

1.5 Solid-State Sintering

1.5.1 Driving Forces

It is generally accepted that the reduction in the surface free energy of a sintering compact, due to the elimination of internal surface area associated with the pores, provides the driving force for sintering. When compared to other processes (e.g. chemical reactions), the decrease in the surface free energy during sintering is rather small ($\sim 100\text{J/mol}$ for particles with an initial diameter of $1\ \mu\text{m}$) but the distance that matter has to be transported is also small (of the order of the particle size), so that sintering occurs at a reasonable rate at sufficiently high temperatures.

The specific energy and curvature of the particle surfaces provide an effective stress on the atoms under the surface. For a curved surface with principal radii of curvature r_1 and r_2 , this stress is given by the equation of Young and Laplace:

$$\sigma = \gamma_{sv} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad \dots (1)$$

where γ_{sv} is the specific surface energy. The *diffusion potential*, μ , which drives matter transport, is in this case found by equating the mechanical work performed by the stress to the thermodynamic work required for the reduction of the surface free energy. A commonly used relation is

$$\mu = \sigma \Omega \quad \dots (2)$$

where Ω is the atomic or molar volume. The equation for μ is actually more complex for polycrystalline ceramics where the pores are in contact with the grain boundaries. For example, in the final stage of sintering where the pores are assumed spherical, one expression is:

$$\mu = \Omega \left(\frac{2\gamma_{gb}}{G} + \frac{2\gamma_{sv}}{r} \right) \quad \dots (3)$$

where γ_{gb} is the specific energy of the grain boundary, G is the diameter of the grains, and r is the radius of the pores. According to Eq. 3, the chemical potential consists of two contributions, one attributed to the pores and the other attributed to the boundaries. A further development is to relate the chemical potential to an externally applied stress. The driving force for sintering is then defined in terms of a *sintering stress*, Σ , which is the *equivalent externally applied stress* that has the same effects on sintering as the curved surfaces of pores and grain boundaries. The formulation of the driving force in terms of a fictitious externally applied stress is advantageous in the analysis of sintering where mechanical stress effects arise (e.g. pressure sintering and constrained sintering).

1.5.2 Stages of Sintering

The microstructure of a powder compact, consisting initially of discrete particles, evolves continuously during sintering. However, it is sometimes convenient to divide the process into three idealized stages defined in terms of the microstructure, to force correspondence between simple, established sintering models. The *initial stage* would begin as soon as some degree of atomic mobility is achieved and, during this stage, sharply concave necks form between the individual particles. The amount of densification is small, typically the first 5% of linear shrinkage, and it can be considerably lower if coarsening mechanisms are very active. In the *intermediate stage*, the high curvatures of the initial stage have been moderated and the microstructure consists of a three-dimensional interpenetrating network of solid particles and continuous, channel-like pores. This stage is considered valid to ~5-10% porosity and therefore covers most of the densification. Grain growth (coarsening) starts to become significant. As sintering proceeds, the channel-like pores break down into isolated, closed voids, which marks the start of the *final stage*. Grain growth can be more extensive in the final stage and difficulties are commonly encountered in the removal of the last few percent of porosity.

1.5.3 Mechanisms of Sintering

Sintering of crystalline materials can occur by several mechanisms (i.e. atomic transport paths and their associated sources and sinks): vapor transport (evaporation/condensation), surface diffusion, lattice (volume) diffusion, grain boundary diffusion, and dislocation motion. Figure 1.5 shows a schematic representation of the matter transport paths for two sintering particles. A distinction is commonly made between *densifying* and *non-densifying* mechanisms.

Vapor transport, surface diffusion, and lattice diffusion from the particle surfaces to the neck lead to neck growth and coarsening of the particles without densification. Grain boundary diffusion and lattice diffusion from the grain boundary to the neck are the most important densifying mechanisms in polycrystalline ceramics. Diffusion from the grain boundaries to the pores permits neck growth as well as shrinkage (densification). Plastic flow by dislocation motion can cause neck growth and densification through deformation (creep) of the particles in response to the sintering stress. Plastic flow is more common in the sintering of metal powders. For glass powders, which cannot have grain boundaries, densification and neck growth occurs by viscous flow, involving deformation of the particles.

In addition to the alternative mechanisms, there are additional complications arising from the diffusion of the different *ionic species* making up the compound. To preserve charge neutrality of the local composition, the flux of the different ionic species will be coupled.

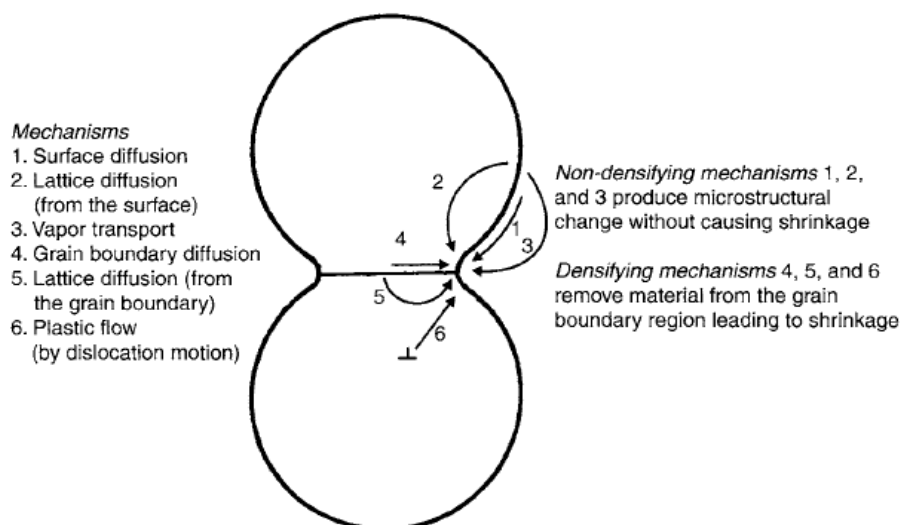


FIGURE 1.5 Schematic representation of the sintering mechanisms for a system of two particles.

A further complication arises because each ionic species can diffuse along different paths. For an oxide with the formula M_xO_y , the effective (*ambipolar*) diffusion coefficient is given by:

$$\bar{D} = \frac{(x + y)[D_l^M + \pi \delta_{gb} D_{gb}^M / G][D_l^O + \pi \delta_{gb} D_{gb}^O / G]}{y[D_l^M + \pi \delta_{gb} D_{gb}^M / G] + x[D_l^O + \pi \delta_{gb} D_{gb}^O / G]} \quad \dots (4)$$

where D is the diffusion coefficient, G is the grain size, δ is the thickness of the grain boundary, the subscripts l and gb refer to lattice and grain boundary diffusion, respectively, and the superscripts M and O refer to the metal and oxygen ions, respectively. According to Eq. 4, whatever the relative magnitudes of the four diffusivities, it is the *slowest diffusing species along its fastest path* that controls the rate. Another complicating factor is that the rate-controlling mechanism for a given material can change with changing conditions of the process variables such as temperature, grain size, and composition. A complicating factor that has been exploited effectively in solid-state sintering is that aliovalent dopants and impurities alter the point defect concentration, thereby altering the diffusion coefficients and the sintering rates.

In general, the effects of dopants on the sintering rates cannot be easily explained because of the multiplicity of the dopant role: for example, influence on more than one diffusion process, segregation at the grain boundaries, influence on surface and grain boundary energies, and the formation of second phases.