

Fig. 10.30 (Continued). (b) Conditions for pore stability.

for shrinkage; when r/ρ is negative, the pore tends to grow. This is illustrated in Fig. 10.30b. For a uniform grain size the space-filling form is a tetrakaidecahedron with 14 surrounding grains. From an approximate relationship between the number of surrounding grains and the pore-diameter to grain-diameter ratio we can derive a relationship for pore stability as a function of dihedral angle and the ratio of pore size to grain size, as shown in Fig. 10.31. From this figure we can see why large pores present in poorly compacted powder such as shown in Fig. 10.32 not only remain stable but grow. It is also seen that an enormous disparity between

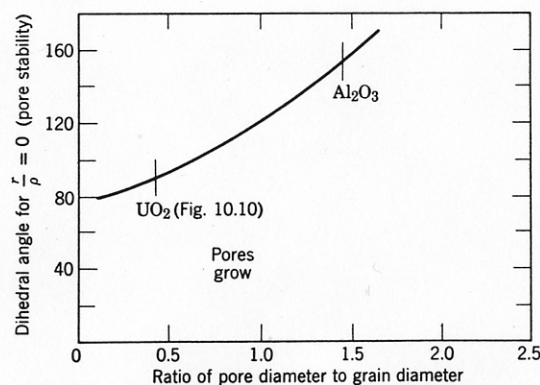


Fig. 10.31. Conditions for pore stability.



Fig. 10.32. Large voids formed by bridging of agglomerates in fine Al_2O_3 powder viewed with scanning electron microscope at $2000\times$. Courtesy C. Greskovich.

grain size and pore size is not necessary for pore stability. That is, the site and size of the porosity relative to the grain-boundary network not only affects the necessary distance for diffusion but also the driving force for the process.

The interaction of grain boundaries and porosity is, of course, a two-way street. When many pores are present during the initial stages of sintering, grain growth is inhibited. However, as discussed in Section 10.1, once the porosity has decreased to a value such that secondary grain growth can occur, extensive grain growth may result at high sintering temperatures. When grain growth occurs, many pores become isolated from grain boundaries, and the diffusion distance between pores and a grain boundary becomes large, and the rate of sintering decreases. This is illustrated in Fig. 10.16b, in which extensive secondary recrystallization has occurred, with the isolation of pores in the interior of grains and a reduction in the densification rate. Similarly, the sample of aluminum oxide shown in Fig. 10.33 has been sintered at a high temperature at which discontinuous grain growth occurred. Porosity is only removed near the grain boundaries, which act as the vacancy sink. The importance of

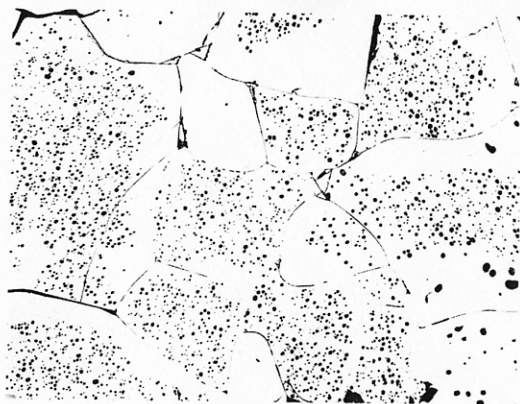


Fig. 10.33. Sintered Al_2O_3 illustrating elimination of porosity adjacent to grain boundaries with residual porosity remaining at grain centers. Courtesy J. E. Burke.

controlling grain growth as an integral part of controlling sintering phenomena cannot be overestimated. Consequently, the grain-growth processes discussed in Section 10.1 must be actively prevented in order to obtain complete densification. Usually densification continues by a diffusion process until about 10% porosity is reached; at this point rapid grain growth occurs by secondary recrystallization, and the rate of densification is sharply reduced. In order to obtain densification much beyond this level, prevention of secondary recrystallization is essential. The most satisfactory way of doing this is with additives which prevent or slow down boundary migration to a point at which it is possible to obtain pore elimination. Additions of MgO to Al_2O_3 , ThO_2 to Y_2O_3 , and CaO to ThO_2 , among others, have been found to slow boundary migration and allow complete pore elimination by solid-state sintering in these systems. The porefree microstructure of a polycrystalline ceramic having optical transparency suitable for use as a laser material is shown in Fig. 10.34.

10.3 Vitrification

To vitrify is to make glasslike and the vitrification process—densification with the aid of a viscous liquid phase—is the major firing process for the great majority of silicate systems. (In some current glossaries vitrification is defined as being identical to densification on firing, but the more specific usage is preferred.) A viscous liquid silicate is formed at the firing temperature and serves as a bond for the body. For

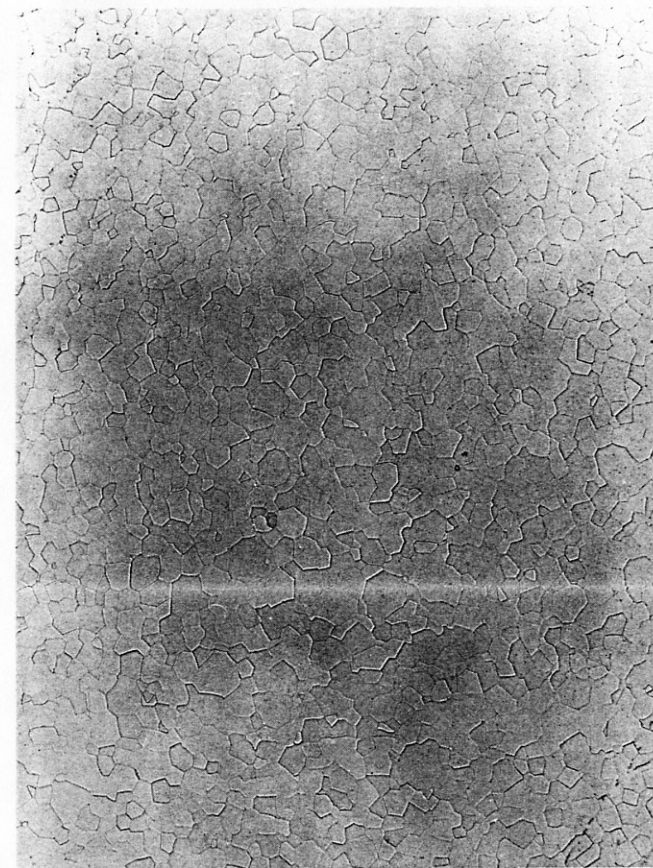


Fig. 10.34. Polished section of $\text{Y}_2\text{O}_3 + 10 \text{ mole } \% \text{ ThO}_2$ sintered to porefree state. 100 \times . Courtesy C. Greskovich and K. N. Woods.

satisfactory firing the amount and viscosity of the liquid phase must be such that densification occurs in a reasonable time without the ware slumping or warping under the force of gravity. The relative and absolute rates of these two processes (shrinkage and deformation) determine to a large extent the temperature and compositions suitable for satisfactory firing.

Process Kinetics. If we consider two particles initially in contact (Fig. 10.21), there is a negative pressure at the small negative radius of

way that the final shape is satisfactory. In the same way, when plates are fired in the horizontal position there is a tendency for the rims to settle; this can be compensated for by adjusting the shape of the initial piece.

Correct setting methods are important in eliminating difficulties caused by firing-shrinkage variations. These have been most extensively developed for porcelain compositions in which complete vitrification is desired and high shrinkages result. Some of the standard setting methods are illustrated in Fig. 10.46. Cups and bowls are commonly boxed as indicated in Fig. 10.46a. This keeps the rim circular, since warpage of one restricts warpage of the other; in addition, it prevents the thin rims from being too rapidly heated. For larger pieces, unfired setters are necessary as a means of controlling shrinkage and maintaining circular rims. A variety of methods is used for setting different kinds of plate compositions, depending on the amount of shrinkage expected. For ware fired to complete vitrification individual setting and support are essential. For ware fired to partial densification, plates can be stacked with no ill effects. In general, large tiles and brick do not cause much difficulty.

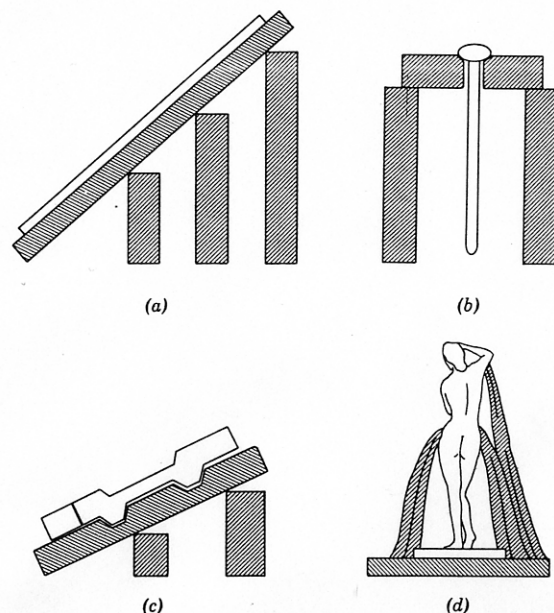


Fig. 10.47. Setting methods for special shapes. (a) Large tiles set at an angle of repose; (b) slender rod supported by collar; (c) special shape; (d) sculptured piece. From F. H. Norton.

Special shapes may require special setting methods to eliminate adverse effects of firing shrinkage. Large refractory tile can be set at an angle of repose on a flat surface (Fig. 10.47a). This allows the tile to shrink without much stress. In the same way rods or tubes may be set in an inclined V groove or supported by a collar from the upper end (Fig. 10.47b). Gravitational forces keep the tubes straight up to lengths of several feet. Unique shapes can always be supported on special setters designed for the particular sample. Some experience is necessary to handle unique shapes efficiently. Small pieces of sculptured vitrified ware are particularly difficult. The safest setting provides complete support from unfired struts (Fig. 10.47d).

Suggested Reading

1. G. C. Kuczyski, N. A. Hooton, and C. F. Gibson, Eds., *Sintering and Related Phenomena*, Gordon and Breach, New York, 1967.
2. G. C. Kuczyski, Ed., "Sintering and Related Phenomena", *Materials Science Research*, Vol. 6, Plenum Press, New York, 1973.
3. R. L. Coble and J. E. Burke, *Progress in Ceramic Science*, Vol. III, J. E. Burke, Ed., Pergamon Press, 1963.
4. W. D. Kingery, Ed., *Ceramic Fabrication Process*, Part IV, Technology Press, Cambridge, Mass., and John Wiley & Sons, New York, 1958.
5. W. D. Kingery, Ed., *Kinetics of High-Temperature Process*, Part IV, Technology Press, Cambridge, Mass., and John Wiley & Sons, New York, 1959.
6. J. E. Burke and D. Turnbull, "Recrystallization and Grain Growth in Metals," *Prog. Met. Phys.*, 3, 220 (1952).
7. E. Schramm and F. P. Hall, "The Fluxing Effect of Feldspar in Whiteware Bodies," *J. Am. Ceram. Soc.*, 15, 159 (1936).
8. For additional papers on sintering see: R. L. Coble, *J. Appl. Phys.*, 41, 4798 (1970); D. L. Johnson and I. B. Cutler, *J. Am. Ceram. Soc.*, 46, 541 (1963).

Problems

- 10.1. Distinguish between primary recrystallization, grain growth, and secondary recrystallization as to (a) source of driving force, (b) magnitude of driving force, and (c) importance in ceramic systems.
- 10.2. Explain why the activation energy for grain-boundary migration corresponds approximately with that for boundary diffusion, even though no concentration gradient exists in the former case.
- 10.3. Can grain growth during sintering cause compaction of ceramics? Explain. Can grain growth affect the sintering rate? Explain.