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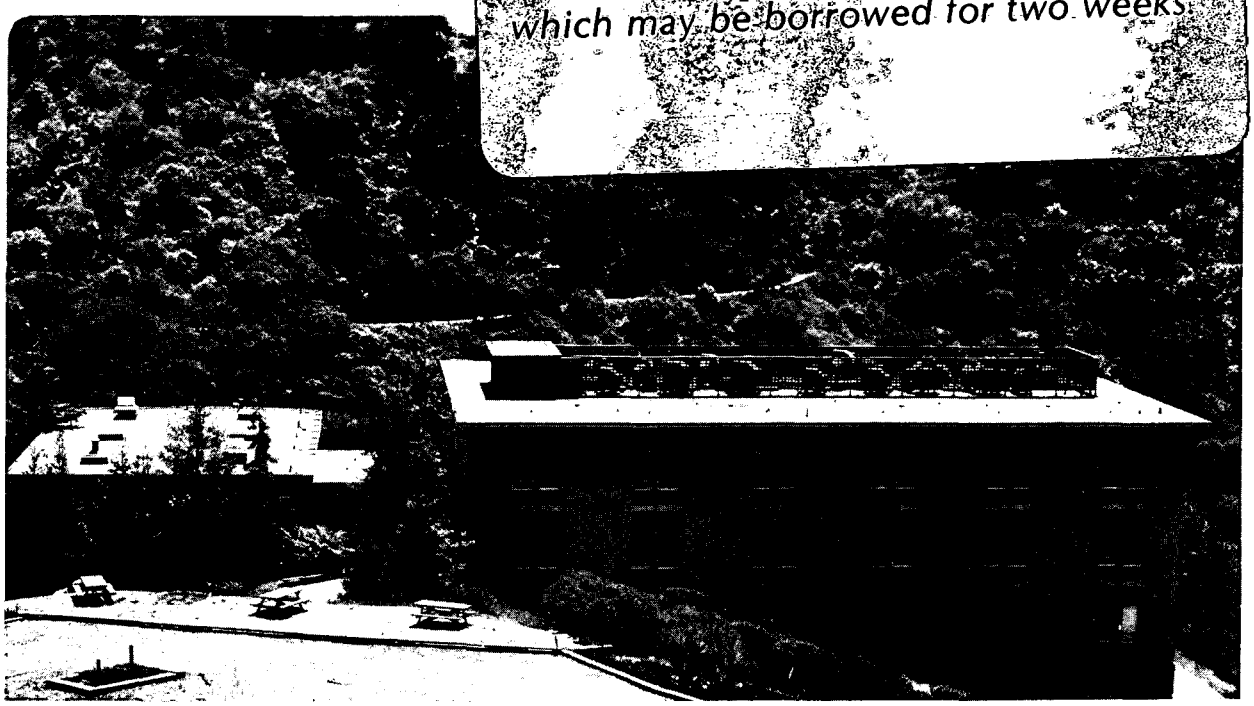

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PORE SHRINKAGE AND SINTERING STRESS

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The criterion for the stability of a large pore in a fine pore matrix is reconsidered, taking into account the pressure exerted by the densifying matrix. The result indicates that progressively larger pores can shrink, even if grain growth is minimal or absent.

When ceramic powders are formed into green bodies, large pores may be produced as the result of imperfect processing. These large pores, as well as the agglomerates, are an important impediment to densification. [1] Whether or not pores can shrink in powder compacts has been considered for some time in thermodynamic terms.[2,3] In this consideration the balance between disappearing pore surface area and appearing grain boundary area leads to a criterion that precribes the maximum coordination number of grains around a pore to still permit pore shrinkage. However, when a large pore is present in a fine pore matrix, the matrix will still be attempting to shrink when the large pore is in a condition where its local geometrical changes would cause it to be invariant. In such a situation, the pore would behave as an undeformable particle, its surface being held by the force balance at the grain junctions, and the shrinking matrix would exert a compressive stress on stress on it. The complete energy balance for the pore stability of a large pore in a fine pore matrix then must include a term of the form

P.dV, where P is the "sintering stress" and V is the volume of the large pore.

A large pore is considered in a matrix composed of fine grains and fine pores, as shown in Fig. 1. When this matrix attempts to densify, around the invariant pore, it will exert a compressive stress on the pore surface, equal to $P = \alpha\gamma_s\varepsilon\bar{H}$, independent of sintering mechanisms or kinetics.[4,5] α is a proportionality factor taken to be 1, γ_s is the surface energy, ε is the porosity, and $\bar{H}$ is the mean curvature of the pore surface in the matrix. The existence of the sintering stress was first demonstrated by Dawihl and Nix[6] and a simplified expression for it was mentioned by Youssef and Eudir.[7] A more general expression was given by Gregg and Rhines, who measured the evolution of the sintering "force" for copper powder compacts.[4] It is clear from the work of Gregg and Rhines that P is inversely proportional to the scale of the system, i.e. to the particle size, D. Thus one might also write:

$$P = \beta\,\gamma_s\varepsilon\,\bar{h}/D \qquad \text{Eq. 1}$$

where β is a proportionality factor, and $\bar{h}$ is the mean pore curvature of the matrix normalized to the particle diameter. The work of Gregg and Rhines also shows that, at constant D, $\bar{h}$ increases significantly with decreasing porosity, up to about 90 or 95% density. The work performed by this sintering pressure must be included in the energy balance that gives the criterion for pore stability.

For a pore that is large compared to the grain size, D, the pore surface area will be approximately equal to $4\pi r^2$, where r is the radius of the large pore. The number of grains around the large pore is $16r^2/D^2$. If

it is assumed that the average coordination number of the grains in the pore surface is 6 then, for an incremental pore shrinkage or and infinitesimal pore radius decrease dr, the following energy balance is obtained at equilibrium:

$$dE/dr \cong -8\pi\gamma_s r + 24\ \gamma_B\ r^2\ /D\ -4\pi P r^2 = 0 \qquad \text{Eq. 2}$$

where γ_B is the grain boundary energy. This leads to a criterion for shrinkage of the following form:

$$r/D < 2\pi\ \gamma_s/\gamma_B\ \{\ 6-\ (\pi PD/\gamma_B)\ \} \qquad \text{Eq. 3}$$

or, in view of Eq. 1:

$$d/D < 4\pi\ \gamma_s/\gamma_B\ \{\ 6-\ (\pi\beta\varepsilon\bar{h}\gamma_s/\gamma_B)\ \} \qquad \text{Eq. 4}$$

where d= 2r, the grain diameter. The qualitative evolution of the sintering pressure follows from the measurements of Gregg and Rhines. This criterion expresses only whether or not a pore will shrink with respect to some fixed reference frame; for complete pore shrinkage, the usual requirement remains that the pore would need to shrink in the absence of a sintering pressure, when the matrix approaches full density. A pore that can shrink according to the criterion expressed by Eqn. 4 would do so to the degree that the surrounding matrix densifies. This could lead the pore to a size that permits complete shrinkage when the compact approaches full density where the sintering pressure becomes insignificant. Thus, the pore shrinkage domain described by Eqn. 4 may be divided into two fields: one for partial shrinkage, and one for complete shrinkage. The criterion for complete shrinkage is:

$$d/D < 2\pi\gamma_s/3\ (1-\varepsilon)\ \gamma_B \qquad \text{Eq. 5}$$

where ε is the porosity.

The pore shrinkage criteria expressed by Eqns. 4 and 5 have been sketched in Fig. 2.

It is thus clear that the microstructural evolution of a densifying compact that contains a bimodal distribution of large and small pores, will first exhibit partial or total shrinking of smaller pores and later of larger pores. The suggestion that grain growth is required before shrinkage of larger pores can occur[8] is therefore too restrictive: the same result follows from the evolution of the sintering pressure, even if grain growth is minimal or absent. If grain growth does occur, then Eqn. 4 also shows that proportionately larger pores can shrink. This evolution of powder compact microstructures is very clear in the work of Greskovich and Lay [9] on densification of Mg doped alumina.

An estimate of the range of sizes of the large pores that possibly can shrink in the absence of grain growth may be made with the data obtained by Gregg and Rhines on copper powder compacts.[4] Insertion of the maximum values of P would indicate that the denominator in Eq. 2 could vary from an initial maximum of 6 to a minimum of 1.4 towards 95% density.

Sintering stresses have not yet been measures for ceramic compacts; such efforts are currently underway in our laboratory.

It should be noted that Eqns. 3 or 4 give a shrinkage criteria for pores that are large compared to the particle size. For small pores, one must consider the shape of the polyhedra in detail. For the tetrahedral packing, encountered in perfect green compacts of equally sized particles, the dihedral angle should not be smaller than about 70 degrees to permit pore shrinkage, as is evident from Ref. 2.

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Figure Captions

Fig. 1 Schematic geometry of a large invariant pore of radius r in a fine pore matrix. The matrix exerts the sintering pressure P during densification if the large pore is invariant.

Fig. 2 Qualitative evolution of the criterion for stability of a large pore in a compact.

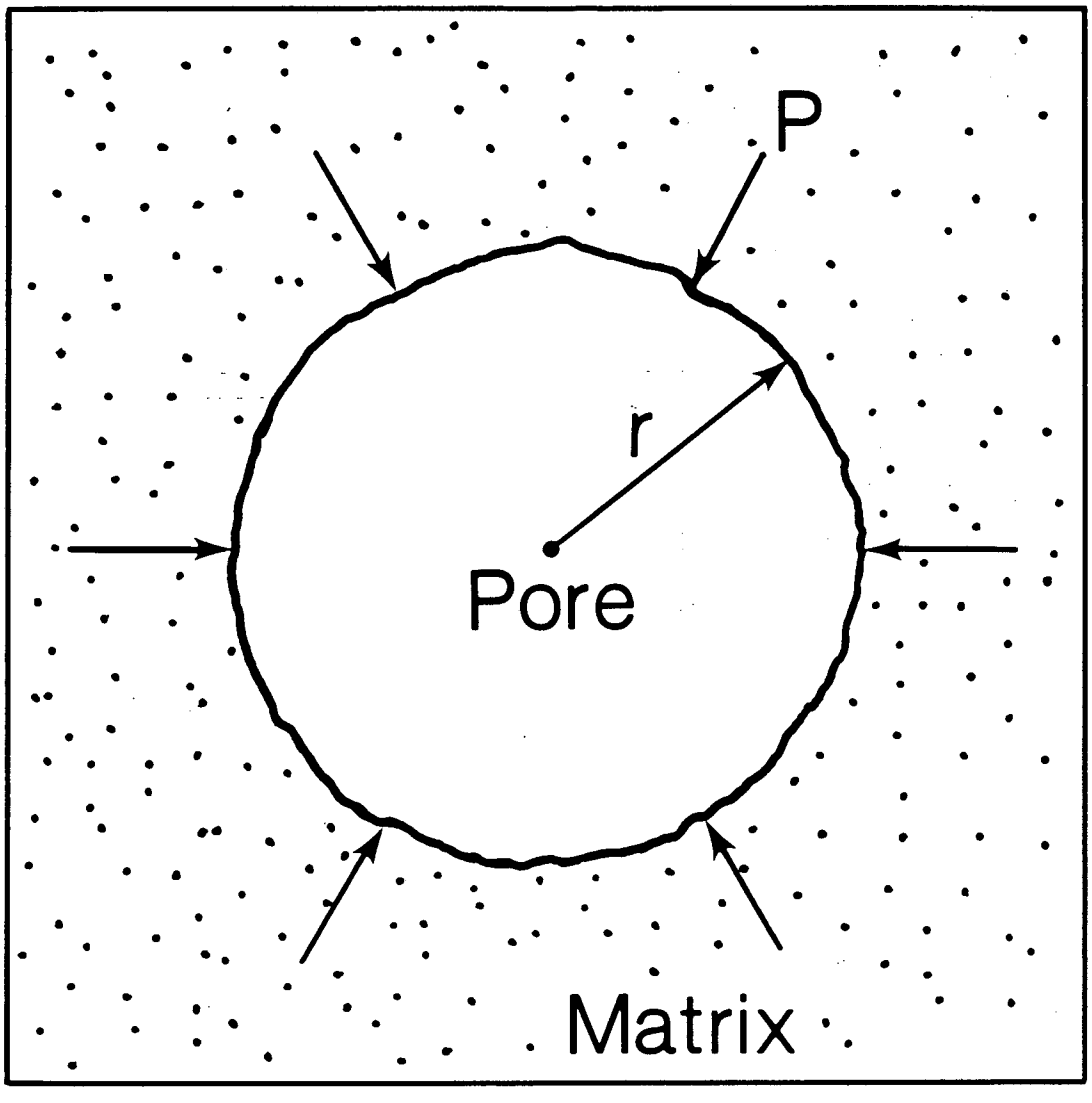

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Fig. 1

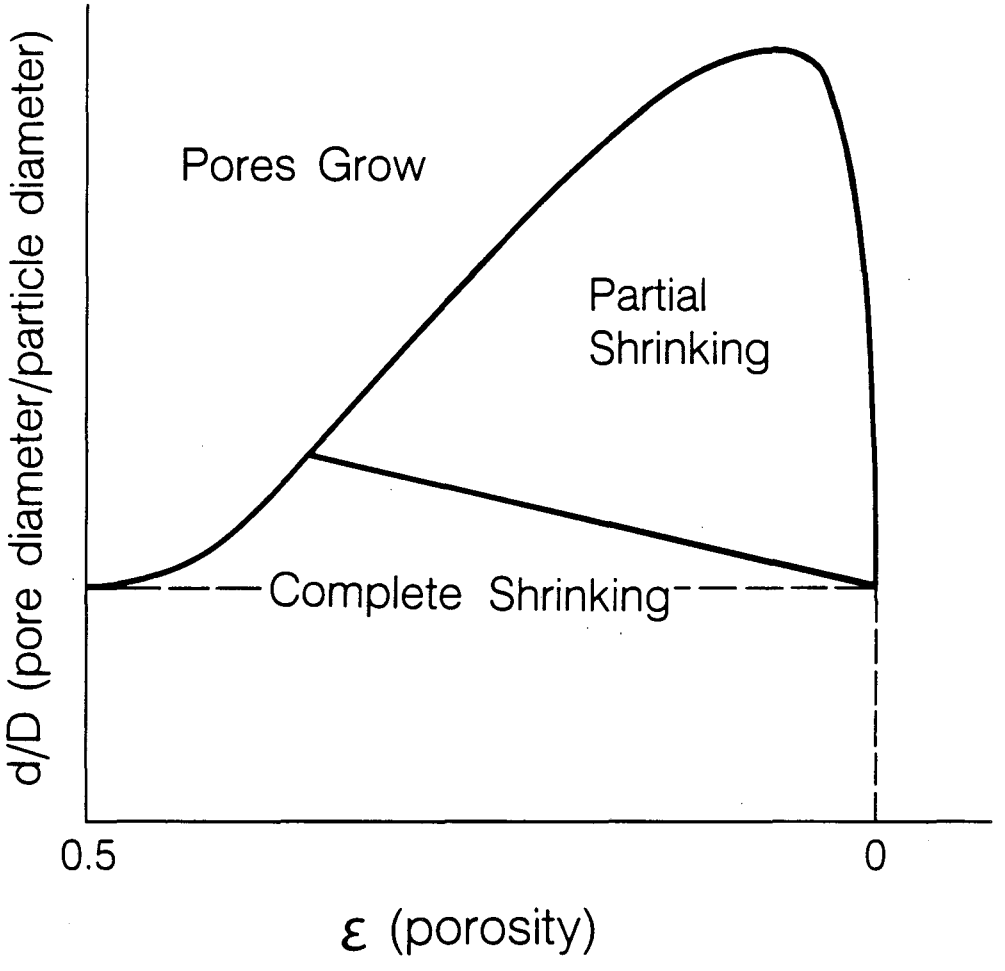

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Fig. 2

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