

1.5.4 Competition between Densification and Coarsening

The various sintering mechanisms do not operate independently. Vapor transport and surface diffusion compete with the densifying mechanism. They lead to coarsening of the microstructure and a reduction of the driving force for sintering, so that a significant reduction in the densification rate can result. Sintering is said to involve a competition between densification and coarsening. The production of ceramics with high density would require choosing the sintering conditions so that the non-densifying mechanisms are not very active. When coarsening mechanisms dominate, the production of a highly porous body is favored.

1.5.5 Effects of Grain Boundaries

In the sintering of polycrystalline materials, part of the energy decrease due to elimination of internal surface area associated with the pores goes into creating new grain boundary area. The grains also have a tendency to grow, by migration of the boundaries, to reduce the energy associated with the grain boundaries, thereby leading to an increase in the diffusion distance.

The presence of the grain boundaries also dictates the equilibrium shape of the pores at the intersection with the boundaries. At equilibrium, the chemical potential of the atoms in the pore surface must be the same everywhere, which is equivalent to saying that the curvature of the pore surface is the same everywhere. This means that the pore surface must consist of circular arcs in two-dimensional models and of spherical caps in a very limited number of three-dimensional geometries, for isotropic solids. There must also be a balance of forces at the junction between the grain boundary and the pore surface. Ignoring possible torque terms, as shown in Figure (1.6 – a) this balance of forces leads to

$$\cos\left(\frac{\psi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{sv}} \quad \dots (5)$$

where ψ is the dihedral angle, γ_{gb} is the specific grain boundary energy, and γ_{sv} is the specific surface energy.

The pore surface in Figure (1.6 - a) is concave (negative curvature) and during sintering, the surface will move towards its center of curvature, so that the pore will shrink. However, as shown in Figure (1.6 -b), when the pore is surrounded by a large number of grains (i.e. the *pore coordination number* is large), the balance of forces at the grain boundary/pore junction dictates that the pore surface will become convex (positive curvature). In this case, the pore will grow or become metastable. Whether or not pores can shrink in a powder compact has been analyzed in thermodynamic.

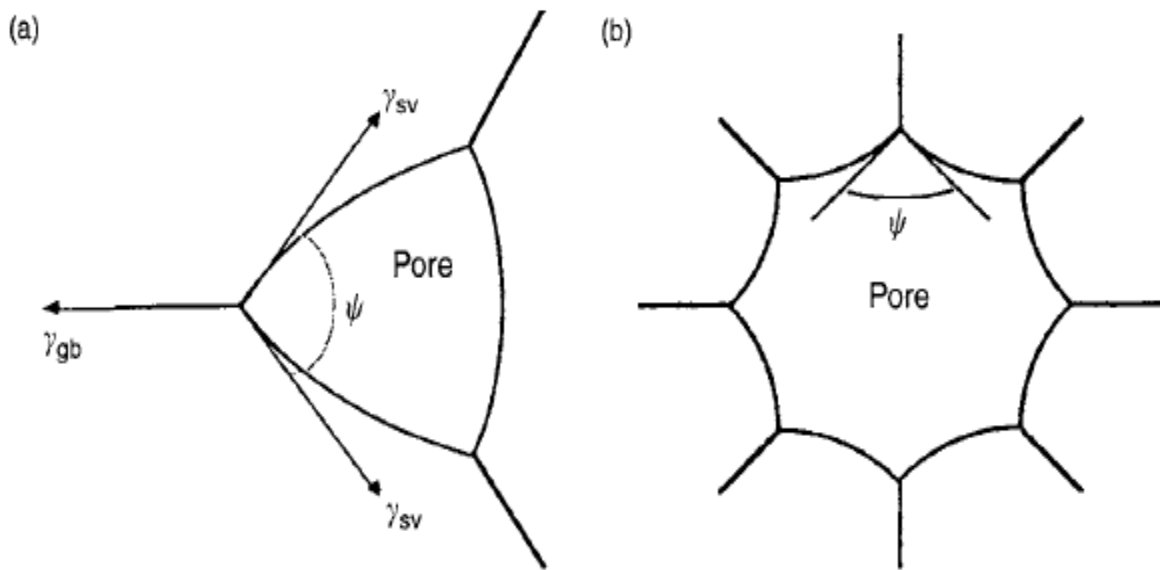


FIGURE (1.6) Pore shape and pore stability are determined by the dihedral angle and the pore coordination number: (a) The pore with the concave surfaces will shrink while (b) the pore with the convex surfaces will grow (or become metastable).

The balance between the reduction in pore surface area and the increase in the grain boundary area leads to a criterion that prescribes the maximum pore coordination number that will permit a pore to shrink. As shown in Figure 1.7, for a given dihedral angle (e.g. 120°), pores with a coordination number less than a certain critical value, ($N_0 = 12$), will shrink while pores with $N > N_c$ will grow. The large pores in a powder compact will have large values of N and will therefore be difficult to shrink, leading to

residual porosity in the sintered material. The importance of controlling particle packing for the achievement of high density is therefore clear.

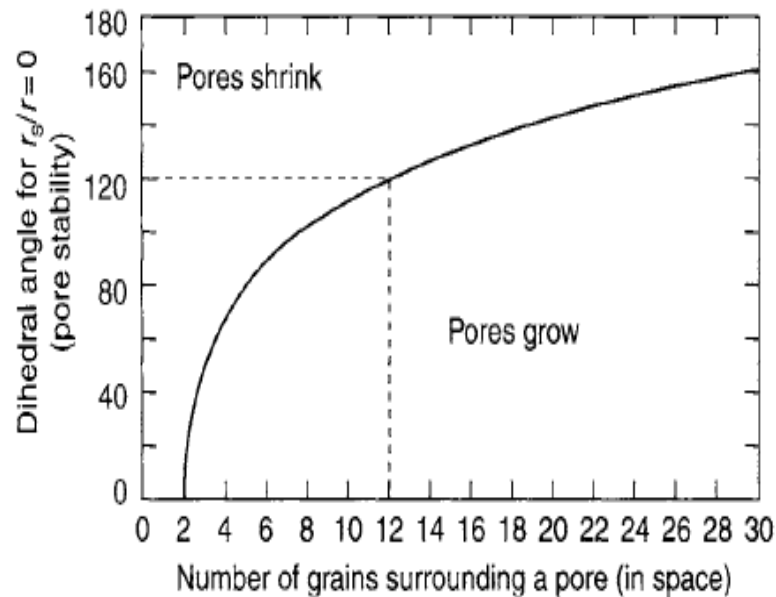


FIGURE 1.7 Conditions for pore stability as a function of pore coordination number and dihedral angle. For a dihedral angle of 120° , pores surrounded by more than 12 grains will grow.