

Equation (2) may now be re-written

$$\left(\frac{\rho}{P}\right)^{\frac{1}{3}} = 4 (\pm 2) 10^3 \frac{\sigma}{l^2} \frac{D_M \Omega_s}{kT} t + \text{constant} \quad (6)$$

4. TEMPERATURE DEPENDENCE OF SHRINKAGE RATE

4.1 Experimental Procedure

It has been reported elsewhere¹ that the gradient of a plot of $(\rho/P)^{\frac{1}{3}}$ versus time for an alumina compact during pressure-sintering is usually constant, in accordance with Equation (2), over a range of relative densities extending from <0.90 to about 0.96. (Outside these limits the gradient was usually again constant, but with slightly different values from that of the main part of the plot, presumably because of changes in pore geometry). However, it was also observed that these gradients could vary considerably amongst different specimens even though the same experimental conditions were used in each case, presumably because of minor differences in pore separation. For this reason it was considered that the effect of a change of temperature on densification rate could not easily be evaluated by comparing the shrinkage rates of different specimens.

The method adopted was to observe the shrinkage of a compact at a given temperature while 2–3% densification took place, and then to lower the temperature by about 50°C and measure the new shrinkage rate.

The detailed procedure was as follows. The alumina powder was inserted in the die and outgassed (under vacuum) for about 12 h at about 350°C. The temperature was then raised to the required value with a pressure of 5000 lb.in.⁻² applied to the compact, after which the load was reduced or removed so that little or no further densification occurred during the hour or more required for the apparatus to reach thermal equilibrium. A suitable load (sufficient to cause a reasonable shrinkage rate at the chosen temperature) was then applied, and the shrinkage of the compact was plotted against time until an estimated density change of 2–3% had been accomplished. At this time the temperature was reduced to a new value about 50°C lower, and the new shrinkage curve was plotted. The general shape of the plot is shown diagrammatically in Figure 2A, the temperature being reduced at point A. The part of the curve immediately following point A represents a combination of compact shrinkage and thermal contraction, eventually becoming a pure shrinkage curve at point B, about 40 min. later. The extent of the thermal contraction was of course unknown, and until it had been evaluated the true pellet lengths represented by the part of the plot prior to point A could not be calculated from the final length of the pellet. To evaluate the amount of the thermal contraction, the pellet was permitted to shrink until the density reached was sufficiently high for the shrinkage rate to have become negligible (point C in Figure 2A). The temperature was then again raised to its initial value, and the amount of thermal expansion evaluated by subtracting the apparent length at C from that at D (about 40 min. later). When the apparatus had been allowed to cool to room temperature, the pellet was removed and its length and density measured. The plot of $(\rho/P)^{\frac{1}{3}}$ versus time for such an experiment possessed the shape shown diagrammatically in Figure

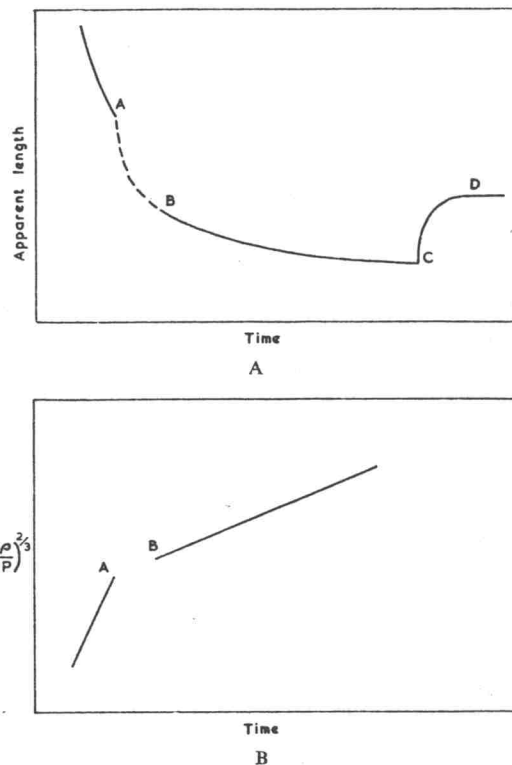


FIGURE 2

Schematic shape of:

- A. Shrinkage plots obtained during temperature-dependence experiments.
B. Plot of densification-data corresponding to shrinkage plot in A.

2B. The activation energy for diffusion could be calculated from the gradients of the two parts of the latter plot, using the relationship

$$Q = R \left(\frac{T_1 T_2}{T_1 - T_2} \right) \ln \left(\frac{S_1 T_1}{S_2 T_2} \right)$$

where S_1 and S_2 are the gradients of the plot of $(\rho/P)^{\frac{1}{3}}$ against time, at temperatures T_1 and T_2 (°K) respectively.

4.2 Experiments with Undoped Alumina

The first experiments in the series were performed using untreated Linde A alumina. Four satisfactory sets of results (in which both parts of the shrinkage plot were obtained at relative densities lower than 0.96) were obtained using four different pairs of temperatures. Details are given in Table 1 and plots of $(\rho/P)^{\frac{1}{3}}$ against time for two of them are shown, as an example of the type of plot obtained, in Figure 3.

The value of the activation energy for diffusion is seen to be $115(\pm 4)$ kcal.mole⁻¹. The quoted uncertainty arises mainly because of the degree of precision with which the temperature could be measured.

4.3 Experiments with Magnesia-doped Specimens

Magnesium was chosen as a doping cation because it possesses a lower valency than that of aluminium, and so small amounts in solid solution in alumina may be expected to cause an excess concentration of oxygen