MANUFACTURING PROCESS IN METALLURGY

POWDER METALLURGY

SINTERING OF GREEN PRODUCTS

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SINTERING

It is the process, by which, assembly of powder particles compacted under pressure or confined in a container/die, chemically bond themselves into a coherent body/sintered products under the influence of controlled temperature and time. In addition to the bonding of the particles, sintering may be used to accomplish other functions; these includes alloying, heat treatment, joining, and densification. Densification refers to shrinkage resulting from elimination of porosity.
Sintering is required to be done to single component (pure metal and ceramics), where shrinkage takes place mainly or multicomponent system, where solid solution formation and liquid/gas phase formation takes place along with densification.

**Types of sintering:**

a) **Solid state sintering:** In case of single component system (pure metal and ceramics) in solid state, densification occurs mainly because of self atomic diffusion, a major transport mechanism and the driving force resulting from a chemical potential gradient due to surface tension and capillary forces between particles.
In case of multicomponent system (alloys - e.g. Cu-Ni etc.) in solid state, densification occurs due to inter-atomic diffusion with the concentration gradient, a major driving force, in addition to self-diffusion caused by surface tension & capillary forces.

In case of single component system, sintering takes place in two stages, adhesion and recrystallization. Adhesion occurs during heating due to atomic attraction and recrystallization occurs at temperatures above 0.7 Tm, consists of diffusion of atoms between adjacent grains. Recrystallization results in changes in microstructure, phase change, grain growth,
Sintering

Heats the powder below the melting point to allow solid-state diffusion and bond the particles together.

FIGURE 18.12 Sintering on a microscopic scale: (1) particle bonding is initiated at contact points; (2) contact points grow into “necks”; (3) the pores between particles are reduced in size; and (4) grain boundaries develop between particles in place of the necked regions.
precipitation and pore shrinkage.
In case of multicomponent component system, sintering takes place in two stages, material transport mechanisms (self-diffusion caused by capillary forces), inter-diffusion of components into one another (due to concentration gradient) through vacancy movement. Diffusion results in homogenization of composition, the extend of which, depends upon diffusion coefficient. This depend upon particle size, sintering temperature and time. The sintering process in such case is due to Kirkendall effect, causing excess vacancy. This can be improved by addition of a
small amount of second phase (dopants e.g. nickel or palladium), which enhanced grain boundary diffusion.

b) **Liquid phase sintering:** This is most suitable for multicomponent system. In this process, the sintering temperature is high enough so that liquid phase is present during all or part of the sintering time. Liquid phase (1-10% vol.) leads to rapid densification, which has some solubility for the solid. Liquid covering solid crystallizes at the grain boundaries and binds the grains resulting rapid rearrangement of solid particles leading to increase in density. Then, liquid dissolves the solid until it is saturated by keeping
sintering temperature above liquid formation temperature. Lastly, solid phase sintering occurs resulting changes in microstructure & phase, grain coarsening and densification. Densification will improve if pressure is applied simultaneously. e.g. W-Cu, Cu-Sn, covalent compound, cemented carbide, etc.

For effective sintering, following conditions must be fulfilled:
1. Presence of an appreciable/minimum amount of liquid phase so that deformation of green compact should not take place.
2. Appreciable solubility of solid in liquid.
3. Complete wetting of the solid by liquid.
4. Initial particle size must be small as smaller particles have higher surface energy/unit volume resulting higher driving force.
5. Temperature is to be properly controlled as diffusion is taking place through liquid phase only. Very high temperature will result in deformation of green compacts.
c) Vapour phase sintering: This is used in case of multicomponent system. In this process, the sintering temperature is high enough so that gas/vapour phase is present during all or part of the sintering time. Gas phase diffuses and then crystallizes at the grain boundaries resulting rapid rearrangement of solid particles leading to increase in density. After this stage, solid phase sintering occurs by inter-atomic diffusion with the concentration gradient, a major driving force, in addition to self-diffusion caused by surface tension & capillary forces resulting change in microstructure & phase, grain coarsening and densification. e.g. Fe-Zn.
Most of the work on sintering has been concerns with the “Why” and “How” of sintering. The “Why” refers to the driving force of the process, the reasons for the changes taking place during sintering and “How” is related to the mechanism of the material transport within the sinter mass that bring about the changes. These changes are usually referred to as the stage of sintering.

**Driving force for sintering:**

The driving force for solid state sintering is excess surface free energy. In this, the powder compact tries to reduce the surface energy by transporting material from different areas by
various material transport mechanisms so as to eliminate pores. The driving forces during sintering are surface tension forces, diffusional flow, pore channel closure, shrinkage, and formation of isolated pores. Material transport during sintering occurs through gas phase, liquid phase or solid state. In solid state sintering, mechanism of mass transport takes place by surface transport, grain boundaries or bulk transportation. The surface transport takes place through diffusion, adhesion or evaporation-condensation or by surface diffusion, viscous flow, plastic flow, grain boundary and volume diffusion.
Stages in solid state sintering:

It takes place in following six stages:
1. Bonding
2. Neck growth
3. Pore channel closure
4. Pore rounding
5. Densification or pore shrinkage
6. Pore coarsening.
1. Bonding:

Bonding between particles takes place very early in the sintering process as the material heats up. The bonding process involves diffusion of atoms leading to the development of grain boundaries at a specific sintering temperature and time. This takes place at those sites where there is contact between particles sufficient in magnitude to allow bonding. This stage of sintering does not lead to any dimensional/volume change of the material. These bonds imparts a high degree of coherency and integrities to the materials. No change in Genus takes place in this stage.
2. Neck growth:

It is 2\textsuperscript{nd} stage of sintering and is related very much to the 1\textsuperscript{st} stage of initial bonding. The newly formed bond areas are termed as neck. In the 2\textsuperscript{nd} stage, these necks grow in size. This signifies a greater degree of bonding within the sinter mass. The neck growth requires the transport of materials within the sinter mass but does not employ any decrease in the amount of porosity i.e. no shrinkage of materials. If original porosity is considered in the sinter mass as somewhat irregular channels of an inter connected nature, then neck growth leads to smoothening of these channels. Although, neck
growth is generally accepted to take place rather rapidly and early in the sintering process, it may in fact continue for some time and overlap some later stage. This is promoted by the formation of new necks during sintering associated with stage 3 and 5. Neck growth also results in growth of the initial grain boundary associated with stage 1. No change in Genus takes place in this stage.

3. Pore channel closure:
This stage represents a major change in the nature of the porosity in the sinter mass i.e. interconnected 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. One of the causes of pore channel closure is neck growth. However, pore shrinkage also leads to channel closure due to new contact formed among pore surfaces. Hence, the pore channel closure stage may proceed for some time and overlap stage 4 & 5. It has been observed that with porosities greater than 10%, most of the porosity is in an interconnected form whereas with porosity less than 10%, most of the porosity is of closed or isolated type. In this stage, Genus decreases.
4. Pore rounding:

It is considered as natural consequences of neck growth. When material is transported to the neck region from the pore surfaces, the pores themselves become rounded. No pore shrinkage is necessary for pore rounding, although, it too mat be taking place during the same time. The rounding process pertains both to isolated and interconnected porosity. It is possible to achieve almost perfectly spherical pores. It should be noted that pore rounding is promoted by high sintering temperature.
5. Densification or pore shrinkage:

It is most important stage of sintering, where eventually elimination pores of sinter mass takes place. For single component systems, densification may be equivalent to pore shrinkage, whereas, in multicomponent systems, both shrinkage and expansion may take place. It is important to realize that the process of pore shrinkage, leading to decrease in the volume of the sinter mass, must involve movement of the solid into the porosity and movement of any gas in the porosity to the external surfaces. Pore shrinkage becomes less important in this stage of sintering with increasing density of the green compact. Genus decreases in this stage.
6. Pore coarsening:

This is the last stage of sintering. The process simply consists of the shrinkage and elimination of small isolated pores and growth of larger ones. The total volume of porosity associated with all these pores remains the same, but, the number of pores decreases and the average size increases. Hence, no densification of the material is associated with this stage. Genus is saturated in this stage. The figures in next two slides show the various stages of sintering.
Initial point contact

Spherical particle
D = diameter

Neck

Early stage
geripiently
neck growth
(short time)

Grain boundary

Late stage
geripiently
neck growth
(long time)

Terminal condition
fully coalesced
(infinite time)
(b) 

Stage I: Before Sintering

Stage II: Formation of Necks

Stage III: Evolution of necks and grain boundaries and elimination of pores

Stage IV: Isolation of pores

Closed pore
The geometrical description of sintering is the topological approach based on the use of several parameters. These are; number of particles in the given mass of powder (P), the number of points at which the powder particles make contact (C), and the topological genus of all the surface in the sinter mass (G).

The Genus is given by:

\[ G = C - P + 1 \]

The term genus describes the connectivity of the two dimensional surface of the sintering body. It represents the number of contacts that would have to be cut to reduce the connectivity of the
Sinter mass to that of a single chain of particles. The genus and the other parameters may be utilized to described sintering in both quantitative and qualitative manner from the view point of the structures changes taking place or the kinetics of the process. For example, three stage of sintering have been described with the context of the approach. An initial stage corresponding to number of substantial change in the topological parameter, this involves neck growth and smoothening of surface irregularities (no change in G, N or V). A second stage in which there are substantial changes in parameter, in particular, the approach of the genus to zero
related to pore channel closure and pore shrinkage & elimination, the decrease in V due to pore shrinkage & elimination and the decrease in Sv related to the decrease in V. The third stage is related to zero or residual genus that is constant, shrinkage of isolated pores & pore coarsening may take place.
Effect of variables on sintering:
Following factors affect sintering process:
1. Particle size
2. Particle shape
3. Particle structure
4. Particle composition
5. Green density
6. Particle straining
7. Temperature of sintering
8. Time of sintering
9. Atmosphere
1. Particle size:
Smaller the particle size, greater the sintering rate/densification because of greater driving force due to larger interfacial area leading to more surface diffusion, grain boundary diffusion and volume diffusion. Particle size effect the final grain size, which effect the properties of the sintered mass. Smaller particle size, greater strength of sintered products.

2. Particle shape:
More the irregular the particle shape, better the sintering rate due to more contact between particles and increase in internal surface area.
3. Particle structure:
Finer the grains size in the particle, better sintering due to favourable material transport mechanism.

4. Particle composition:
Particle composition have two effect; either it restricts the migration of grain boundary or favours the migration of grain boundary. Reaction between impurities with base metal or alloying additions at high temperature decreases the sintering rate. Dispersed phase is desirable for the sintering rate, which hinders the migration of the grain boundary.
5. Green density:
Decrease in green density improves the sintering rate due to increase in amount of internal surface area by increasing the driving force. However, the theoretical density of sintered mass will be higher for the higher green density.

6. Particle straining:
Cold worked metal compacts sinters at faster rate.
7. Temperature of sintering:
Increasing the sintering temperature significantly increases the rate and magnitude of any change occurring during sintering.

8. Time of sintering:
Degree of sintering increases with increase in sintering time. However, increase in sintering time enhances the grain coarsening and thus affect the mechanical properties of sintered products. The effect of increasing sintering time is less effective as compare to increase in sintering temperature. Hence, it is better to perform sintering at high temperature and shorter time to get desired properties of parts.
The effect of sintering temperature and time on density of sintered products can be co-related as follow:

\[ t = A \cdot \exp\left(\frac{Q}{RT}\right) \]

Where,
- \( t \) is sintering time to achieve the desired density
- \( Q \) is activation energy
- \( R \) is constant
- \( T \) is sintering temperature
- \( A \) is constant
The magnitude/extent of sintering is represented by densification parameter \((P_s)\), which is as follow:

\[
P_s = \frac{\text{Sinter product density} - \text{Green density}}{\text{Theoretical density} - \text{Green density}}
\]
9. Atmosphere:
Special sintering atmosphere (gas or mixture of gases) protects the sintering mass from undesirable action/reaction from gases present in the environment and also influences the bonding of the particles thereby properties of the sintered products. The selection of sintering atmosphere should be made in such a manner that it must not react with the materials being sintered. The sintering atmosphere used may be reducing (hydrogen, carbon monoxide), oxidizing (carbon dioxide, air, steam, oxygen), or neutral (argon, helium, vacuum) atmosphere. In similar conditions, vacuum gives higher sintering rate.
Sintering atmosphere has following functions:

1. **To clean the surface:**
To remove all the absorbed films. A proper atmosphere can remove the undesirable lubricants or binders from the green products. Similarly, surface oxides can be removed by using hydrogen atmosphere while sintering is taking place simultaneously.

2. **To prevent chemical reactions:**
Any undesirable chemical reaction between sinter mass and environment can be prevented by using proper atmosphere. For example: Oxidation, re-oxidation, carburization, decarburization, etc.
3. To maintain the equilibrium conditions without loss of alloying additions/dopants:

The final composition / loss of alloying / dopants additions of sintered products during sintering can be controlled by maintaining the equilibrium conditions of the atmosphere. These additions further enhance the rate of sintering and improve densification.

- Steam is used during sintering of UO$_2$.

- Ni is used during sintering of tungsten. Use of 0.01% Ni brings down the sintering temperature from 2700$^0$C to 1400$^0$C. It also clean the interior or pore of the compact.
- Iron powder sintered at 1000\(^0\) C gives 5% shrinkage and 10% at 1200\(^0\) C. Same iron powder with NiC\(_2\)O\(_4\) at 1000\(^0\) C gives 8% shrinkage and 15.5% at 1200\(^0\) C.

- final composition of carbon content in steel

- adjusting the impurities levels such as nitrogen content in steel.

4. **Transfer heat to the compacts:**

It helps in transferring heat through atmospheric gas to the compacts thus sintering rate is improved.