Sintering

Sintering is the most common thermal consolidation technique in powder metallurgy. Sintering can be defined as “The thermal treatment of a powder or compact at a temperature below the melting point of the main constituent, for the purpose of increasing its strength by bonding together of the particles”.

Sintering can be related to the “firing” of ceramics, which has been used for thousands of years. The main difference, however, owes to the fact that metals are typically not in chemical equilibrium at ambient atmosphere; i.e., sintering in air would result in catastrophic oxidation regarding the large specific surface and thus high chemical reactivity of powder based systems. Therefore, sintering of metallic systems needs protective atmospheres, which has a pronounced impact both on the mechanisms of sintering and on industrial sintering processes.

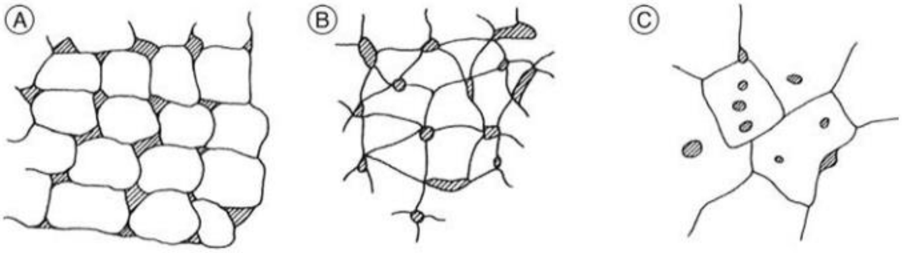
Sintering Mechanisms: Solid-State Sintering

Sintering can be performed in different variants, depending on the phases present and the components of which the respective systems consists: solid state, activated, liquid phase (persistent or transient).

The most straightforward variant of sintering is solid-state sintering of single component systems. Here, the driving force is elimination of defects among which the surface is dominant; the disperse system lowers its energy primarily by reducing its surface. One pronounced difference between dispersed metallic systems and ceramic or polymer systems is the much higher surface energy of metals. Another consequence of the high surface energy is that reduction of oxidized surface promotes sintering by increasing the energy of the surface and thus the driving force.

This sintering process can be split into different sections: Initially, in the bulk or the pressed (green) state, the particles meet at points or highly deformed pressing contacts. In the early stages of sintering, metallic interparticle contacts are formed and grow; the interparticle porosity is still interconnected and open. In the later stage, rapid shrinkage occurs; the pores are closed and become isolated against one another. In the final stage, any remaining porosity decreases slowly, and grain coarsening occurs because the pores that inhibit grain growth even if scarcely present tend to disappear.

The dominating stage depends on the starting powder used. With fine and highly active starting powders, shrinkage is pronounced, and close to 100% density can be attained. The improvement of the mechanical properties is reached through the increase of the load bearing cross-section; i.e., the fraction of the specimen taken by metallic bridges, which is, however, lower than the fraction of the metallic phase itself. Although dimensionally stable sintering is aimed at for precision parts, anisotropic density distribution originating from uniaxial compaction must be considered here.



In most PM materials, more than one component is contained, and particularly if starting from powder mixes, heterodiffusion and homogenization processes have to be considered. In the case of alloy formation, the driving forces, especially, the mixing entropy, are much higher than those caused by the surface energy, and, therefore, the formation of new pores during mutual diffusion can occur (“Kirkendall effect”).

Such phenomena are observed, for example, if Ti–Al mixes are sintered and they are enhanced by exothermic reactions (“reactive sintering”). In special cases, sintering can be activated by the addition of a small amount of a second element that is virtually insoluble in the main constituent but has high solubility for this constituent. In this case, a thin layer of the additive is formed on the particle surfaces of the main constituent through which the main constituent can diffuse rapidly, thus enhancing sintering. A typical example is the system W–Ni: whereas for the sintering of plain W to reasonable density levels, 2700°C are required, the addition of 0.3% Ni results in a virtually dense material already at 1400°C. However, by addition of Ni, W also loses its character as high-temperature material, especially, its creep resistance, a phenomenon that underlines the close relationship between creep and sintering.

Liquid Phase Sintering

Even faster sintering can be reached if offering mass transport not through a solid layer but a liquid, the so-called liquid phase sintering, which requires two constituents at minimum. Two variants of liquid phase sintering can be distinguished: if at sintering temperature the liquid phase is in chemical equilibrium with the solid phase (which forms the major part of the system), this is termed sintering with persistent liquid phase.

The liquid phase enhances material transport and typically also densification; therefore, persistent liquid phase sintering is the process applied if full density is required, such as for hard metals and tungsten heavy alloys.

An essential criterion is wetting of the solid by the liquid phase. Solubility of the main constituent in the liquid phase usually promotes densification. Densification mechanisms are particle rearrangement, which is supported by the lubricating effect of the liquid phase, as well as solution–reprecipitation processes that change the shape of the solid phase towards higher packing density. Grain growth depends on the interfacial energy of solid–liquid; it is very distinct in the system W–Ni but much less so in hard metals in which low-energy WC surfaces are formed. However, with ultrafine hard metal grades, grain growth stabilizers have to be added to retain the submicron microstructure.

Classical sintering with persistent liquid phase occurs in powder mixes, such as W–Ni or WC– Co, in which an additive metal generates the liquid phase. which may occur through solid-state sintering.

If the melting point of the minor constituent is below the sintering temperature or if a low melting eutectic is formed, a liquid phase is formed that is not thermodynamically stable but rapidly disappears, forming a solid solution. This liquid phase is called “transient,” and transient liquid phase sintering is a common process, for example, with sintered steels, the most widely used steel grade for precision parts, Fe–Cu–C, is sintered in such a way.

This type of sintering has the advantage that it does not result in densification but, in contrast, slight swelling is observed—frequently called “copper swelling”, which is used in industrial practice to compensate for the natural shrinkage of pressed compacts; thus, net dimensional change +/- 0 can be established. The second benefit of the transient liquid phase is enhanced distribution and homogenization of the alloy elements, which improves the mechanical properties.

Activated sintering

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