

## Grain Growth, Sintering, and Vitrification

We have previously discussed phase changes, polymorphic transformations, and other processes independent of, or subsequent to, the fabrication of ceramic bodies. Phenomena that are of great importance are the processes taking place during heat treatment before use; these are the subject of this chapter.

During the usual processing of ceramics, crystalline or noncrystalline powders are compacted and then fired at a temperature sufficient to develop useful properties. During the firing process changes may occur initially because of decomposition or phase transformations in some of the phases present. On further heating of the fine-grained, porous compact, three major changes commonly occur. There is an increase in grain size; there is a change in pore shape; there is change in pore size and number, usually to give a decreased porosity. In many ceramics there may be solid-state reactions forming new phases, polymorphic transformations, decompositions of crystalline compounds to form new phases or gases, and a variety of other changes which are frequently of great importance in particular cases but are not essential to the main stream of events.

We shall be mainly concerned with developing an understanding of the major processes taking place. There are so many things which can happen, and so many variables that are occasionally important, that no mere cataloging of phenomena can provide a sound basis for further study. In general, we shall be concerned first with recrystallization and grain-growth phenomena, second with the densification of single-phase systems, and finally with more complex multiphase processes. There are many important practical applications for each of these cases.

### 10.1 Recrystallization and Grain Growth

The terms recrystallization and grain growth have had a very broad and indefinite usage in much of the ceramic literature; they have sometimes been used to include phase changes, sintering, precipitation, exsolution, and other phenomena which produce changes in the microstructure. We are mainly concerned with three quite distinct processes. *Primary recrystallization* is the process by which nucleation and growth of a new generation of strainfree grains occurs in a matrix which has been plastically deformed. *Grain growth* is the process by which the average grain size of strainfree or nearly strainfree material increases continuously during heat treatment without change in the grain-size distribution. *Secondary recrystallization*, sometimes called abnormal or discontinuous grain growth, is the process by which a few large grains are nucleated and grow at the expense of a fine-grained, but essentially strain-free, matrix. Although all these processes occur in ceramic materials, grain growth and secondary recrystallization are the ones of major interest.

**Primary Recrystallization.** This process has as its driving force the increased energy of a matrix which has been plastically deformed. The energy stored in the deformed matrix is of the order of 0.5 to 1 cal/g. Although this is small compared with the heat of fusion, for example (which is a 1000 or more times this value), it provides a sufficient energy change to effect grain-boundary movement and changes in grain size.

If the isothermal change in grain size of strainfree crystals in a deformed matrix is measured after an initial induction period, there is a constant rate of grain growth for the new strainfree grains. If the grain size is  $d$ ,

$$d = U(t - t_0) \quad (10.1)$$

where  $U$  is the growth rate (cm/sec),  $t$  is the time, and  $t_0$  is the induction period. This is illustrated in Fig. 10.1 for recrystallization of a sodium chloride crystal which had been deformed at 400°C and then annealed at 470°C. The induction period corresponds to the time required for a nucleation process, so that the overall rate of recrystallization is determined by the product of a nucleation rate and a growth rate.

The nucleation process is similar to those discussed in Chapter 8. For a nucleus to be stable, its size must be larger than some critical diameter at which the lowered free energy of the new grain is equal to the increased surface free energy. The induction period corresponds to the time required for unstable embryos present to grow to the size of a stable nucleus. If an unlimited number of sites is available, the rate of nucleation increases to some constant rate after an initial induction period. In

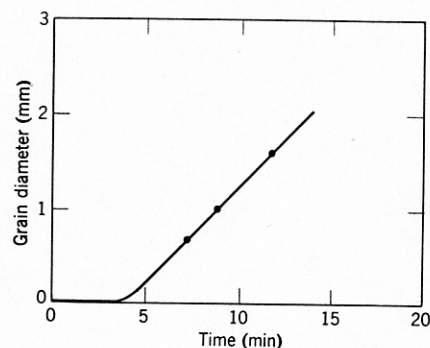


Fig. 10.1. Recrystallization of NaCl deformed at 400°C (stress = 4000 g/mm<sup>2</sup>) and recrystallized at 470°C. From H. G. Müller, *Z. Phys.*, **96**, 279 (1935).

practice the number of favorable sites available is limited, and the rate of nucleation passes through a maximum as they are used up. H. G. Müller\* observed that nuclei in sodium chloride tended to form first at grain corners, for example. As the temperature is increased, the rate of nucleation increases exponentially:

$$\frac{N}{dt} = N_0 \exp\left(-\frac{\Delta G_N}{RT}\right) \quad (10.2)$$

where  $N$  is the number of nuclei and  $\Delta G_N$  is the experimental free energy for nucleation. Consequently, the induction period,  $t_0 \sim 1/(dN/dt)$ , decreases rapidly as the temperature level is raised.

As indicated in Eq. 10.1, the growth rate remains constant until the grains begin to impinge on one another. The constant in growth rate results from the constant driving force (equal to the difference in energy between the strained matrix and strainfree crystals). The final grain size is determined by the number of nuclei formed, that is, the number of grains present when they finally impinge on one another. The atomistic process necessary for grain growth is the jumping of an atom from one side of a boundary to the other and is similar to a diffusional jump in the boundary. Consequently the temperature dependence is similar to that of diffusion:

$$U = U_0 \exp\left(-\frac{E_U}{RT}\right) \quad (10.3)$$

where the activation energy  $E_U$  is normally intermediate between that for boundary and lattice diffusion. The growth-rate-temperature curve for

\**Z. Phys.*, **96**, 279 (1935).

recrystallization of sodium chloride has a knee similar to that observed for diffusion and conductivity data, as discussed in Chapter 6.

Since both the nucleation rate and the growth rate are strongly temperature-dependent, the overall rate of recrystallization changes rapidly with temperature. For a fixed holding time, experiments at different temperatures tend to show either little or nearly complete recrystallization. Consequently, it is common to plot data as the amount of cold work or the final grain size as a function of the *recrystallization temperature*. Since the final grain size is limited by impingement of the grains on one another, it is determined by the relative rates of nucleation and growth. As the temperature is raised, the final grain size is larger, since the growth rate increases more rapidly than the rate of nucleation. However, at higher temperatures recrystallization is completed more rapidly, so that the larger grain size observed in constant-time experiments (Fig. 10.2) may be partly due to the greater time available for grain growth following recrystallization. The growth rate increases with increasing amounts of plastic deformation (increased driving force), whereas the final grain size decreases with increasing deformation.

In general, it is observed that (1) some minimum deformation is required for recrystallization, (2) with a small degree of deformation a higher temperature is required for recrystallization to occur, (3) an increased annealing time lowers the temperature of recrystallization, and

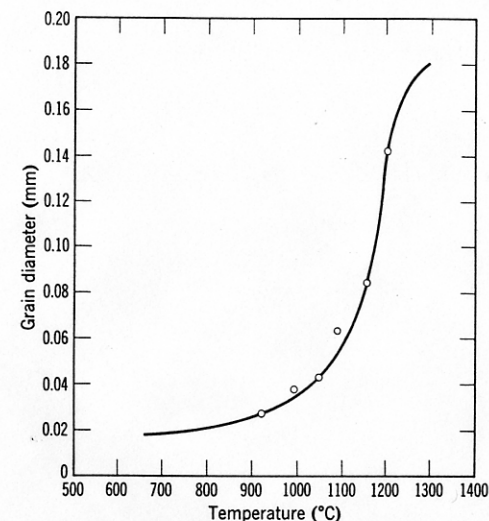


Fig. 10.2. Effect of annealing temperature on grain size of CaF<sub>2</sub> following compression at 80,000 psi and 10 hr at temperature. From M. J. Buerger, *Am. Mineral.*, **32**, 296 (1947).



(4) the final grain size depends on the degree of deformation, the initial grain size, and the temperature of recrystallization. In addition, continued heat after recrystallization is completed leads to the continuation of grain growth.

Primary recrystallization is particularly common in metals which are extensively deformed in normal processing techniques. Ceramic materials are seldom plastically deformed during processing, so that primary recrystallization is not commonly observed. For relatively soft materials, such as sodium chloride or calcium fluoride, deformation and primary recrystallization do occur. It has also been observed directly in magnesium oxide; also, the polygonization process described in Chapter 4 (see Fig. 4.24) for aluminum oxide has many points of similarity.

**Grain Growth.** Whether or not primary recrystallization occurs, an aggregate of fine-grained crystals increases in average grain size when heated at elevated temperatures. As the average grain size increases, it is obvious that some grains must shrink and disappear. An equivalent way of looking at grain growth is as the rate of disappearance of grains. Then the driving force for the process is the difference in energy between the fine-grained material and the larger-grain-size product resulting from the decrease in grain-boundary area and the total boundary energy. This energy change corresponds to about 0.1 to 0.5 cal/g for the change from a 1-micron to a 1-cm grain size.

As discussed in Chapter 5, an interface energy is associated with the boundary between individual grains. In addition, there is a free-energy difference across a curved grain boundary which is given by

$$\Delta G = \gamma \bar{V} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (10.4)$$

where  $\Delta G$  is the change in free energy on going across the curved interface,  $\gamma$  is the boundary energy,  $\bar{V}$  is the molar volume, and  $r_1$  and  $r_2$  are the principal radii of curvature. (This relationship has been derived and discussed in Chapter 5. That part of Chapter 5 should be reviewed if its meaning is not clear.) This difference in the free energy of material on the two sides of a grain boundary is the driving force that makes the boundary move toward its center of curvature. The rate at which a boundary moves is proportional to its curvature and to the rate at which atoms can jump across the boundary.

Grain growth provides an opportunity to apply the absolute-reaction-rate theory already discussed in Chapter 6. If we consider the structure of a boundary (Fig. 10.3), the rate of the overall process is fixed by the rate at which atoms jump across the interface. The change in energy with an atom's position is shown in Fig. 10.3b, and the frequency of atomic jumps

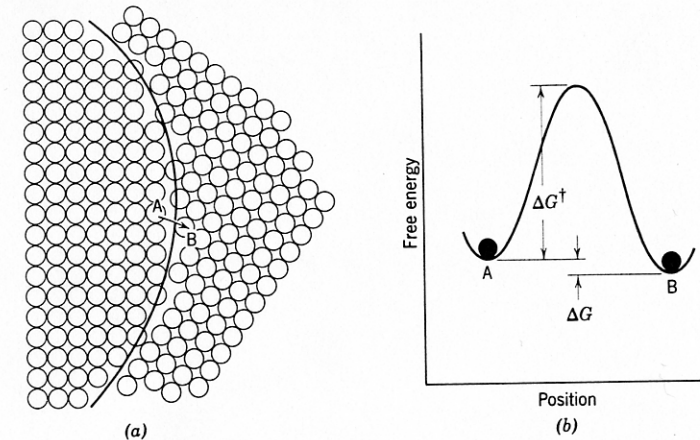


Fig. 10.3. (a) Structure of boundary and (b) energy change for atom jump.

in the forward direction is given by

$$f_{AB} = \frac{RT}{Nh} \exp \left( -\frac{\Delta G^\ddagger}{RT} \right) \quad (10.5)$$

and the frequency of reverse jumps is given by

$$f_{BA} = \frac{RT}{Nh} \exp \left( -\frac{\Delta G^\ddagger + \Delta G}{RT} \right) \quad (10.6)$$

so that the net growth process,  $U = \lambda f$ , where  $\lambda$  is the distance of each jump is given by

$$U = \lambda f = \lambda (f_{AB} - f_{BA}) = \frac{RT}{Nh} (\lambda) \exp \left( -\frac{\Delta G^\ddagger}{RT} \right) \left( 1 - \exp \frac{\Delta G}{RT} \right) \quad (10.7)$$

and since  $1 - \exp \frac{\Delta G}{RT} \cong \frac{\Delta G}{RT}$ , where  $\Delta G = \gamma \bar{V} \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$  and  $\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$ ,

$$U = \left( \frac{RT}{Nh} \right) (\lambda) \left[ \frac{\gamma \bar{V}}{RT} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \right] \exp \frac{\Delta S^\ddagger}{R} \exp \left( -\frac{\Delta H^\ddagger}{RT} \right) \quad (10.8)$$

which is equivalent in form to Eq. 10.3 given previously. That is, the rate of growth increases exponentially with temperature. The unit step involved is the jump of an atom across the boundary, so that the activation energy should correspond approximately to the activation energy for boundary diffusion.

If all the grain boundaries are equal in energy, they meet to form angles of  $120^\circ$ . If we consider a two-dimensional example for illustrative purposes, angles of  $120^\circ$  between grains with straight sides can occur only for six-sided grains. Grains with fewer sides have boundaries that are concave when observed from the center of the grain. Shapes of grains having different numbers of sides are illustrated in Fig. 10.4; a sample with uniform grain size is shown in Fig. 10.5. Since grain boundaries migrate toward their center of curvature, grains with less than six sides tend to grow smaller, and grains with more than six sides tend to grow larger. For any one grain, the radius of curvature of a side is directly proportional to the grain diameter, so that the driving force, and therefore the rate of grain growth, is inversely proportional to grain size:

$$\dot{d} = \frac{d(d)}{dt} = \frac{k}{d} \quad (10.9)$$

and integrating,

$$d - d_0 = (2k)^{1/2} t^{1/2} \quad (10.10)$$

where  $d_0$  is the grain diameter at time zero. Experimentally it is found that when  $\log d$  is plotted versus  $\log t$ , a straight line is obtained (Fig. 10.6). Frequently the slope of curves plotted in this way is smaller than one-half,

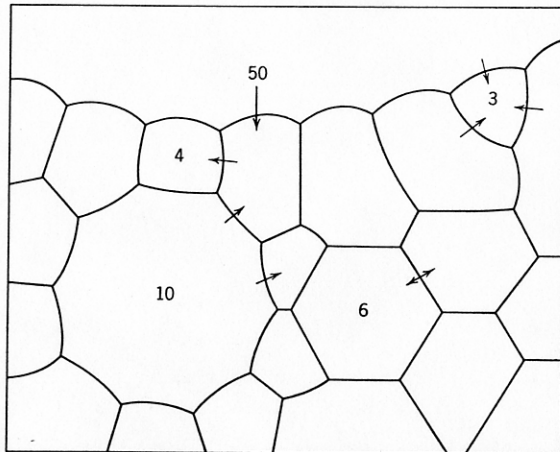


Fig. 10.4. Schematic drawing of polycrystalline specimen. The sign of curvature of the boundaries changes as the number of sides increases from less than six to more than six, and the radius of curvature is less, the more the number of sides differs from six. Arrows indicate the directions in which boundaries migrate. From J. E. Burke.

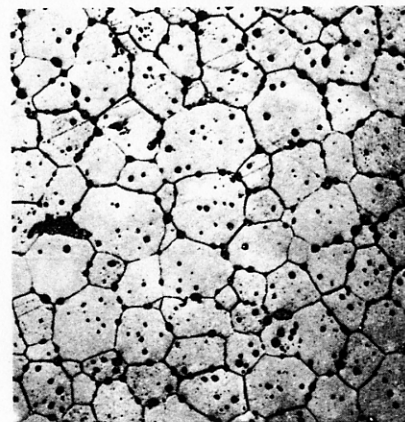


Fig. 10.5. Polycrystalline  $\text{CaF}_2$  illustrating normal grain growth. Average angle at grain junctures is  $120^\circ$ .

usually falling between 0.1 and 0.5. This may occur for several reasons, one being that  $d_0$  is not a large amount smaller than  $d$ ; another common reason is that inclusions or solute segregation or sample size inhibits grain growth.

A somewhat different approach is to define a grain-boundary mobility  $B_i$  such that the boundary velocity  $v$  is proportional to the applied driving force  $F_i$  resulting from boundary curvature:

$$v = B_i F_i \quad (10.11a)$$

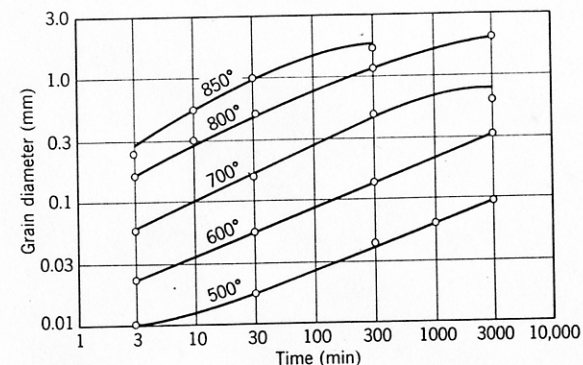


Fig. 10.6. Log grain diameter versus log time for grain growth in pure  $\alpha$ -brass. From J. E. Burke.



For the atomic-jump mechanism illustrated in Fig. 10.3, the boundary mobility is given by the atomic mobility divided by the number of atoms involved,  $n_a$ :

$$B_i = \frac{B_a}{n_a} = \left( \frac{D_b}{kT} \right) \left( \frac{\Omega}{Sw} \right) \quad (10.11b)$$

where  $D_b$  is the grain-boundary diffusion coefficient,  $\Omega$  is the atomic volume,  $S$  is the boundary area, and  $w$  is the boundary width. Since the average boundary velocity is equal to  $v$  and the driving force is inversely proportional to grain size, a grain-growth law of the form of Eqs. 10.9 and 10.10 results. However, as discussed in Chapter 5, the actual structure of a ceramic grain boundary is not quite so simple as pictured in deriving Eqs. 10.8 and 10.11b. Even for a completely pure material there is a space-charge atmosphere of lattice defects associated with the boundary and usually solute segregation as well, as shown in Figs. 5.11, 5.12, 5.17, and 5.18. The effect of this lattice defect and impurity atmosphere is to sharply reduce the grain-boundary velocity at low driving forces, as shown in Fig. 10.7 and analysed by J. Cahn\* and K. Lücke and H. D. Stuwe.† The influence of this atmosphere becomes stronger as the grain

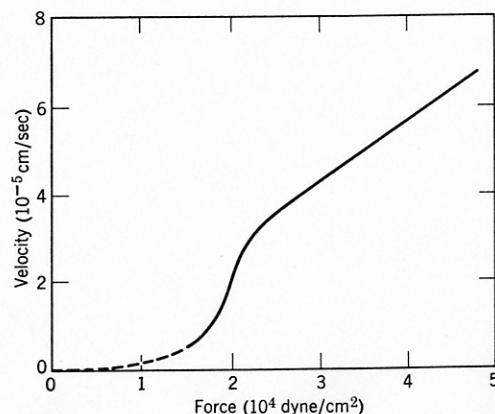


Fig. 10.7. Variation of boundary velocity  $v$  with driving force  $F$  at 750°C for a 20° tilt boundary in NaCl. From R. C. Sun and C. L. Bauer, *Acta Met.*, 18, 639 (1970).

size increases, the solute segregate concentration increases, and the average boundary curvature decreases. Additions of MgO to  $Al_2O_3$ ,  $CaCl_2$

\**Acta Met.*, 10, 789 (1962).

†*Acta Met.*, 19, 1087 (1971).

to KCl and of  $ThO_2$  to  $Y_2O_3$  in amounts below the solubility limit have proved effective as grain-growth inhibitors.

When grains grow to such a size that they are nearly equal to the specimen size, grain growth is stopped. In a rod sample, for example, when the grain size is equal to the rod diameter, the grain boundaries tend to form flat surfaces normal to the axis so that the driving force for boundary migration is eliminated and little subsequent grain growth occurs. Similarly, inclusions increase the energy necessary for the movement of a grain boundary and inhibit grain growth. If we consider a boundary such as the one illustrated in Fig. 10.8, the boundary energy is decreased when it reaches an inclusion proportional to the cross-sectional area of the inclusion. The boundary energy must be increased again to pull it away from the inclusion. Consequently, when a number of inclusions are present on a grain boundary, its normal curvature becomes insufficient for continued grain growth after some limiting size is reached. It has been found that this size is given by

$$d_i \approx \frac{d_l}{f_{d_i}} \quad (10.12)$$

where  $d_i$  is the limiting grain size,  $d_l$  is the particle size of the inclusion, and  $f_{d_i}$  is the volume fraction of inclusions. Although this relationship is only approximate, it indicates that the effectiveness of inclusions increases as their particle size is lowered and the volume fraction increases.

For the process illustrated in Fig. 10.8, the boundary approaches, is attached to, and subsequently breaks away from a second-phase particle. Another possibility is that the grain boundary drags along the particle

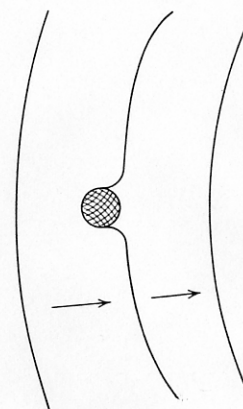


Fig. 10.8. Changing configuration of a boundary while passing an inclusion.