingling of lubricant with powders to modify metal to powder interaction during compaction

Mixing–Process of combining powders of different chemistries such as elemental powder mixes (Cu-Sn) or metal-nonmetal powders. This may be done in dry or wet condition. Liquid medium like alcohol, acetone, benzene or distilled water are used as milling medium in wet milling. Ball mills or rod mills are employed for mixing hard metals such as carbides

Mixing methods

The various types of mixing methods are, (i) convective mixing: transfer of one group of particles from one location to another, (ii) diffusive mixing: movement of particles on to newly formed surface, (iii) shear mixing: deformation & formation of planes within the powders

Depending on the extent of mixing, mixing can be classified as (i) perfectly mixed or uniform mixing, (ii) random mixed, & (iii) totally un-mixed. The mixing should be stopped when random mixture is achieved. Overmixingleads to reduced flow characteristics of the mix

Heat Treatment Of Powders

Heat treatment is generally carried out before mixing or blending the metal powders. Some of the important objectives are,

i)Improving the purity of powder:Reduction of surface oxides from powders by annealing in hydrogen or other reducing atmosphere. Dissolved gases like hydrogen and oxygen, other impurities are removed by annealing of powders. Lowering impurities like carbon results in lower hardness of thepowder and hence lower compaction pressures & lower die wear during compaction. For eg., atomized powders having a combined carbon and oxygen content as high as 1% can be reduced after annealing to about 0.01% carbon and 0.2% oxygen. Heat treatment is done at protective atmosphere like hydrogen, vacuum.

ii)Improving the powder softness:Aim is to reduce the work hardening effect of powders that has be crushed to obtain fine powders; while many powders are made by milling, crushing or grinding of bulk materials. Powder particles are annealed under reducing atmosphere like hydrogen. The annealing temperature is kept low to avoid fusion of the particles.

iii)Modification of powder characteristics: The apparent density of the powders can be modified to a higher or lower value by changing the temperature of treatment.

Toxicity Of Powders

•Toxicity leads to undesirable health effects like eye, skin irritation, vomiting, respiratory problems, blood poisoning etc.

•powder like lead, nickel are highly toxic & Al, iron are less toxic

•Precautions: Use of protective gloves, respiratory masks, protective clothing etc.; use of well ventilated storage, workplace; careful handling, disposal of wastes

•flammability & reactivity data is required

•Health effects: Inhalation –disturbs the respiratory track; remedial measures include moving the person to fresh air. Artificial breathing is requiredif patient not breathing properly.

Skin, eyes –Brushing, washing skin and eyes with water and soap. Clean eyeswith fresh water for 15 mts.

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) isostaticpressing, iii) powder rolling, iv) powder extrusion, v) explosive compaction

Pressurelesscompaction 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, pressurelesssintering. 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. Themain 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 andfuel cells are typical examples.

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

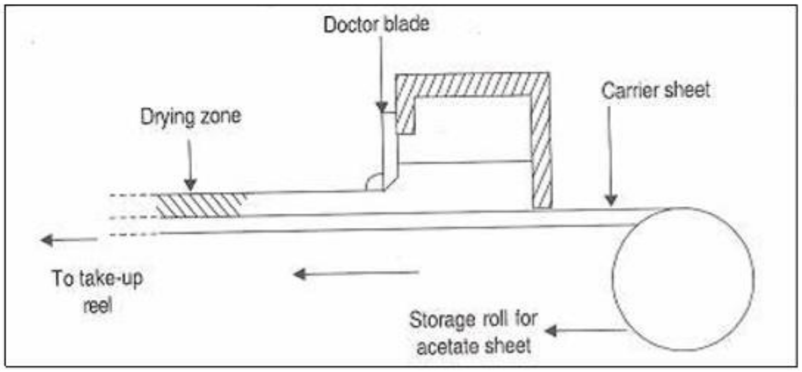
-A slip is a suspensionof metal or ceramic powder (finer than 5 μm) in water or other soluble liquid which is pored into a mould, dried and further sintered.

-Slip is usually made of, 1) a dispersion agentto stabilize the powder against colloidal forces, 2) a solventto control the slip viscosity and facilitate casting, 3) a binderfor giving green strength to the cast shape, 4) plasticizerto modify the properties of the binder

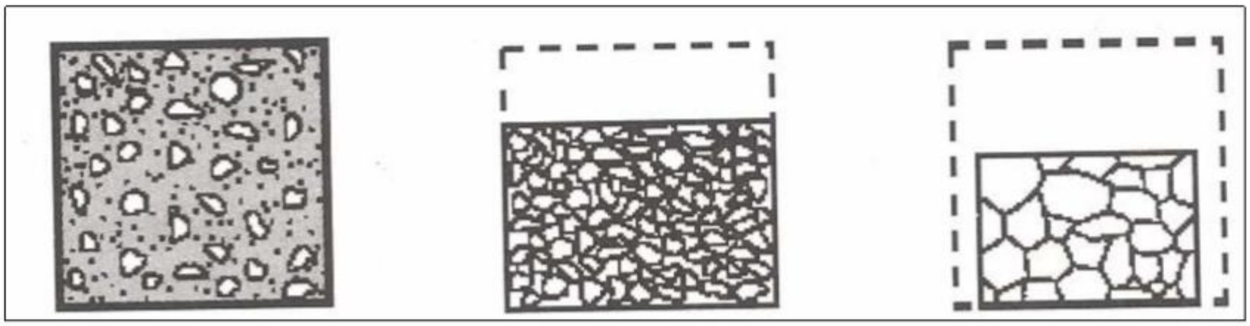
-For successful slip casting, formation of appropriate and a consistent slip is important. This is achieved by proper control of particle size, size distribution, order of component addition, their mixing time, addition of proper deflocculant-to prevent the settling and aggregation of powders and maintains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

-Mostly water is used as suspending medium, but absolute alcoholor 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 thatit 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.
•For coarser, spherical stainless steel powder, a mixer of 80.7%metal powder, 19% water, 0.3% of sodium alginate as deflocculanthaving 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 guidancefins; Also products with excellent surface finish like basins, water closets.
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 nickelcadmium 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 ceramicpowder 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



Stages in tape casting

V) Vibratory compaction:-

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 developcrack 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. inertia of system:larger the system, more the energy required for packing
2. friction force between particles:more friction results in need of more KE for compaction
3. particle size distribution:more frequency required if more large particles are present. Vibration cycle is important and not period of vibration.

Pressure compaction techniques

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

•**Die compaction:**

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.

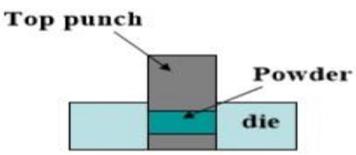
•Unidirectional and bidirectional compaction involves same number of stages and are described in this figure. They are, i) charging the powder mix, ii) applying load using a punch (uni-) or double punch (bi-) to compact powders, iii) removal of load by retracting the punch, iv) ejection of green compact.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

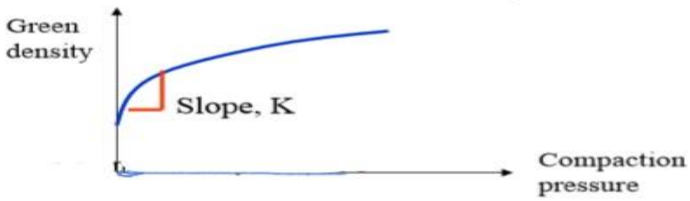
Effect of powder characteristics

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.





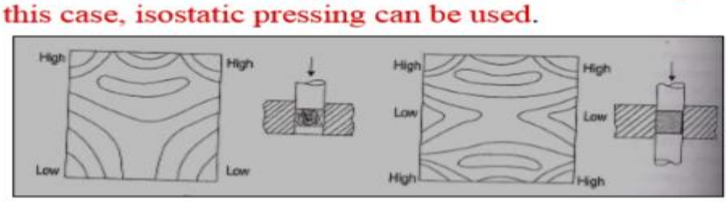
- The green compact produced can be considered as a two-phase aggregate consisting of powder particles and porosity each having own shape and size.

- 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.

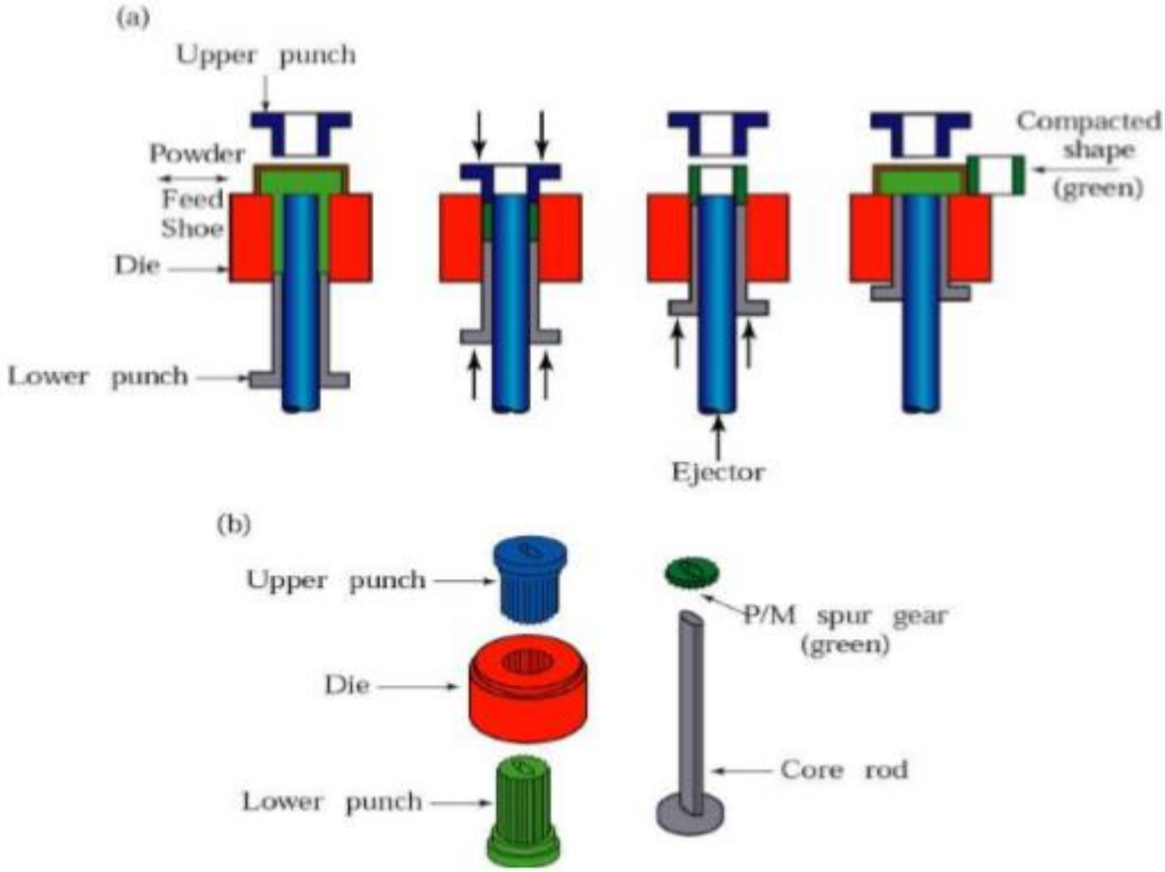
- This density variation and hence final property variation can be greatly reduced by having **double ended die compaction**. In this case, powder experiences more uniform pressure from both top and bottom, resulting in minimization of density variation. But this variation will still be considerable 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



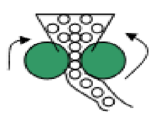
Double ended compaction

Schematic of powder compaction



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.

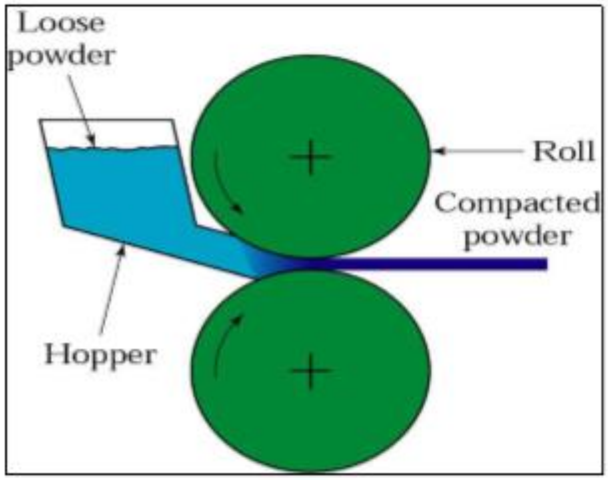


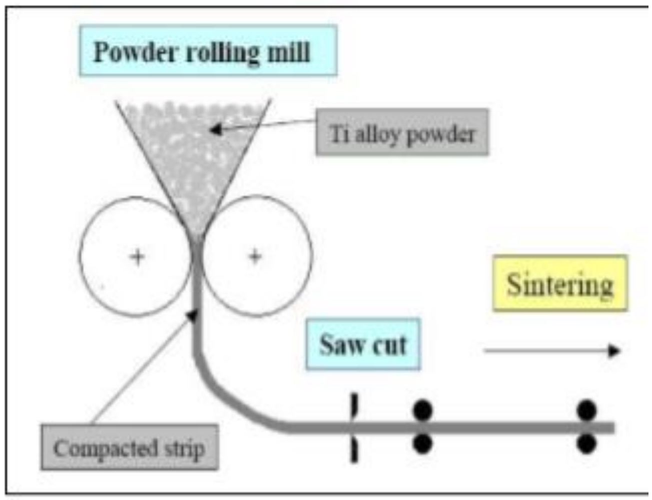
Steps: 1) preparation of green strip, 2) sintering, 3) densification of sintered strip, 4) final cold rolling and annealing

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.





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.

-HIP presses are available in diameters up to 2m with pressures ranges from 40 to 300 MPawith 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 diffusionand creep, but also bonded across the interface to form a continuous material.

-Commonly used heating elements:Kanthalheating element –up to 1200 °C; Molybdenum heating element –1200 to 1700 °C; Graphite heating element –2000 to 2600 °C

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

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). .

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 $\gamma_{SS.}$ 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., $\boldsymbol{dE = \gamma_{SS}\, dA_{SS} + \gamma_{SV}\, dA_{SV} \leq 0}$

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 $dE = 0$,

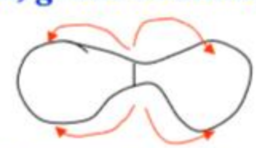
i.e., $\boldsymbol{\gamma_{SS}\, dA_{SS} + \gamma_{SV}\, dA_{SV} = 0 \Rightarrow \gamma_{SS} / \gamma_{SV} = - dA_{SV} / dA_{SS}}$

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.

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, $\boldsymbol{\mu - \mu_0 = RT \ln(p/p_0) = (-\gamma)(\Omega)/r}$ 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

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

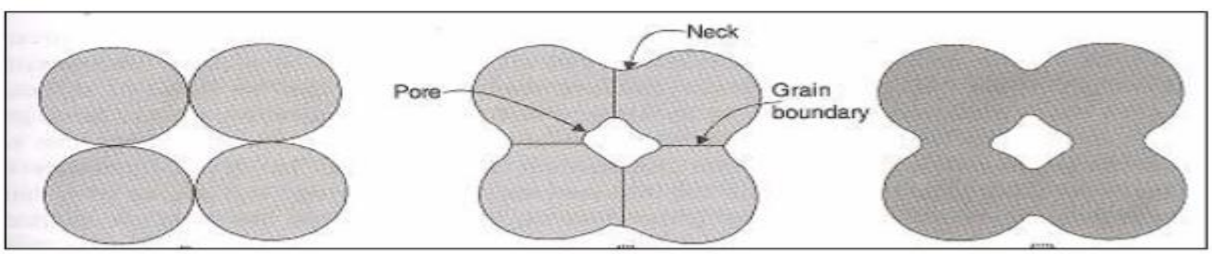
transport can be through adhesion, surface diffusion. Many models available to describe sintering process –like viscous flow, plastic flow, grain boundary and volume diffusion models. These models will be briefly described here.

Stages in solid state sintering

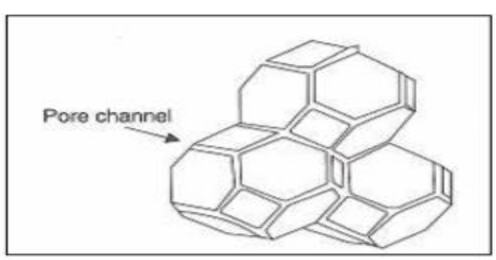
• In general, solid state sintering can be divided into three stages – 1^{st} stage: *Necks are formed at the contact points between the particles*, which continue to grow. During this rapid neck growth takes place. Also the pores are interconnected and the pore shapes are irregular.

• 2^{nd} 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.

• 3^{rd} 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.



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



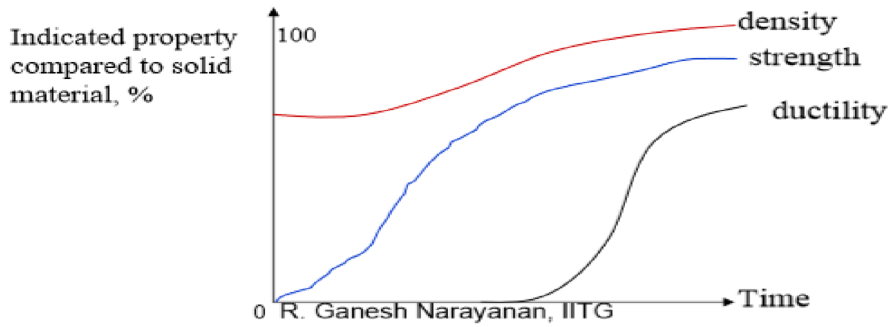
Pore channel formation

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.



Mechanism during liquid phase sintering

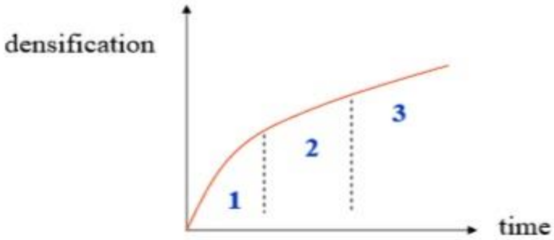
In the sintering of multi-component systems, the material transport mechanisms involve self diffusion and interdiffusion of components to one another through vacancy movement. **Sintering of such systems may also involve liquid phase formation, if the powder aggregate consists of a low melting component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

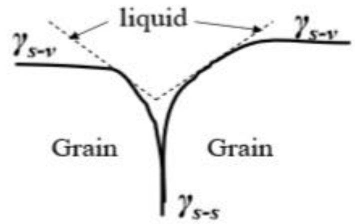
Liquid phase sintering: In this, the liquid phase formed during sintering aids in densification of the compacts. **Liquid phase sintering employs a small amount of a second constituent having relatively low melting point. This liquid phase helps to bind the solid particles together and also aids in densification 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.

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	Surface tension

Selected Application Of Powder Metallurgy

P/M porous filters: 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 fluidflow in a system with controlled pressure drop. Distribution involves providing a uniform flow over a wide area.

Production of porous metal filters: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.

Made by Gravity sintering:-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.

-Bronze filtersare made by gravity sintering using either atomized spherical bronze powder or from spherical Cu powder coated with Snlayer. The powders are sintered in graphite or stainless steel moulds at temperatures near the solidustemperature of the bronze composition. Porosities of the range 40 to 50 % can be formed

-Porous nickel filtersare made in the same fashion. Hollow, cylindrical stainless steel filterswith thin wall thickness can be fabricated by cold extrusion ofthe 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 andlength 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 toobtain the porous part