

1.6 Grain Growth and Coarsening

Grain growth is the term used to describe the increase in the average grain size of a polycrystalline material. The grain boundary is a region with a complex structure, about 1-2 unit cells wide, between two crystalline domains. It has a higher energy than the bulk crystal and, hence, a reduction in the grain boundary area will reduce the free energy of the system. The grain boundary moves by diffusion of atoms (ions) from one side of the boundary to the other so that atoms previously aligned with one grain becomes aligned with the other, causing it to grow at the expense of its neighbor. Growth occurs in such a way that the convex grain loses atoms while the concave grain gains atoms with the result that the boundary moves towards its center of curvature.

The term *coarsening* is frequently used to describe the process in porous ceramics whereby the increase in the average grain size is accompanied by an increase in the average pore size. Coarsening reduces the driving force for sintering and increases the diffusion distance for matter transport, thereby reducing the rate of sintering. The suppression of coarsening mechanisms therefore forms a key requirement for the achievement of high density. Another requirement is that the microstructure be stabilized such that the pores and the grain boundaries remain attached. This second requirement depends primarily on the ability to reduce the intrinsic (pore-free) mobility of the grain boundaries.

Coarsening of precipitates or particles in a solid, liquid, or gaseous medium is commonly referred to as *Ostwald ripening*. It is especially important in liquid phase sintering where matter transport driven by chemical potential differences causes the smaller grains to become smaller and the larger particles to grow, resulting in an increase in the average grain size. Grain growth in ceramics is generally divided into two types: (i) *normal* grain growth and (ii) *abnormal* grain growth, which is sometimes referred to as *exaggerated grain growth* or *discontinuous grain growth*. In normal grain growth, the average grain size increases with time but the grain size distribution remains self-similar (invariant in time). Abnormal grain growth is the process whereby a few large grains grow rapidly at the expense of the smaller grains, giving a **bimodal**

grain size distribution. *Anisotropic grain growth* is a type of abnormal grain growth in which the abnormal grains grow in an elongated manner, commonly with faceted, straight sides. In porous ceramics, abnormal grain growth is accompanied by breakaway of the boundaries from the pores and, as outlined earlier, must be avoided if high densities are to be achieved.

1.6.1 Normal Grain Growth

Normal grain growth in pure, dense, and single-phase materials has been analyzed by a number of different approaches. *Mean field theories* consider the change in size of an isolated grain embedded in a matrix that represent the average effect of the whole array of grains. In real systems grain growth, certain *topological requirements* of a space-filling array of grains must be balanced with the requirements of interracial tension. More recently, the use of computer simulations has provided a valuable technique for the analysis of grain growth. The grain growth models predict a kinetic equation of the form

$$G^m = G_0^m + Kt \quad \dots (15)$$

where G is the grain size at time t , G_0 is the grain size at $t = 0$, and K is a temperature-dependent rate constant obeying the Arrhenius equation. For the mean field theories, $m = 2$ (i.e. parabolic growth kinetics) while the topological model $m = 3$. In practice, grain growth data for dense ceramics yield m values ranging from 2 to 4. In the model of Burke and Turnbull, the rate constant K for a pure, pore-free material is related to the *intrinsic* mobility of the boundary, M_b , by [2]

$$K = 2\alpha M_b \gamma_{gb} \quad \dots (16)$$

where α is a numerical constant that depends on the shape of the grains and γ_{gb} is the grain boundary energy. The mobility is related to the diffusion coefficient for the atoms across the boundary, D_a , by

$$M_b = \frac{D_a}{kT} \left(\frac{\Omega}{\delta_{gb}} \right) \quad \dots (17)$$

where k is the Boltzmann constant, T is the absolute temperature, Ω is the atomic volume, and δ_{gb} is the grain boundary thickness.

The grain growth models based on the evolution of a single, identified grain do not consider the evolution of the *distribution* of grain sizes with time. As a first approximation, the grain growth rate depends on the difference between the grain size at the mode and at the mean of the distribution. Practically, this means that the rate of grain growth will be higher for a highly skewed distribution (i.e. a distribution with a wide distribution of grain sizes in which the mean grain size is significantly greater than the mode). The rate of grain growth should also be zero for a symmetrical distribution, although it would become broader and shallower with time. A monosize or narrow initial distribution, as may be produced from particles with the same size, will first broaden without an increase in the average grain size. After some incubation time, grain growth takes off, with the average grain size increasing with time.

1.6.2 Abnormal Grain Growth

Microstructures of polycrystalline ceramics that have been heated for some time at a sufficiently high temperature often show very large (abnormal) grains in a matrix of finer grains (Fig. 1.8). It is important to understand and to be able to control abnormal grain growth for two main reasons. First, the occurrence of abnormal grain growth during sintering limits the attainment of high density. For example, the pores trapped in the abnormal grain shown in Figure (1.8) are difficult to remove. Second, the large abnormal grains are commonly detrimental to the properties of the material. An important goal in practical sintering is therefore the suppression of abnormal grain growth.

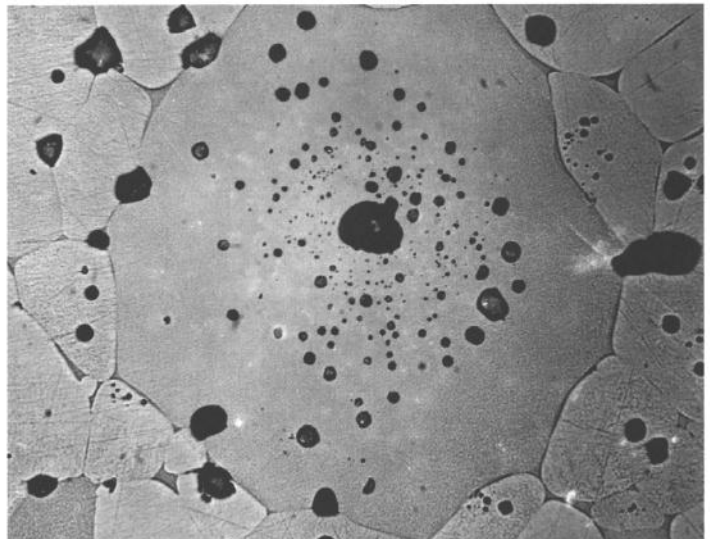


FIGURE (1.8) Abnormal grain growth in an MgO ceramic. The pores trapped inside the abnormal grain are difficult to remove, thereby leading to residual porosity in the sintered material (magnification = 700).

Earlier explanations considered that the grain size distribution of the starting material was the major factor leading to abnormal grain growth. They were based on the Hillert theory of grain growth, which predicted that any grain with a size greater than twice the average grain size would be predisposed to growing abnormally. This explanation is not supported theoretical analysis, which show that although the large grains grow, they do not outstrip the normal grains. The normal grains grow at a faster relative rate so that the large (abnormal) grains eventually return to the normal size distribution. The size effect is therefore not a sufficient criterion for abnormal grain growth. Inhomogeneities in chemical composition, liquid phases, and particle packing have long been suggested as possible causes of abnormal grain growth.

Grain orientation and grain boundary structure are two factors that can lead to variations in the mobility and energy of grain boundaries. Boundaries of large abnormal grains often show faceting on low-index crystallographic orientations. Frequently, the growth planes are those with low surface energy. Low-energy boundaries often have a lower mobility. Growth that is slow normal to and rapid parallel to the low-energy surfaces often lead to plate-like abnormal grains.