values appropriate to the less strain rates predicted by r by the factor $(1 + z_a - z_c)/f$, pends on the valencies of the xample, for alumina $z_c = -3$ $z_c)/f > 6$. Thus a value of D_T (5) will be at least six times ent value calculated using

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25.—The Pressure-sintering of Alumina

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ABSTRACT

E13/C525

The theoretical equation for the final-stage densification of a polycrystalline compact during pressure-sintering, based on a model involving the stress-induced diffusion of vacancies, is discussed. Experiments are described which confirm the predictions of the equation with regard to the dependence of shrinkage rate on the amount of remaining porosity, the applied pressure, and the pore separation.

Le frittage sous pression de l'alumine

Discussion relative à l'équation théorique de la densification finale d'un produit polycristallin compacté par frittage sous pression, basée sur un modèle tenant compte de la diffusion des vacances sous l'effet des contraintes. L'auteur décrit les expériences qui confirment ce que l'équation laissait prévoir au sujet de la corrélation entre la vitesse de retrait d'une part, et la porosité résiduelle, la pression appliquée et la répartition des pores, d'autre part.

Drucksintern von Aluminiumoxid

Es wird eine theoretisch abgeleitete Gleichung für die endgültige Verdichtung eines polykristallinen Preßlings beim Drucksintern diskutiert, wobei ein Modell zugrunde gelegt wird, das die druckinduzierte Diffusion von Leerstellen berücksichtigt. Experimente werden beschrieben, die Voraussagen der Gleichung bezüglich der Abhängigkeit der Schwindingsgeschwindigkeit von Porositätsgrad, vorliegendem Druck und Porentrennung bestätigen.

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1. INTRODUCTION

In an earlier publication¹ a new equation was proposed to describe the final-stage densification of a polycrystalline compact during pressure-sintering, where the necessary change of grain shape occurred by the stress-induced diffusion of vacancies. The proposed equation was

$$\frac{1}{V_s}\frac{\mathrm{d}V}{\mathrm{d}t} = -Z \frac{\sigma}{l^2} \frac{D\Omega}{kT} \left(\frac{P}{\rho}\right)^3 \qquad . \qquad (1)$$

where V_s is the volume of solid material, dV/dt is the rate of change of volume of the compact, Z is a geometrical constant, σ is the applied pressure, l is the mean pore separation, D has the dimensions of a self-diffusion coefficient, Ω is the relevant vacancy volume, k is Boltzmann's constant, T is the absolute temperature, P is the fractional porosity and ρ the relative density $(\rho=1-P)$. Evidence was reported that the rate of volume change of pressed alumina compacts was indeed proportional to $(P/\rho)^{i}$, but experiments to test the other predictions of the equation were incomplete at the time of publication. These later experiments are reported in the present paper.

2. THE PRESSURE-SINTERING EQUATION

2.1 Corrections to the Method of Derivation

Equation (1) is not entirely satisfactory as it stands, because the factors D and Ω are not satisfactorily defined.

A theory is now available which describes the ion flux in a binary ionic crystal subjected to a stress gradient,² and this theory will be used as the starting point for a new derivation of the pressure-sintering equation.

From reference 2, it may be assumed that the effective flux of complete "molecules" in such a crystal is given by

$$J_M = -\frac{D_M}{kT} \frac{\mathrm{d}\sigma}{\mathrm{d}x} \qquad . \qquad . \qquad (2)$$

where $d\sigma/dx$ is the stress gradient and D_M is the effective "molecular" diffusion coefficient.

$$D_M = -(D_T)_a \left(\frac{1 + z_a - z_c}{f_a z_c}\right) \text{ if } (D_T)_c \gg (D_T)_a$$

$$(D_T)_c \left(\frac{1+z_a-z_c}{f_c z_a}\right)$$
 if $(D_T)_a \gg (D_T)_c$

where the subscripts a and c refer to anions and cations respectively, D_T is the tracer diffusion coefficient, z is the ionic charge expressed as a multiple of the charge on the electron, so that z_c is always negative, and f is the jump correlation factor.

The rate of volume change dV/dt of a pressuresintered sample is given by

$$\frac{1}{V_s}\frac{\mathrm{d}V}{\mathrm{d}t} = -J_M\Omega_s A$$

where Ω_s is the volume of a "molecule" of the ionic crystal (i.e. of the least number of ions of both species which maintain electrical neutrality), A is the total pore surface area in unit volume of solid material. J_M is now the "molecular" flux imediately below the pore surfaces. As has been suggested elsewhere,¹

 $(P)^{\frac{1}{2}}/, \quad d\sigma \quad \sigma (P)$

$$A \propto \left(\frac{1}{\rho}\right) / l$$
 and $\frac{d\sigma}{dx} \propto -\frac{\sigma}{l} \left(\frac{1}{\rho}\right)$

where l is the pore separation. Combining these relationships with Equations (2) and (3) results in

$$\frac{1}{V_s}\frac{\mathrm{d}V}{\mathrm{d}t} = -Z\frac{\sigma}{l^2}\frac{D_M\Omega_s}{kT}\left(\frac{P}{\rho}\right)^3 \qquad . \qquad (4)$$

This equation is identical in form with Equation (1), but with the advantage of a properly-defined diffusion coefficient.

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Equation (4) has little in common with, and is in no way related to, any earlier theory of pressure-sintering.³ At present it is probably best regarded as a semiempirical equation, although it is hoped to present a detailed analysis of its theoretical basis in a later publication.

2.2 The Integrated Form of the Equation

The results obtained in previously-reported experiments¹ were plotted as -dV/dt versus $(P/\varphi)^3$, which necessitated measuring gradients on a graph of pellet length versus time. This plotting process was lengthy and liable to error, and the gradients of densification plots could be compared only after the solid volume V_s of each pellet had been determined. The integrated form of Equation (4), derived below, provides a much simpler method of plotting experimental data.

Equation (4) may be rewritten

$$\frac{\mathrm{d}}{\mathrm{d}t}(1/\rho) = -Z \frac{\sigma}{l^2} \frac{D_M \Omega_s}{kT} \left(\frac{1}{\rho} - 1\right)^{\frac{\alpha}{2}}$$

so that

or

$$\frac{(1-1)^{-3}}{d}\left(\frac{1}{\rho}\right) = -\frac{Z\sigma}{l^2}\frac{D_M\Omega_s}{kT}\int dt$$

$$\left(\frac{\rho}{P}\right)^{\frac{3}{4}} = \frac{2Z}{3l^2} \frac{D_M \Omega_s}{kT} \sigma \ t + \text{constant} \qquad . \tag{5}$$

Thus a plot of $(\rho/P)^3$ versus time will yield a straight line with a gradient equal to two-thirds that of a plot of $(dV/dt)/V_s$ versus $(P/\rho)^3$.

3. APPARATUS

The general arrangement of the pressure-sintering apparatus is shown in Figure 1. The die-and-plunger as-



Schematic diagram of pressure-sintering apparatus.

sembly was arranged vertically within the steel pressingframe and was enclosed within a sintered-alumina vacuum envelope tube. This in turn was encircled by an eightelement molybdenum-in-alumina furnace constructed in two halves, hinged together. When the furnace was opened and the envelope tube was removed, the die assembly was easily accessible. A miniature platinum resistance thermometer, mounted between two of the furnace elements, was coupled through a proportional controller to a saturable reactor wired into the power supply to the furnace. This equipment enabled the temperature to be

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controlled to within one or two degrees centigrade of the set value.

The load was applied to the upper plunger using a 7:1 lever. This arrangement was preferred to the more customary hydraulic systems because the applied pressure could be calculated accurately and would remain essentially constant during the entire course of a pressing experiment. The displacement of the upper plunger could be measured at any time during pressing using a sensitive dial gauge mounted at the top of the steel frame: changes of displacement as little as one micron could be detected.

The die and plunger assembly (Figure 2) were made of



graphite (grade EY 110, Morganite Carbon Ltd, London S.W.11). The die body, 13 cm long and 2.5 cm O.D., was furnished with a 9.5 mm diameter bore through its lower half, closed at the bottom by a plug, and a 15 mm diameter bore through its upper half to act as an alignment guide for the plunger. The plunger was shaped as shown in Figure 2, with dimensions such that its upper part (15 mm diameter) engaged the die body before its tip entered the 9.5 mm bore. A recess was drilled in the die wall just below the position of the pressed compact, to accommodate the bead of the Pt-20%Rh/Pt-40%Rh thermocouple used to measure the die temperature.

When in position within the apparatus the die-andplunger assembly was stacked with pyrolytic graphite spacers above and below (the total thickness of pyrolytic graphite at each end being 4 cm) to reduce loss of heat from the die by conduction. The stacked assembly stood upon a tubular alumina anvil and pressure was transmitted to the upper plunger by a 12 mm diameter alumina push rod, passing through an O-ring piston seal at the upper end of the vacuum envelope tube.

4. EXPERIMENTAL PROCEDURE

The alumina powder nominal particle size $0.3 \,\mu\text{m}$. (Linde A, Union Carbide Ltd, London W.1.) was first weighed out (about 0.9 g, sufficient to produce a pellet about 3 mm thick after densification) and poured into the die body. The die plunger was then placed loosely in position and the whole pressing assembly was placed within the apparatus. The envelope system was then evacuated (ultimate pressure less than 10^{-2} torr) and the furnace temperature was raised to about 350 °C. After a to the 5000 lb particle final p least of equilib the rel final p plun ze the ren I-min. but at decrea-At tl the fu pressec was m density absolu of sing time t density measu to obt throug then F plots v indica being

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At the end of the experiment the load was removed and the furnace was switched off. Having cooled, the pressed pellet was removed from the die and its thickness was measured with a precision micrometer. The pellet density was then determined by weighing in air and in absolute alcohol, the density of a high-quality specimen of single-crystal alumina being determined at the same time to act as a calibration. The final thickness and density of the pellet could be combined with the periodic measurements of plunger displacement during pressing, to obtain a series of pellet densities at regular intervals throughout the experiment. The data so obtained were then plotted on a graph of $(\rho/P)^3$ versus time. These plots were always straight lines for most of their length, indicating that the porosity factor in Equation (4) was being obeyed.

5. EFFECT ON DENSIFICATION OF CHANGES IN APPLIED PRESSURE

Equation (4) predicts that the shrinkage rate of a compact during pressure-sintering should be proportional to the applied stress, but it is difficult to test this prediction by comparing the shrinkage rates of different compacts to which different pressures are applied. This is because small differences in mean pore separation (which markedly affect shrinkage rates) arise amongst compacts even when great care is taken to reproduce the experimental conditions exactly, and it is difficult to allow for the effect because of the difficulty of obtaining accurate values of pore separation. For this reason the pressure-dependence of shrinkage rate is best determined by changing the pressure applied to a particular compact at some time during the experiment.

Experiments were attempted in which the initial applied pressure was 5000 lb.in-2, which was then reduced to lower values as the experiment progressed. The results were confusing, because the shrinkage rate tended to fall much more rapidly than expected for some hours after the load had been reduced. The reason was not clear; possibly some grain growth occurred which had been inhibited under the higher stress. Whatever the reason, it was clear that stress-dependence comparisons could best be made in experiments in which the applied load was initially low, and then increased in stages. A further difficulty was the discovery that an increase of pressure applied to a compact with a relative density lower than about 0.9 resulted in an unexpectedly large increase in shrinkage rate: possibly the higher pressure imposed caused a change of microstructure through grainboundary sliding or some other effect which did not occur at higher densities.

Figures 3 to 5 show the data obtained in two stressdependence experiments, in which all the measurements were obtained after the compacts had achieved densities greater than $90 \frac{1}{6}$.



Densification data: 1st pressure-dependence experiment.



Shrinkage plot: 1st pressure-dependence experiment.



Densification data: 2nd pressure-dependence experiment.

The first of these experiments was performed at 1300° C. After initial pressing to reach the required starting density, followed by a period of 2 h to allow the apparatus to reach thermal equilibrium, a pressure of 2000 lb.in⁻² was applied. After 2½ h, the pressure was increased to 3000 lb.in⁻², and after a further 3 h to 5000 lb.in⁻². Regular measurements of plunger displacement were, of course, taken in the usual fashion throughout the experiment. A plot of plunger displacement against time displayed a discontinuity each time the load was changed, because of

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changes in the elastic deformation of the pressing assembly, but it was a simple matter to correct the displacement readings to eliminate these discontinuities, and thence to calculate pellet densities throughout the experiment.

Figure 3 shows $(\rho/P)^4$ plotted against time. The plot is seen to consist of three straight-line regions, corresponding to the three applied stresses. The gradients of the three regions are plotted against the applied stress on the smaller graph in Figure 3, and it is seen that a straight line through the origin is obtained, so confirming the relationship predicted in Equation (4). For the purpose of comparing the two methods of plotting data, the same results are plotted as $(dV/dt)/V_s$ versus $(P/\rho)^3$ in Figure 4. Again, the gradients of the three regions vary in the ratio 2:3:5.

A further stress-dependence experiment was conducted at 1400°C, the various applied pressures being 2000, 3000, 4000 and 5000 lb.in⁻². The data are plotted in Figure 5, and again it is seen that the gradient of the plot of $(\rho/P)^{\dagger}$ versus time is proportional to the applied pressure, confirming the prediction of Equation (4).

6. EFFECT ON DENSIFICATION OF VARIATIONS IN MEAN PORE SEPARATION

Equation (4) predicts that the shrinkage rate of a compact during pressure-sintering should be inversely proportional to the square of the mean pore separation. To check this prediction, it was necessary to press a number of samples under the same conditions of temperature and pressure, so that any differences in shrinkage rate amongst the samples would be known to be caused by differences in mean pore separation.

A series of nine pressing experiments was conducted at 1300° C with an applied pressure of 5000 lb.in⁻². Details of all these experiments are set out in Table 1, and

Table 1

	Aubie 1				
Expt No. (cf Fig. 6)	Relative density at termination	Pressing time (h)	$\left \frac{d}{dt} \left(\frac{\rho}{P} \right)^{\frac{3}{4}} \right $	Pore count	
I	0.997	44	1.65	35	
2	0.965	1.75	1.95	55	
3	0.976	3.5	2.15	60	
4	0.954	1.25	2.20	62	
5	0.990	9.5	2.15	48	
6	0.998	68	1.55	31	
7	0.999	56	1.08	18	
8	0.989	26	0.88	18	
9	0.988	20	0.85	21	

the shrinkage data are plotted as $(\rho/P)^{i}$ versus time in Figure 6. It can be seen that a range of gradients was obtained, although the same temperature and pressure were used for all the experiments.

Those plots ending in arrows (Figure 6) were continued to higher densities but, for convenience in plotting, only the first few hours are shown: for instance, a plot of results extending to a relative density of 0.997 would require a $(\rho/P)^{\text{f}}$ axis extending to 48 and a time axis extending to several tens of hours. Occasionally plots



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FIGURE 6 Densification data: 9 experiments at 1300°C, pressure 5000 lb.in-2.

Time (h)

would be divided into two straight-line portions with slightly different gradients: examples are Plots 3 and 6 in Figure 6. Usually the change of gradient occurred at a relative density of about 0.96, and a possible explanation may be that a proportion of the pore population ceases to shrink, resulting in an increase in the effective mean pore separation. The gradients for Plots 3 and 6 (Figure 6) recorded in Table 1 are those of the first parts of the plots.

All nine specimens were sectioned and polished, using 6 μ m and 1 μ m diamond paste on successive lead laps, and examined by optical microscopy. The remaining porosity could be seen clearly when the specimens were examined in reflected light using a × 140 oil immersion objective, when the pores appeared as bright spots of light. Even pores which were too small to be optically resolved, and which were quite invisible under oblique illumination, could be detected in this way: for such pores the bright spots were actually diffraction patterns. Photographs were obtained of the pore pattern below the polished surface of each of the specimens: Figure 7 is an example of the type of photograph obtained.





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FIGURE 7 surface of a pressed specimen (p=0.999)

PRESSURE-SINTERING OF ALUMINA-

The number of pores visible in a fixed area (equivalent to about 50 µm²) of each negative was counted. This number was, in each case, proportional to the number of pores lying within a layer of the specimen equal in thickness to the depth of field of the objective lens, and so was proportional to the pore density. Several pore counts were obtained for each specimen; average values are recorded in the last column of Table 1. If equations (4) and (5) are correct, then the gradient of the plot of $(o/P)^{i}$ versus time should be inversely proportional to the square of the pore separation (at any given temperature and pressure), i.e. the gradient raised to the power $\frac{3}{2}$ should be proportional to the pore density. In Figure 8 the gradients of the plots in Figure 6, raised to the power 3, are plotted against the pore counts obtained from the photomicrographs. The points lie quite closely on a straight line through the origin, thus confirming the pore separation factor in Equation (4).



Correlation between the gradients of the plots in Figure 6 and pore densities.

7. CONCLUSIONS

The experiments described in Sections 5 and 6 confirm that the shrinkage rate of an alumina specimen during the final stage of densification ($\rho \ge 0.89$) is dependent on the applied pressure and on the mean pore separation in the manner predicted by Equation (4). In addition, the fact that straight-line plots of $(\rho/P)^{\dagger}$ against time were obtained indicates that the predicted relationship between shrinkage rate and porosity is also correct.

In most experiments at constant load the gradient of the plot of $(\rho/P)^3$ against time was constant over a range of relative densities from well below 0.89 to about 0.96, indicating that no significant change in grain size or pore geometry was occurring. As has been mentioned, the gradient often decreased at a density of about 0.96, indicating some change in the effective pore geometry, but the experiments reported in Section 6 showed that the pore densities measured from the final compacts could be correlated with the shrinkage rates during the density range 0.90-0.94, which suggests that pores do not vanish altogether during densification, although they become very small before they stop shrinking. The observation that very high densities can be reached provided that sufficient pressing time is allowed suggests that pores do not become isolated from grain boundaries (at the temperatures and pressures used), for this would presumably hinder further shrinkage.

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