

# **6 SINTERING**

## **6.1. Introduction**

Sintering may be considered the process by which an assembly of particles, compacted under pressure or simply confined in a container, chemically bond themselves into a coherent body under the influence of an elevated temperature. The temperature is usually below the melting point of the major constituent. Much of the difficulty in defining and analyzing sintering is based on the many changes within the material that may take place simultaneously or consecutively. Densification or shrinkage of the sintered part is very often associated with all types of sintering. However, sintering can take place without any shrinkage; expansion or no net dimensional change is quite possible. From the tooling point of view it is preferred to avoid very large amount of dimensional changes. The driving force for solid state sintering is the excess surface free energy. Sintering is a complex process and for any given metal and set of sintering conditions there are likely to be different stages, driving forces and material transport mechanisms associated with the process.

Various stages of sintering can be grouped in the following sequence:

- (1) Initial bonding among particles
- (2) Neck growth
- (3) Pore channel closure
- (4) Pore rounding
- (5) Densification or pore shrinkage
- (6) Pore coarsening

A detailed description of these stages is given by Hirschhorn<sup>1</sup> and German.<sup>2</sup> Sometimes some stage overlaps over the later stages.

Among various mechanisms evaporation and condensation, surface, grain boundary and volume diffusion and plastic deformation mechanisms are prevalent. The description of such topic is beyond the scope of this book. However, a detailed account is given in the book by Lenel.<sup>3</sup>

## **6.2. Liquid Phase and Activated Sintering**

Liquid phase sintering method is getting more and more common, in which the presence of liquid phase during all or part of the sintering cycle of material is used for enhanced densification. There are two variations of the process:

- (a) normal liquid phase sintering for which the formation of the liquid

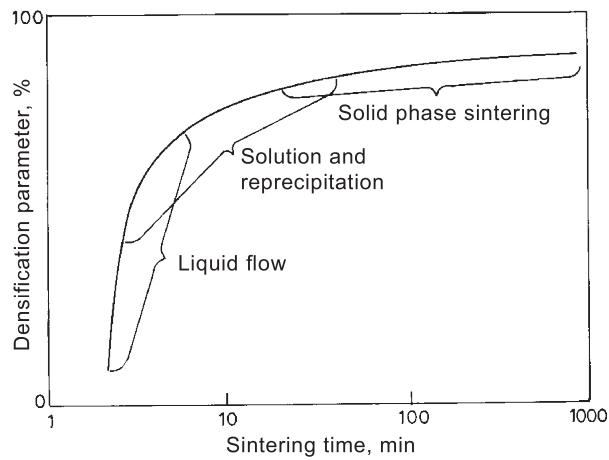
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phase is associated with one or more components contained in the original green compact.

(b) infiltration of the original green compact with a liquid formed outside the compact during the very early period of sintering. Although simultaneous infiltration and sintering appears to be dominant, infiltration of a previously sintered part is also practised.

During liquid phase sintering three stages ‘rearrangement’ or ‘liquid flow’, ‘accommodation’ or ‘dissolution and reprecipitation’ and ‘coalescence’ or ‘solid phase sintering’ take place. These stages follow in the approximate order of their occurrence, but there may be significant overlapping for any specific system. Figure 6.1 shows the densification stages during liquid phase sintering. With progress in liquid phase sintering the densification kinetics is lowered. Increasing the liquid content up to approximately 35 volume percent aids initial densification. A coarse particle size and a high green density act to offset the favourable effects of the melt. In case the second stage is not effective, the melt will penetrate along the interparticle interfaces and cause particle separation. This will contribute in swelling. A small dihedral angle inhibits coalescence of neighbouring particles. A detailed account on the theory of liquid phase sintering is given in the book by German.<sup>4</sup> Application of liquid phase sintering technology is widely made in the field of sintered steels, cemented carbides, heavy alloys, bronzes and silicon nitride systems.

**Activated sintering**, in general, refers to process in which the activation energy for sintering is lowered. This is mostly achieved by chemical addition to the powder. For certain metals, particularly refractory metals, the addition of dopant causes the densification kinetics to increase as much as 100 times compared with undoped compacts. The best activators are palladium and nickel. Nickel is often added as a solution of its salt which



**Fig. 6.1** A schematic plot of the densification of a powder compact during liquid phase sintering, showing the three stages.

is reduced to the metal and forms a layer several monatomic layers thick on the surface of the tungsten powder particles.

### **6.3. Loose Sintering**

This method is quite widely used for manufacture of highly porous parts like filters. Basically, metal powder is poured or vibrated into a mould which is then heated to the sintering temperature in an appropriate atmosphere. The form and complexity of shape which can be made by this method depend to a large extent on the flow characteristics of the powder. Since shrinkage usually takes place during sintering, only shapes where this can occur without mould constraint causing cracking can be used. The characteristics required of the mould material for loose sintering are:

(i) It should be easily machined or formed into the required shape, (ii) it should withstand the sintering temperature without appreciable deformation and (iii) it should not weld to the powder during sintering. For most applications machined or welded metal moulds are used, although graphite may also be employed where no reaction with the powder is likely, and even here a refractory mould wash may suffice to prevent reaction. Since no pressure is applied to the powder any unreduceable oxide skin on the particle will prevent metal-to-metal contact and inhibit sintering. For this reason it is virtually impossible to loose sinter aluminium powder.

### **6.4. Process Variables**

The most important factors involved during sintering process are temperature, time and furnace atmosphere. The influence of these factors on the sintering process is described below:<sup>5</sup>

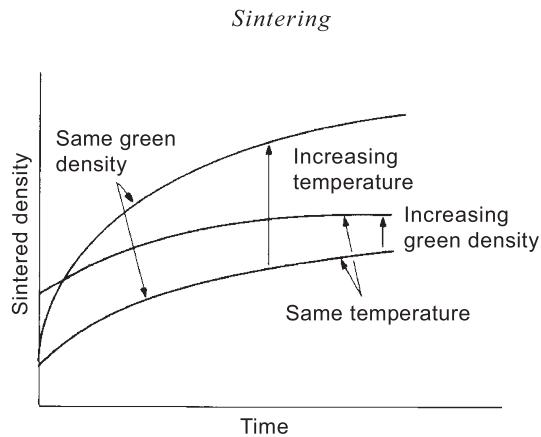
**Sintering Temperature:** Increasing the sintering temperature greatly increases the rate and magnitude of any changes occurring during sintering. Figure 6.2 illustrates the effect of increasing temperature for a constant green density.

**Sintering Time:** Although the degree of sintering increases with increasing time the effect is small in comparison to the temperature dependence. The loss of driving force with increasing time at any temperature is one of the reasons why it is so very difficult to remove all porosity by sintering. An attempt should be made to achieve the desired properties of the sintered parts by shorter sintering times and correspondingly higher temperatures. However, the maintenance costs and energy consumption of a furnace increase when its operating temperature is raised.

**Sintering Atmosphere:** The proper production, use and control of sintering atmospheres which are essential for the optimum use of the powder metallurgy process are described in a later section.

### **6.5 Material Variables**

**Particle Size:** In terms of the basic stages of sintering, decreasing particle size leads to increased sintering. The smaller particle size has a greater



**Fig. 6.2** Sintered density time curves illustrating effects of increasing green density and sintering temperature on densification.

pore/solid interfacial area producing a greater driving force for sintering. It promotes all types of diffusion transport, e.g. greater surface area leads to more surface diffusion, small grain size promotes grain boundary diffusion and a larger interparticle contact area to volume diffusion.

**Particle Shape:** The factors that lead to greater intimate contact between particles and increased internal surface area promote sintering. These factors include decreasing sphericity and increasing macro- or microsurface roughness.

**Particle Structure:** A fine grain structure within the original particles can promote sintering because of its favourable effect on several material transport mechanisms.

**Particle Composition:** Alloying additions or impurities within a metal can affect the sintering kinetics. The effect can either be deleterious or beneficial depending upon the distribution and reaction of the impurity. Surface contamination, such as oxidation is usually undesirable. Dispersed phases within the matrix may promote sintering by inhibiting grain boundary motion. Reaction between impurities and either the base metal or alloying additions at the relatively high sintering temperature may be undesirable.

**Green Density:** A decreasing green density signifies an increasing amount of internal surface area and consequently, a greater driving force for sintering. Although the percentage change in density, increases with decreasing green density, the absolute value of the sintered density remains highest for the higher green density material.

## 6.6 Dimensional Changes

Changes in dimensions resulting from sintering represent an important field in powder metallurgy, especially with respect to large scale production of parts with small dimensional tolerance. The fundamental process of sintering leads to a reduction in volume because of pore shrinkage and elimina-

tion. Following factors in this regard may be considered:

**Entrapped Gases:** The expansion of gas in closed porosity has been postulated as producing compact expansion.

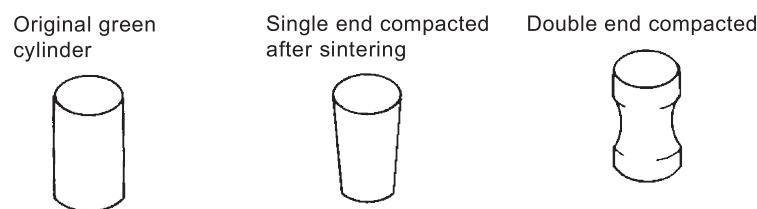
**Chemical Reactions:** Hydrogen is a common component of sintering atmospheres and can often diffuse through the metal to isolated portions of the compact where it reacts with oxygen to form water vapour. The pressure of the water vapour can lead to expansion of the entire mass. It is also possible to have reactions that lead to the loss of some element from the sinter mass to the atmosphere, such as volatilizing, and result in a shrinkage of the material.

**Alloying:** Alloying that may take place between two or more elemental powders very often leads to compact expansion. This effect which is due to the formation of a solid solution is often offset by shrinkage of the original porosity. Dimensional changes may also occur in a binary system where the rate of diffusion of each metal into the other is different.

**Shape Changes:** Green parts invariably contain variations in green density. Such variations can lead to substantial changes in shape because of the strong dependence of sintering, especially shrinkage, on green density. Low green density regions will exhibit a greater amount of shrinkage during sintering. For example, a cylinder with a relatively high  $L/D$  ratio compacted by a single action method would have a gradually decreasing green density from one end to the other. Such a cylinder would change during sintering into a truncated cone, as shown in Fig.6.3. A cylinder prepared by a double action method, on the other hand, would likely achieve an ‘hour-glass’ shape (Fig.6.3). Many times, the shrinkage (or expansion) is different in two directions – axial and radial, and must be taken into account during design of the compacting tools. Parts with complex and asymmetrical shapes, exhibit uneven shrinkage during sintering and loss of the desired tolerances. To restore lost tolerance sizing operation is generally carried out. This will be described later in Chapter 8. For the users point of view it is easier to maintain narrow tolerances on the contours than on the axial dimensions.

### 6.7 Microstructural Changes

When a green compact is sintered, the original particle boundaries can no longer be observed. Instead, the structure becomes similar to that of the



**Fig. 6.3** Illustration of changes in shape of cylindrical compact due to sintering for single and double end compaction.

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metal in wrought and annealed conditions, except that it contains pores. Pores are of two types open or closed. With progression of sintering, pores continue to shrink. At about 5% total porosity, the formation of closed pores commences. Many of the microstructures seen in P/M parts are caused by porosity and by the blends of elemental powders that constitute many alloys. These blends do not always result in homogeneous, well diffused structures. Such heterogeneity is not necessarily detrimental and in certain nickel steels and diffusion alloy steels, may be advantageous.

The heating or annealing of cold worked metals leads to three distinct microstructural changes: recovery, recrystallization and grain growth. Grain growth is the most important one for sintering. There is normally a large driving force for grain growth. Grain growth in a sinter mass can be somewhat different than the conventional metal, since the former can be treated as a two phase material, the second phase being pore. Porosity in green compacts and in the developing sinter mass represents a very effective hindrance to grain growth. The addition of other component in the powder blend may drastically hinder bonding between adjacent particles and the formation of grain boundaries. Grain boundary grooves, may also tend to inhibit grain growth, since the movement of grain boundary away from its groove leads to an increase in grain-boundary area and energy.

The control of grain growth so that grain boundaries do not pull away from pores is an essential part of sintering to zero porosity. The more nonuniform the grain structure, particularly if it develops discontinuous grain growth, the earlier in the sintering process is the separation of pores from grain boundaries likely to occur. It is therefore important to have as uniformly sized a starting powder as possible, so as to reduce this tendency. Many times a proper additive also plays a vital role. An ideal example for this is the sintering of MgO (0.05 %) doped alumina where the additive is preferentially concentrated at the grain boundaries. Such a control has been able to impart full densification to alumina.

Many types of phase transformations may occur in the solid state during sintering at a constant temperature or during the cooling of the metal from the sintering temperature. Porosity and fine grain structure influence on the transformation. The best example of a phase transformation associated with sintering is the production of sintered steels. Since the porosity reduces the thermal conductivity of the mass, for a given set of cooling conditions the actual cooling rate throughout a sintered metal is considerably less than for a conventional solid one. Such an effect would have bearing on martensitic transformation, which is dependent on cooling rate. Precipitation from solid solution is also a very common type of transformation associated with sintering.

During liquid phase sintering porosity level falls down, while grain size increases. The shape of the pores varies rapidly during liquid phase sintering. In the first stage, the pores are irregular. Later they form a cylindrical network and finally attain a spherical shape. The interfacial ener-