26.—Effect of Some Impurities on the Pressure-sintering of Alumina

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ABSTRACT E137/C525

Pressure-sintering experiments are described, from which were obtained activation energies for ionic diffusion in un-doped alumina, and in alumina doped with either magnesia or tantalum pentoxide. The thermodynamics of vacancy formation in alumina have been examined, and six theoretical activation energies for diffusion have been calculated using the three measured values. The calculated activation energies have been correlated with published values for tracer diffusion in alumina. Calculations of diffusion coefficients from the pressure-sintering work show satisfactory agreement with published tracer diffusion coefficients.

Effet de quelques impuretés sur le frittage sous pression de l'alumine

L'auteur décrit des expériences de frittage sous pression qui ont conduit à des énergies d'activation pour la diffusion ionique dans l'alumine non dopée et dans l'alumine dopée soit avec de la magnésie, soit avec du pentoxyde de tantale. Les aspets thermodynamiques de la formation de vacances dans l'alumine sont examinés et six énergies d'activation théoriques sont calculées pour la diffusion à l'aide des trois valeurs mesurées. Les énergies d'activation calculées sont comparées aux valeurs publiées pour la diffusion de traceurs dans l'alumine. Les calculs de coefficients de diffusion, basés sur le frittage sous pression effectué en pratique, fournissent des résultats qui concordent de façon satisfaisante avec les coefficients publiés pour la diffusion des traceurs.

Einflüße einiger Verunreinigungen auf das Drucksintern von Aluminiumoxid

Experimente über Drucksinterung werden beschrieben, aus denen die Aktivierungsenergien der Ionendiffusion in undotiertem Aluminiumoxid und in solchem, das mit Magnesiumoxid oder Tantalpentoxid dotiert war, ermittelt wurden. Die Thermodynamik der Leerstellenbildung in Aluminiumoxid wurde untersucht und es ließen sich sechs theoretische Diffusionsaktivierungsenergien unter Benutzung der drei gemessenen Werte berechnen. Die berechneten Aktivierungsenergien wurden mit Literaturwerten der Tracer-Diffusion in Aluminiumoxid in Beziehung gesetzt. Die Berechnung der Diffusionskoeffizienten aus den Drucksinter-Versuchen zeigen befriedigende Übereinstimmung mit den aus der Literatur bekannten Tracer-Diffusionskoeffizienten.

1. INTRODUCTION

It has been shown elsewhere[1] that the shrinkage of an alumina polycrystal during the final stages of pressure-sintering is well described by the equation

$$\frac{1}{V_s}\frac{dV}{dt} = -Z\frac{\sigma}{l^2}\frac{D_M\Omega_s}{kT}\left(\frac{P}{\rho}\right)^{\frac{1}{3}} \quad . \quad . \quad . \quad (1)$$

or

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

where V_s is the volume of solid material, dV/dt is the rate of volume change of the compact, σ is the applied pressure, l is the mean pore separation, D_M is the effective "molecular" diffusion coefficient, Ω_s is the volume of a "molecule" of the crystal, k is Boltzmann's constant, T is the absolute temperature, P is the fractional porosity and ρ the relative density ($P = 1-\rho$). Z is a constant of proportionality, which must be evaluated before the equation may be used to determine diffusion coefficients. The effective "molecular" diffusion coefficient is defined by the relationships:[2]

$$D_M = -(D_T)_a\left(\frac{1+z_a-z_c}{f_a z_c}\right), \text{ if } (D_T)_c \gg (D_T)_a \quad (3a)$$

or

$$D_M = (D_T)_c\left(\frac{1+z_a-z_c}{f_c z_a}\right), \text{ if } (D_T)_a \gg (D_T)_c \quad . \quad (3b)$$

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, and f is the jump correlation factor. D_M can be expressed as $D_0 \exp(-Q/RT)$, where D_0 is a constant, Q is an activation energy, and R is the gas constant per gram molecule. The present paper describes experiments undertaken to determine the values of Q and D_0, firstly in compacts of undoped alumina, and then in compacts doped with impurities chosen for their effect on the vacancy equilibrium in alumina.

2. APPARATUS

The pressure-sintering apparatus has been fully described elsewhere.[1] The alumina powder (Linde A nominal particle size 0·3 μm) was pressed in a graphite die with a 9·5 mm bore, enclosed within a sintered-alumina vacuum envelope tube. This in turn was surrounded by a multi-element molybdenum-in-alumina furnace, the temperature of which could be controlled to within one or two degrees centigrade of the set value by

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