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
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25.—The Pressure-sintering of Alumina

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ABSTRACT

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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.

1. INTRODUCTION

In an earlier publication[1] 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

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

where V_s is the volume of solid material, $\mathrm{d}V/\mathrm{d}t$ 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 $(P/\rho)^{\frac{2}{3}}$, 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

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

where $\mathrm{d}\sigma/\mathrm{d}x$ is the stress gradient and D_M is the effective "molecular" diffusion coefficient.

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

or

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

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 $\mathrm{d}V/\mathrm{d}t$ of a pressure-sintered 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]

$$A \propto \left(\frac{P}{\rho}\right)^{\frac{2}{3}}\Big/ l \quad \text{and} \quad \frac{\mathrm{d}\sigma}{\mathrm{d}x} \propto -\frac{\sigma}{l}\left(\frac{P}{\rho}\right)$$

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

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

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

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