1.11 SINTERING PRACTICE

A wide variety of techniques has been developed to obtain dense ceramics with a desired microstructure and phase composition. In general, these methods involve a combination of a heating schedule and applied pressure.

Heating schedules can be simple, as in isothermal sintering, or have a complex temperature-time relationship, as in rate-controlled sintering, while pressure may be applied either uniaxial, with or without a die, or by the surrounding gas. Control of the sintering atmosphere is also important and precise control of oxygen or nitrogen partial pressure as a function of temperature may in some cases be beneficial or essential. Insoluble gases trapped in closed pores may obstruct final stages of densification or lead to post-densification swelling and, in these cases; a change of sintering atmosphere or vacuum sintering is indicated. Atmosphere protection may also be provided by packing the sample in an appropriate powder. The practice of sintering further includes a control of the particle characteristics, green compact structure, and consideration of chemistry.

1.11.1 Heating Schedules

A general heating schedule is shown in Figure 1.21. Binder burnout, removal of volatiles such as water, and conversion of additives such as organometallics or polymers take place. Typically, the first hold temperature is, at most, a few hundred degrees centigrade. The heat-up rate should be carefully controlled, since it is quite possible that rapid heating causes boiling and evaporation of organic additives leading to specimen bloating or even shattering. Stage 2 can be included to promote chemical homogenization or reaction of powder components. Stage 3 represents the heat-up to the isothermal sintering stage 4, during which the majority of the densification and microstructure development takes place, which is then followed by a cool-down. An additional hold in stage 5, prior to the final cool-down of stage 6, may also be included to relieve internal stresses or allow for precipitation or other reactions.

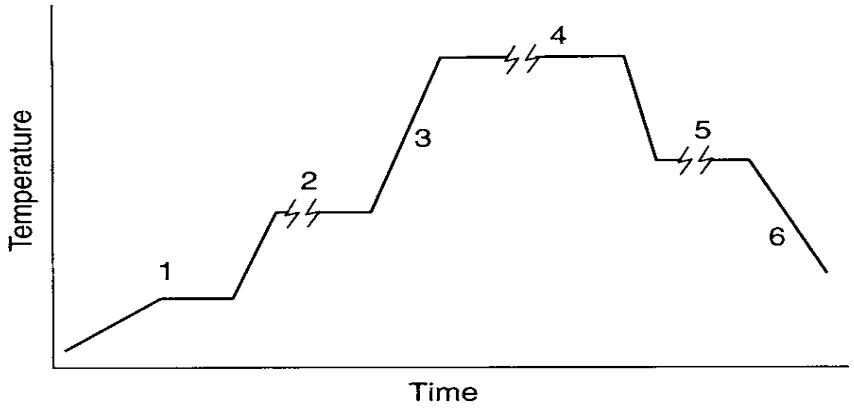

FIGURE 1.21 Generalized heating schedule.

1.11.1.1 Isothermal Sintering

In isothermal sintering, perhaps better called isothermal-stage sintering, the temperature is increased monotonically to a sintering hold temperature and lowered to room temperature afterwards. The holding time is long compared to the heat-up time. This is the most common heating schedule. The heat-up times are limited by the sample size and by the thermal characteristics of the furnace. Heat-up times for large bodies can stretch over many hours, to avoid temperature gradients that could lead to cracking or to the formation of an outer dense layer on an incompletely densified core, as would result from differential densification.

During the heat-up phase of the isothermal sintering, significant densification and microstructural changes can take place. In addition, generally, densification processes should be carried out significantly above the intended service temperature.

1.11.1.2 Constant Heating Rate Sintering

In this case, the sample is heated to a specified temperature at a controlled heating rate, and immediately cooled. Constant heating rate experiments may actually be simpler to analyze theoretically than the "isothermal" ones, because strict isothermal sintering is not possible. In practice, the use of constant heating rates is again limited by the sample size. High constant heating rates are then most useful in laboratory studies. Manipulation of the heating rate can be useful in the case where reactions take place during densification. For example, densification and crystallization of a glass

powder in which densification was inhibited by crystallization at 1 K/min, but densification was complete prior to crystallization at 15 K/min. In general, higher heating rates lead to a finer grain size. The relative density versus temperature clustered in a narrow band, for heating rates between 0.5 and 15 K/min.

1.11.1.3 Multi-stage Sintering

Multi-stage sintering is frequently used in practice, sometimes introducing extended temperature plateaus or more complex temperature-time sequences in the heating schedule, with the purpose of achieving specific either chemical or microstructural features. An example of staged sintering, involving two separate peak temperatures in which the temperature is reduced between the stages is in the sintering of the ion-conducting ceramic sodium beta alumina. Optimum results with respect to microstructure and strength were achieved in this case by reducing the sintering temperature by about 150°C after reaching the first peak temperature (about 1500°C). A reduction in grain size and an increase in uniformity were also found for MgO, $A1_2O_3$, and ZnO using a two-stage sintering technique. The first stage consisted of an extended hold at a temperature where shrinkage was 0.5-1% after 48 h. At the holding temperatures, limited coarsening occurs that appears to have the effect of homogenizing the porous powder compact. Figure 1.22 shows the change in pore size distribution after limited coarsening for an alumina powder.

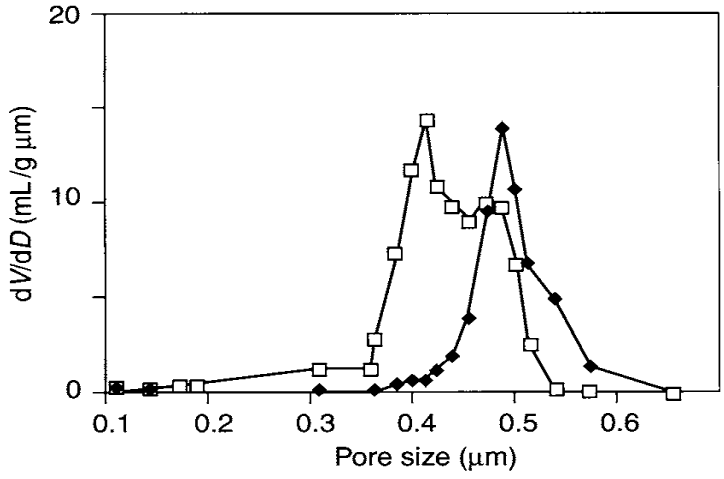

FIGURE 1.22 Pore size distribution narrowing after 50 h at 800°C for an alumina powder compact, determined by mercury porosimetry.

1.11.1.4 Rate-Controlled Sintering

In rate-controlled sintering, the densification rate is coupled with the temperature control of the sintering furnace in such a way as to keep the densification rate constant or limited. The result is a complicated temperature history that at times approaches the staged sintering processes. The beneficial effects on microstructure have been reported in several instances, including where chemical reactions occur during densification. Manipulation of the sintering temperature is necessarily limited by the thermal impedance of the sintering furnace and by the size of the sample.

1.11.1.5 Fast-Firing

Ratio-controlled sintering and fast firing are based on the principle of increasing the densification rate relative to the coarsening rate. In ratio-controlled sintering, a temperature is selected that depends on the relative activation energies of these competing processes. This is shown schematically in Figure 1.23. The preferred sintering temperature is one where the densification rate is higher than the coarsening rate. The most common situation is one where at higher temperatures densification rates are faster than coarsening rates. This leads to the process of fast firing, in which the sample is taken to the high sintering temperature as rapidly as the system allows.

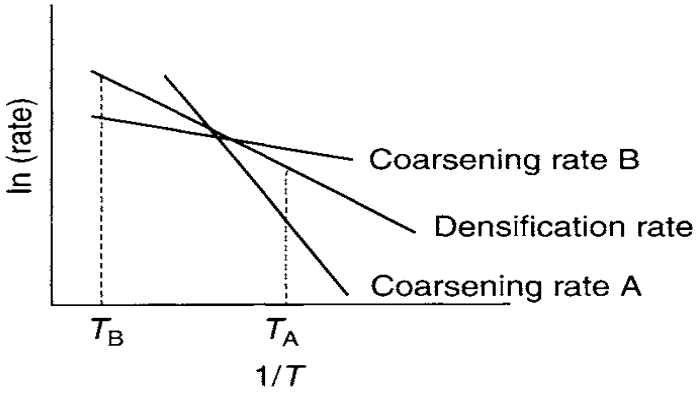

FIGURE 1.23 Possible relation of coarsening rates to densification rate. The preferred sintering temperatures TA or TB correspond to the coarsening rates A or B.