

1.5.6 Sintering Models

Matter transport during sintering is driven by chemical potential gradients arising from differences in the curvature of the free surfaces in the compact of particles. When compared to atoms under a flat surface at the same temperature and composition, the atoms under a convex surface have a higher chemical potential while the atoms under a concave surface have a lower chemical potential. This gradient in the chemical potential produces a driving force for matter transport from the (convex) particle surfaces and from the grain boundaries between the particles to the (concave) necks between the particles (Figure 1.5). Mathematical models have been developed to analyze the rate of matter transport along these paths. The models can be classified into three types: (a) analytical models; (b) scaling laws; and (c) numerical models.

1. Analytical Models

The analytical models assume a simplified, highly idealized geometry for each stage of sintering and, for each mechanism, the diffusional flux equations are solved analytically to provide equations for the sintering kinetics. They have often been criticized for their simplified and generalized assumptions about the microstructure of the sintering compact (e.g. monodisperse particles, uniform packing, generalized grain and pore shapes, absence of grain growth). However, they are useful for providing an excellent *qualitative* understanding of sintering in terms of primary variables (e.g. particle size, temperature, applied pressure, heating rate, and atmosphere).

For the two-sphere geometry assumed for the initial stage (Fig. 1.5), equations for neck growth (and shrinkage for the densifying mechanisms) have been derived for each mechanism and are summarized elsewhere. The initial-stage equations played a key role in the early development of sintering theory but their usefulness in practical sintering is quite limited. For the intermediate and final stages of sintering, Coble assumed the grain shape to be a tetrakaidecahedron and derived equations for conventional sintering by lattice and grain boundary diffusion, and for sintering with an applied pressure. The most useful feature of the sintering equations is the predicted dependence of the densification rate on the primary processing variables. For any stage of the sintering process, the model predictions for the densification rate, $\dot{\epsilon}_\rho = (1/\rho) dp/dt$, can be expressed in general form:

$$\dot{\epsilon}_\rho = \left(\frac{1}{\rho} \right) \frac{d\rho}{dt} = \frac{HD\Omega\phi^{(m+1)/2}}{G^m kT} (p_a + \Sigma) \quad \dots (6)$$

where H is a numerical constant that depends on the assumed geometry of the model and on the sintering mechanism, Ω is the atomic volume of the rate controlling species, G is the grain (or particle) size, k is the Boltzmann constant, and T is the absolute

temperature. The diffusion coefficient D and the grain size exponent, m , take on their appropriate values for a given mechanism: $D = D_1$ and $m = 2$ for lattice diffusion, where D_1 is the lattice diffusion coefficient; $D = D_{gb}\delta_{gb}$ and $m = 3$ for grain boundary diffusion, where δ_{gb} is the grain boundary thickness. The term Σ is the sintering stress, defined earlier as the *equivalent externally applied stress* that has the same effects on sintering as the curved surfaces of pores and grain boundaries. The term ϕ , referred to as the *stress intensification factor*.

2. Herring's Scaling Law

Herrings scaling law does not assume a specific geometrical model. Instead, it assumes that the geometrical changes remain similar. The law considers the effect of change of scale (e.g. particle size) on the rate of matter transport for individual mechanisms. The times for equivalent geometric change can be expressed as:

$$\frac{t_2}{t_1} = \left(\frac{G_{2,0}}{G_{1,0}} \right)^m \quad \dots (7)$$

where the subscripts 1 and 2 represent two different powders with initial particle size $G_{1,0}$ and $G_{2,0}$, respectively and m is an integer that depends on the mechanism of matter transport: $m = 4$ for surface diffusion and for grain boundary diffusion, $m = 2$ for vapor transport, and $m = 3$ for lattice diffusion. For an equivalent geometrical change, the law states that the rate of sintering varies as $1/G^m$. Since the densification rate varies as $1/G^4$ for grain boundary diffusion and as $1/G^3$ for lattice diffusion, the grain boundary path is favored for fine particles. The rate of coarsening by surface diffusion also varies as $1/G^4$ so that grain boundary diffusion and surface diffusion are expected to be in competition during the sintering of fine particles. Because of the general approach used in its derivation, the scaling law might be expected to have some advantage over the analytical models that assume a specific geometry. A problem is that the requirement of geometrically similar microstructural change is not easy to achieve for real powder compacts and the law has not found any significant applicability in sintering.

1.5.7 The Sintering Stress

The formulation of the driving force for sintering, the *sintering stress*, in terms of an equivalent external stress. In the loading dilatometry experiments, the hydrostatic component of the applied uniaxial stress is small compared to the sintering stress, so that the sintering mechanism of the loaded powder compact is expected to be identical to that for a freely sintered compact. Equation 6 can be written as.

$$\dot{\epsilon}_p = \frac{HD\Omega\phi^{(m+1)/2}}{G^m kT} \Sigma \quad \dots (8)$$

Assuming the same mechanism for creep under the low uniaxial stress, P_z , an equation for the creep rate is

$$\dot{\epsilon}_c = \frac{H'D\Omega\phi^{(m+1)/2}}{G^m kT} P_z \quad \dots (9)$$

where H' is a numerical constant. The ratio of the densification rate to the creep rate can be found from Eqs 8 and 9 as

$$\frac{\dot{\epsilon}_\rho}{\dot{\epsilon}_c} = \frac{F\Sigma}{p_z} \quad \dots (10)$$

where F is a constant. Measurement of the densification rate and the creep rate at a fixed value of P_z for identical samples.

1.5.8 The Stress Intensification Factor

Solid-state sintering involves atomic transport from the grain boundaries to fill up the pores and is dependent on the *effective stress* on the grain boundaries. We therefore require a way to relate the externally applied stress, σ_a , to the effective stress on the grain boundary, σ_e . This has been commonly achieved (see Eq. 6) by using a parameter, ϕ , referred to as the *stress intensification factor* that depends on the geometry of the porous compact:

$$\sigma_e = \sigma_a \phi \quad \dots (11)$$

The stress intensification factor is equal to the ratio of the total cross-sectional area (of the solid phase plus the pores), A_t , to the effective cross-sectional area (of the solid-phase only), A_e . For a polycrystalline material, ϕ is equal to the cross-sectional area of the grain, A_g , divided by the grain boundary area, A_{gb} :

$$\phi = \frac{A_t}{A_e} = \frac{A_g}{A_{gb}} \quad \dots (12)$$

If the pores are spherical and randomly distributed through the porous compact, such as a glass in the final stage of sintering, ϕ takes a simple form:

$$\phi = 1/\rho \quad \dots (13)$$

where ρ is the relative density of the compact. In general, the relationship may be expected to be complex. However, computer calculations by Beere [40] on the equilibrium shapes of pores in a porous compact yield results that can be well fitted to simple analytical expressions. One expression is

$$\phi = \exp[a(1 - \rho)] \quad \dots (14)$$

where a is a constant that depends on the dihedral angle of the pores.