

which remains attached to the boundary as it moves. This requires material transport across the particle, which may occur by interface or surface or volume diffusion, by viscous flow, or by solution (precipitation in a liquid or glass inclusion), or by evaporation (condensation in a gas inclusion). We can define an inclusion particle mobility B_p relating the driving force and particle velocity $v_p = B_p F_p$ in the same way as has been done for the boundary (Eq. 10.11b) and for atomic diffusion in Chapter 6. When the inclusion is dragged by the boundary, their velocities are identical; in the case in which $B_p \ll B_b$ we can neglect the intrinsic boundary mobility, and the resulting grain-boundary velocity is controlled by the driving force on the boundary together with the mobility and number of inclusions per grain boundary, p :

$$v_b = \frac{B_p F_b}{p} \quad (10.13)$$

The inclusion particle moves along with the boundary, gradually becoming concentrated at boundary intersections and agglomerating into larger particles as grain growth proceeds. This is illustrated for the special case of pore agglomeration in Figs. 10.9 and 10.10.

Thus, second-phase inclusions can either (1) move along with boundaries, offering little impedance; (2) move along with boundaries, with the inclusion mobility controlling the boundary velocity; or (3) be so immobile that the boundary pulls away from the inclusion, depending on the relative values of the boundary driving force (inversely proportional to grain size), the boundary mobility (Fig. 10.7), and the inclusion particle mobility, which, depending on the assumed mechanism and particle shape, may be proportional to r_p^{-2} , r_p^{-3} , or r_p^{-4} .* As grain growth proceeds, the driving force diminishes, and any inclusions dragged along by the boundary increase in size so that their mobility decreases. As a result, the exact way in which second-phase inclusions inhibit grain growth not only depends on the properties of the particular system but also can easily change during the grain-growth process. Sorting out these effects requires a careful evaluation of the microstructure evolution in combination with the kinetics of grain growth and a detailed knowledge of system properties. Inhibition of grain growth by solid second-phase inclusions has been observed for MgO additions to Al_2O_3 , for CaO additions to ThO_2 , and in other systems.

A second phase that is always present during ceramic sintering and in almost all ceramic products prepared by sintering is residual porosity

*P. G. Shewmon, *Trans. A.I.M.E.*, **230**, 1134 (1964); M. F. Ashby and R. M. A. Centamore, *Acta Met.*, **16**, 1081 (1968).

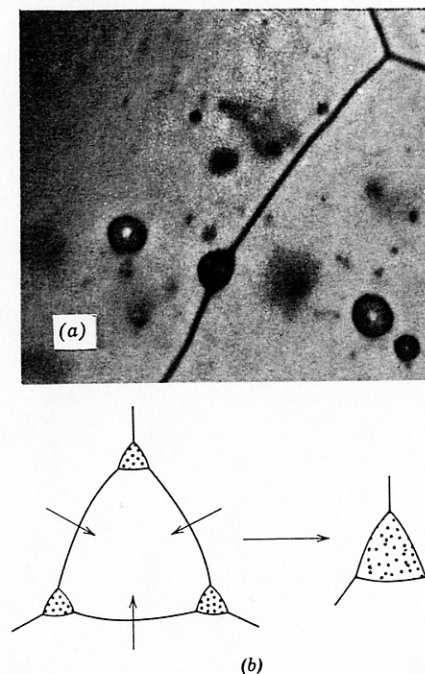


Fig. 10.9. (a) Pore shape distorted from spherical by moving boundary and (b) pore agglomeration during grain growth.

remaining from the interparticle space present in the initial powder compact. This porosity is apparent both on the grain boundaries (intergranular) and within the grains (intragranular) in the sintered CaF_2 sample shown in Fig. 10.5. It is present almost entirely at the grain corners (intergranular) in the sintered UO_2 samples shown in Fig. 10.10. As with particulate inclusions, pores on the grain boundaries may be left behind by the moving boundary or migrate with the boundary, gradually agglomerating at grain corners, as illustrated in Figs. 10.9 and 10.10. In the early stages of sintering, when the boundary curvature and the driving force for boundary migration are high, pores are often left behind, and a cluster of small pores in the center of a grain is a commonly observed result (see Fig. 10.5). In the later stages of sintering, when the grain size is larger and the driving force for boundary migration is lower, it is more usual for pores to be dragged along by the boundary, slowing grain growth.

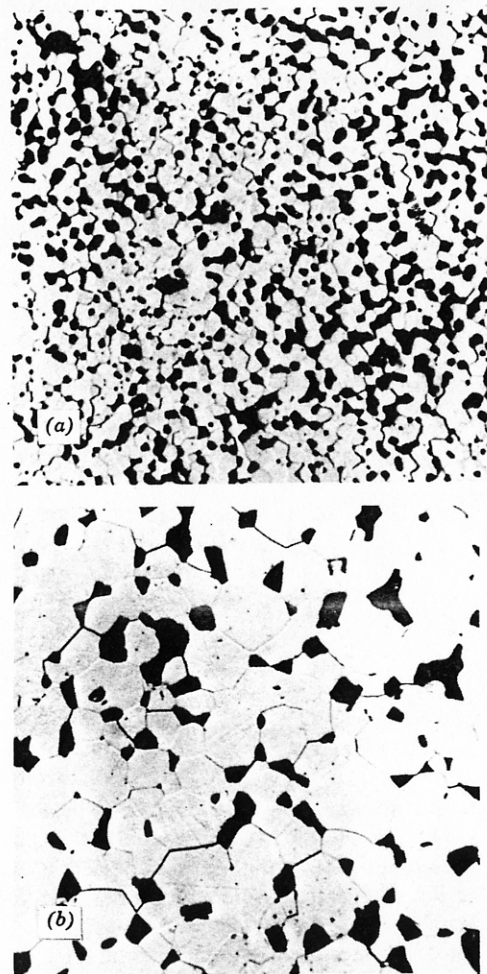


Fig. 10.10. Grain growth and pore growth in sample of UO_2 after (a) 2 min, 91.5% dense, and (b) 5 hr, 91.9% dense, at 1600°C (400 \times). From Francois and Kingery.

Another factor that may restrain grain growth is the presence of a liquid phase. If a small amount of a boundary liquid is formed, it tends to slow grain growth, since the driving force is reduced and the diffusion path is increased. There are now two solid-liquid interfaces, and the driving force is the difference between them, that is, $(1/r_1 + 1/r_2)_A - (1/r_1 + 1/r_2)_B$, which

is smaller than either alone; in addition, if the liquid wets the boundary, the interface energy must be lower than the pure-grain-boundary energy. Also, the process of solution, diffusion through a liquid film, and precipitation is usually slower than the jump across a boundary. However, this case is more complex in that grain growth may be enhanced by the presence of a reactive liquid phase during the densification process, as discussed in Section 10.4. In addition, a very small amount of liquid may enhance secondary recrystallization, as discussed later, whereas larger amounts of liquid phase may give rise to the grain-growth process described in Chapter 9. In practice, it is found that addition of a moderate amount of silicate liquid phase to aluminum oxide prevents the extensive grain growth which frequently occurs with purer materials.

Secondary Recrystallization. The process of secondary recrystallization, sometimes called discontinuous or exaggerated grain growth, occurs when some small fraction of the grains grow to a large size, consuming the uniform-grain-size matrix. Once a single grain grows to such a size that it has many more sides than the neighboring grains (such as the grain with fifty sides illustrated in Fig. 10.4), the curvature of each side increases, and it grows more rapidly than the smaller grains with fewer sides. The increased curvature on the edge of a large grain is particularly evident in Fig. 10.11, which shows a large alumina crystal growing at the expense of a uniform-particle-size matrix.

Secondary crystallization is particularly likely to occur when continuous grain growth is inhibited by the presence of impurities or pores. Under these conditions the only boundaries able to move are those with a curvature much larger than the average; that is, the exaggerated grains with highly curved boundaries are able to grow, whereas the matrix material remains uniform in grain size. The rate of growth of the large grains is initially dependent on the number of sides. However, after growth has reached the point at which the exaggerated grain diameter is much larger than the matrix diameter, $d_g \gg d_m$, the curvature is determined by the matrix grain size and is proportional to $1/d_m$. That is, there is an induction period corresponding to the increased growth rate and the formation of a grain large enough to grow at the expense of the constant-grain-size matrix. Therefore, the growth rate is constant as long as the grain size of the matrix remains unchanged. Consequently, the kinetics of secondary recrystallization is similar to that of primary recrystallization, even though the nature of the nucleation and driving force is different.

Secondary recrystallization is common for oxide, titanate, and ferrite ceramics in which grain growth is frequently inhibited by minor amounts of second phases or by porosity during the sintering process. A typical resultant structure is illustrated for barium titanate in Fig. 10.12, and the

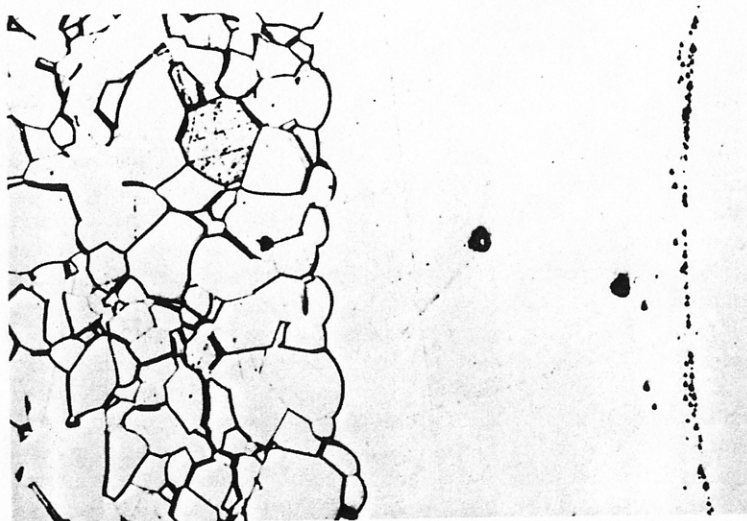


Fig. 10.11. Growth of a large Al_2O_3 crystal into a matrix of uniformly sized grains (495 \times). Compare with Fig. 10.4. Courtesy R. L. Coble.

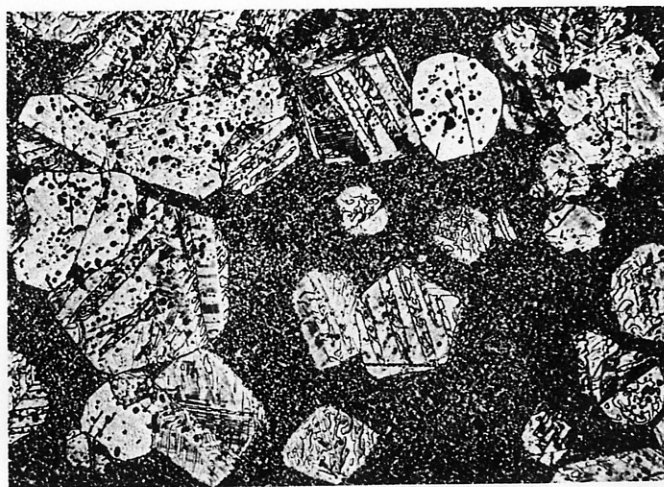


Fig. 10.12. Large grains of barium titanate growing by secondary recrystallization from a fine-grained matrix (250 \times). Courtesy R. C. DeVries.

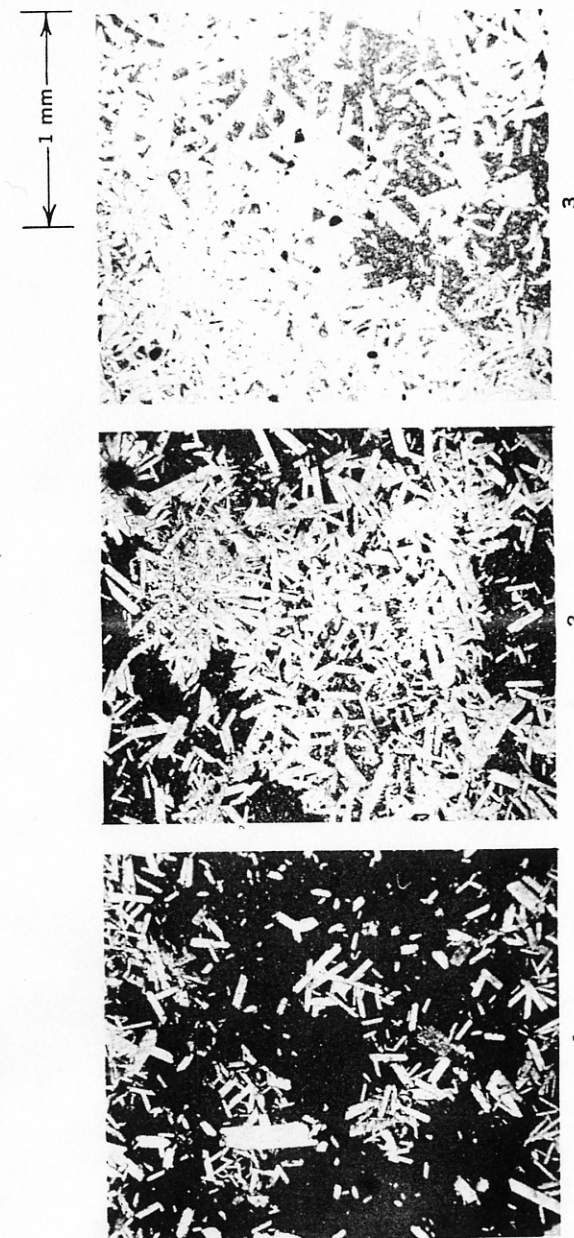


Fig. 10.13. Large grains of Al_2O_3 growing by secondary recrystallization from a fine-grained matrix. Courtesy I. B. Cutler, in reference 5.

progressive growth of aluminum oxide crystals during secondary recrystallization is illustrated in Fig. 10.13.

When polycrystalline bodies are made from fine powder, the extent of secondary recrystallization depends on the particle size of the starting material. Coarse starting material gives a much smaller relative grain growth, as illustrated in Fig. 10.14 for beryllia. This is caused by both the rate of nucleation and the rate of growth. There are almost always present in the fine-grained matrix a few particles of substantially larger particle size than the average; these can act as embryos for secondary recrystallization, since already $d_s > d_m$, and growth proceeds to a rate proportional to $1/d_m$. In contrast, as the starting particle size increases, the chances of grains being present which are much larger in particle size than the average are much decreased, and consequently the nucleation of secondary recrystallization is much more difficult; the growth rate, proportional to $1/d_m$, is also smaller. In the data shown in Fig. 10.14, material having a starting particle size of 2 microns grows to a final particle size of about 50 microns, whereas material with an initial particle size of 10 microns shows a final grain size of only about 25 microns. This result of a much larger final grain size for a smaller initial particle size would be very puzzling if the process of secondary recrystallization was not known to occur.

Secondary recrystallization has been observed to occur with the boundaries of the large grains apparently perfectly straight (Fig. 10.15). Here the previous discussion of the surface tension and curvature of the phase boundary does not apply directly. That is, the boundary energy is

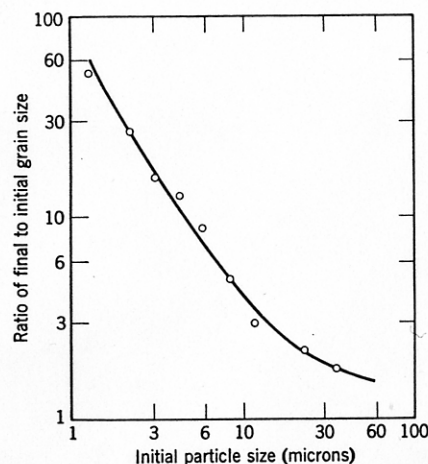


Fig. 10.14. Relative grain growth during secondary recrystallization of BeO heated $2\frac{1}{2}$ hr at 2000°C . From P. Duwez, F. Odell, and J. L. Taylor, *J. Am. Ceram. Soc.*, 32, 1 (1949).

not independent of crystal directions, and the growth planes are those of low surface energy. These structures all seem to occur in systems having a small concentration of impurity which gives rise to a small amount of a boundary phase. The driving force for secondary recrystallization is the lower surface energy of the large grain compared with the high-surface-energy faces or small radius of curvature of adjacent grains. Transfer of material under these conditions can only occur when there is an intermediate boundary phase separating the surfaces of the small and large grains. The amount of second phase present tends to increase at the boundaries of the large crystals compared with that at other boundaries in the system, and a large grain continues to grow once it is initiated. If the amount of boundary phase is increased, however, normal grain growth and this kind of secondary recrystallization are both inhibited, as discussed previously.

Secondary recrystallization affects both the sintering of ceramics and resultant properties. Excessive grain growth is frequently harmful to mechanical properties (see Sections 5.5 and 15.5). For some electrical and magnetic properties either a large or a small grain size may contribute to improved properties. Occasionally grain growth has been discussed in the literature as if it were an integral part of the densification process. That this is not true can best be seen from Fig. 10.16. A sample of aluminum oxide with an initial fine pore distribution was heated to a high temperature so that secondary recrystallization occurred. The recrystallization has left almost the same amount of porosity as was present in the initial

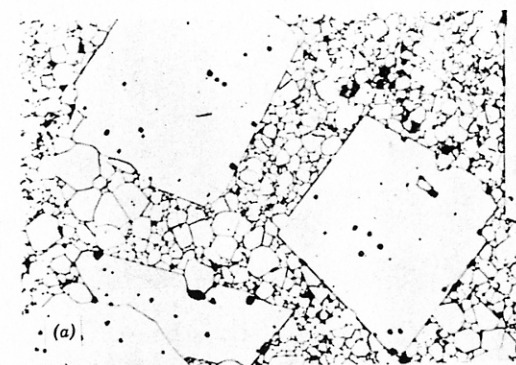


Fig. 10.15. (a) Idiomorphic grains in a polycrystalline spinel. The large grain edges appear straight, whereas the shape of the small grains is controlled by surface tension ($350\times$). Courtesy R. L. Coble.

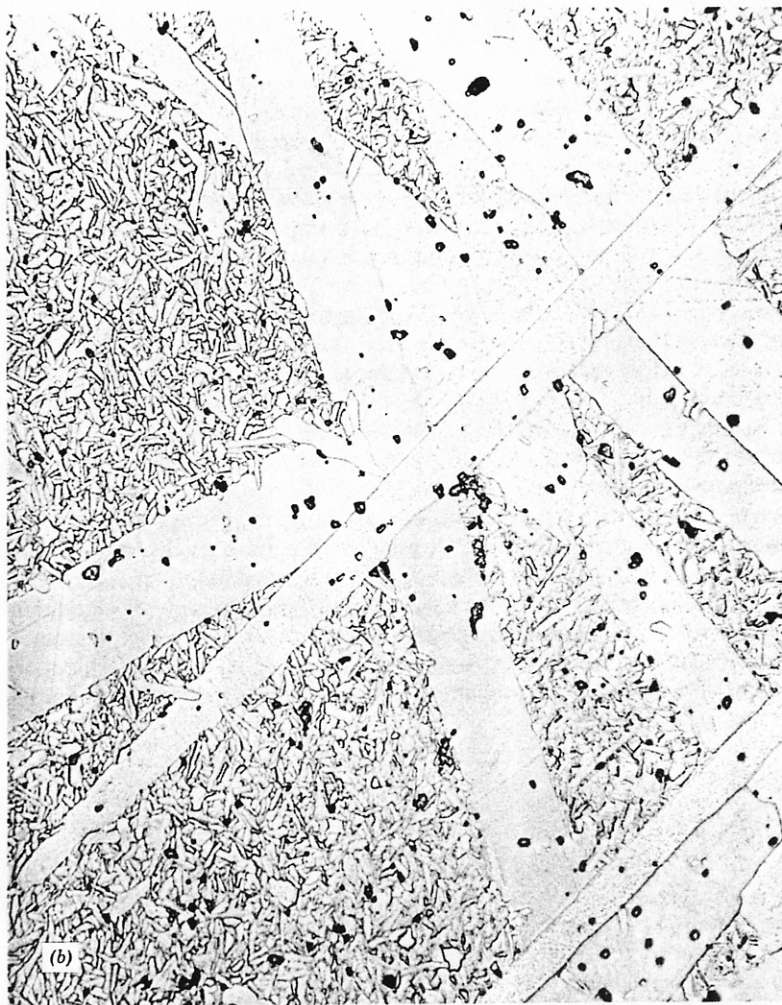


Fig. 10.15 (Continued). (b) Idiomorphic grains of α -6H SiC in a β -SiC matrix (1000 \times).

compact. Elimination of porosity is a related but separate subject and is considered in following sections. An application in which secondary recrystallization has been useful is in the development of preferred orientation on firing of the magnetically hard ferrite, $\text{BaFe}_{12}\text{O}_{19}$.^{*} For this

^{*}A. L. Stuijts, *Trans. Brit. Ceram. Soc.*, 55, 57 (1956).



Fig. 10.15 (Continued). (c) Detail of boundary (75,000 \times). Courtesy S. Prochazka.

magnetic material it is desirable to obtain a high density as well as a high degree of preferred orientation in the sintered product. Particles of the powdered material can be oriented to a considerable extent by subjecting them to a high magnetic field while forming. On sintering there was a 57% alignment after heating at 1250°C. On further heating at 1340°C the