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SINTERING STRESS OF HOMOGENEOUS AND HETEROGENEOUS POWDER COMPACTS

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ABSTRACT

The thermodynamic meaning of the sintering stress is considered for some simple 2-dimensional porous bodies. The sintering stress acts as an effective mean grainboundary stress and can thus be meaningfully combined with applied stresses. The sintering stress can, in general, not be described in rigorous thermodynamic terms, especially for heterogeneous compacts. Simplifications do allow, however, to assess the effects of some microstructural heterogeneities, including the presence of large pores or of dispersed second phases, on the sintering stress.

INTRODUCTION

In recent considerations of the sintering of porous bodies¹⁻⁴ expressions for the densification rates have been used and experimentally verified, introducing a sintering stress,¹ sintering pressure² or sintering potential⁴ as an experimentally accessible quantity. The meaning of these quantities is examined in somewhat more detail, using a simplified, 2-dimensional model. While, in some aspects, closely related to the earlier work of Cannon,^{3,5} the treatment brings out additional complexities in defining the

driving forces for sintering and considers heterogeneous systems.

Model Considerations

Following Johnson⁶ and limiting the treatment to exclusive grainboundary transport, one has, see Fig. 1

$$j_b = -\frac{D_b \delta_b}{\Omega k T} \nabla \mu \quad (1)$$

for each grainboundary intersecting the pore. The quasi steady-state further requires that

$$\nabla \cdot j_b = B \quad (2)$$

where B, the amount of matter removed from the grainboundary per unit area and per unit time, is constant. Transport in an interface can readily be written in terms of stress, since

$$\nabla \sigma = \nabla \mu / \Omega \quad (3)$$

where σ is the local normal stress and μ is the chemical potential of the atom.

The solution to the stress or chemical potential distribution in the boundary is of the form

$$\sigma = \alpha X^2 + \beta \quad (4)$$

α and β follow from the boundary conditions and the force balance at the grainboundary. Thus, if an effective stress, σ_{eff} , is exerted on the boundary as well:

$$\int_{X=0}^{X_0} \sigma dX = \gamma_s \sin \left(\frac{\psi}{2} \right) + \sigma_{\text{eff}} X_0 \quad (5)$$

with

$$\nabla \sigma = 0 \text{ at } X=0 \quad (6)$$

and

$$\sigma(X_0) = \Delta\sigma_0$$

when

$$\Delta\sigma_0 = \Delta\mu_0/\Omega \quad (7)$$

where $\Delta\mu_0$ is the chemical potential difference between a grainboundary atom and an atom at $X = X_0$.

It is customary, in a two-dimensional geometry, to put $\Delta\mu_0 = 2\gamma_s/r$, where r is the radius of curvature of the pore in contact with the grainboundary, Fig. 1b. Actually, the expression for $\Delta\mu_0$ is more complex, as pointed out by Cannon.⁵ The cell shown in Fig. 1 contains a pore and is space filling. In the present case, the cell size is taken to be the grainsize. The choice of this geometry is a simplification and assumes the grainboundaries, connecting the pores, to be of equal length. In general this can not be the case.

For now:

$$\Delta\mu_0 \frac{dv_b}{\Omega} = \gamma_s ds + \gamma_b db \quad (8)$$

where

s = pore surface area

b = grain boundary area

The change in pore volume, dv_p is related to the volume of atoms removed from the grainboundary, dv_b , by

$$dv_p = -\phi dv_b \quad (9)$$

where ϕ is the ratio of the grain boundary area for the grain if the boundaries were to contain no pores, to the actual grainboundary area:

$$\phi = A_{\text{grain}}/A_{\text{grainboundary}} \quad (10)$$

The external volume change, dV of the cell is thus:

$$dV = dv_p = -\phi dv_b \quad (11)$$

ϕ is analogous to the stress intensification factor described by Beere.^{10,11} Thus, dV is larger than the atomic volume Ω if $\Delta\mu_0$ is to correspond to the chemical potential per atom in Eqn. 8.

The pore surface area, s , and the pore volume, v_p are related by

$$s = g_1 R \quad (12)$$

$$v_p = g_2 R^2 \quad (13)$$

where R is a pore dimension as shown in Fig. 1a (not necessarily the radius of curvature, r , Fig. 1b). Eqns 12 and 13 will hold unless the pores are fractal. Also:

$$ds = g_1 dR + R dg_1 \quad (14)$$

and

$$dv_p = 2g_2 R dR + R^2 dg_2 \approx 2g_2 R dR \quad (15)$$

The cell volume, V , for Fig. 1 is in two dimensions:

$$V = g_4 G^2 \quad (16)$$

so that also

$$dV = 2g_4 G dG + G^2 dg_4 \approx 2g_4 G dG \quad (17)$$

For simplicity, it will be assumed that the shape factors, g_i , remain constant, although this is not exact. The error should be minor, unless dramatic topological changes occur in small density intervals.

For the boundary area, b , one may also write, Fig. 1:

$$b = A_G - A_P \quad (18)$$

where A_G is the total grainboundary area, disregarding the presence of the pore, and A_G accounts for the amount of grainboundary area eliminated by the pore. When the pore

is small compared to the grain size A_P can be expressed as Ng_3R , where N is the pore coordination number. When the pore is large compared to the grain size, A_P should be proportional to R^2/G^2 . Staying with the geometry of Figure 1, for which the pore is small compared to the grain size one has: the

$$db \approx d(A_G) - Ng_3dR \quad (19)$$

where N , is considered fixed. In general, the relation of b to G and R will be more complex since a space filling cell geometry does not usually exists for which all boundaries in the cell can be of equal length. Combination of Eqns. 11-19 finally leads to

$$\Delta\mu_o = -\Omega\phi \left[\frac{\gamma_s}{R} \left(\frac{g_1}{2g_2} - \frac{\gamma_b}{\gamma_s} \frac{g_3}{g_2} N \right) + g_5 \frac{\gamma_b}{G} \right] \quad (20)$$

since

$$d(A_G)/dV = g_5/G$$

where g_5 is on the order of 1; eg., for spheres, $g_5 = 1$, (not 2, since a grainboundary is shared between two adjacent grains) while for regular truncated octahedra $g_4 \approx 0.8$. If, in this 2-D case $N = 4$, one expects $g_1 = \sqrt{2}/2$, $g_2 = 2$, $g_3 = 1$. Equilibrium, if the term in $1/G$ is ignored, is then reached for $\gamma_b/\gamma_s = \sqrt{2}/2$, i.e. $\psi = 90^\circ$, as is expected. If the term in $1/G$ is not ignored, then equilibrium would be reached for ψ somewhat smaller than 90° , leading to slightly negatively curved pore surfaces, as pointed out by Cannon.⁵

In general, one would expect

$$\Delta\mu_o = -\Omega\phi \left[\frac{\gamma_s}{R} \left(f_1 - N \frac{\gamma_b}{\gamma_s} f_2 \right) + g_5 \frac{\gamma_b}{G} \right] \quad (21)$$

where, for the simple geometry shown in Fig. 1:

$$f_1 = g_1/2g_2 \quad (22)$$

$$f_2 = g_3/g_2 \quad (23)$$

It is clear that $\Delta\mu_o$ will be difficult to derive rigorously, even if extensive geometrical information exists on the sample microstructure and its evolution.

Combination of Eqns. 1-7 leads to:

$$\dot{\epsilon}_p = \frac{-12D_b\delta_b}{kT} \frac{1}{X_o^2} \frac{1}{G} \left(\frac{\Delta\mu_o}{\Omega} - \frac{\gamma_s}{X_o} \sin\left(\frac{\psi}{2}\right) + \sigma_{\text{eff}} \right) \quad (24)$$

A relationship between X_o and G can be established involving the stress intensification factor, ϕ .^{1,10-11} One can write for ϕ :

$$\phi = \frac{N\alpha_1 G^2}{N\beta_1 X_o^2} \quad (25)$$

where X_o is the mean grain facet diameter and α_1 and β_1 are shape factors. N is the number of facets per grain and is equal to the grain coordination number. This expression was used earlier¹ with the assumption that $\alpha_1 = \beta_1$ which can be a fair approximation. If the grain shape remains constant during the intermediate stage of sintering then α_1 and β_1 are constant as well. Eqn. 24 can thus be written as

$$\dot{\epsilon}_p = -\frac{K}{G^m} \Sigma \phi^{(m-1)/2} \quad (26)$$

where m is a transport path dependent constant and where

$$\Sigma = -\phi \left[\frac{\gamma_s}{R} \left(f_1 - N \frac{\gamma_b}{\gamma_s} f_2 \right) + g_4 \frac{\gamma_b}{G} \right] - \frac{\gamma_s}{X_o} \sin\left(\frac{\psi}{2}\right) + \sigma_{\text{eff}} \quad (27)$$

or

$$\Sigma = \Sigma_o + \sigma_{\text{eff}} \quad (28)$$

Σ and Σ_o both have dimensions of stress. The creep-sintering experiments^{1,7} make Σ an experimentally measurable parameter. If an externally applied hydrostatic stress, σ_a^h , is included, exerting the effective mean stress

$$\sigma_{\text{eff}} = \phi \sigma_a^h \quad (29)$$

on the grain boundaries, then the total sintering stress, Σ becomes

$$\Sigma = \Sigma_o + \sigma_a \phi \quad (30)$$

The quantity Σ_o/ϕ can thus be considered as an equivalent, externally applied stress leading to the same densification rate as caused by surface tension, at identical geometry, and is legitimately termed the "sintering stress". The term $\gamma_s \sin(\psi/2)/X_o$ is sometimes neglected since the error is small when X_o is large compared to the pore curvature. This would imply that the mean stress on the boundary, in the absence of an applied stress, is zero. The stress gradient, and thus the local stress, caused by $\Delta\mu_o$, remains a physically measurable entity. The sintering stress need not necessarily be isotropic. Microstructural anisotropy, such as described by Exner⁷ can lead to heterogeneous shrinkage, so that shear deformation will accompany densification, even if no load is applied. For uniaxial loading the relationship between the applied stress and the effective grainboundary stress should also involve a stress intensification factor as used in Eqn. 29. However, since stress redistributions occur in uniaxial creep, as for diffusion controlled grainboundary sliding, one cannot expect these intensification factors to be completely equivalent. This difficulty is, at present, ignored and the two factors will be assumed to be equal. A more detailed study of the exact expression for the stress intensification factor in uniaxial creep should shed further light on this issue. The uniaxial creep rate, $\dot{\epsilon}_c$, may then be expressed in a similar form as the linear densification strain rate, Eqn. 26:

$$\dot{\epsilon}_c = -\frac{K}{G_m} \sigma_a \phi^{(m+1)/2} \quad (31)$$

Bimodal Pore Distributions

For more complex microstructures, as for example bimodal pore distributions, the procedure outlined here is not straightforward. In such a case, a sintering stress, Σ_o/ϕ , and an applied stress $\sigma_a = \Sigma_o/\phi$ lead to a different mass distribution on a microscopic

scale. The applied stress produces a symmetrical flow of matter out of the grainboundaries into the large and small pores, while the asymmetrical boundary conditions for the sintering stress lead to preferential filling of the small pores. The instantaneous relation between the creep rate and the densification rates is, however, not affected. It should also be pointed out that in a practical measurement of Σ_o , ie. a creep-sintering experiment,^{1,9} the applied stress should be small so that creep-strain induced microstructural anisotropies are minimal and constant volume creep prevails. This usually requires the applied stress to be less than $1/5$ of Σ_o/ϕ .

It is useful to introduce some simplifications to examine how the sintering stress could be expected to relate to structure for compacts containing a bimodal pore distribution. For the bimodal pore case shown in Fig. 2, it will be assumed that the chemical potential difference for atoms on the surface of the large and the small pores can be represented by expressions similar to Eqn. 21, in which the terms in $1/G$, may be neglected. Thus:

$$\Delta\mu_o = -\Omega\phi\frac{\gamma_s}{R_s}\left(f_1 - 2\frac{\gamma_b}{\gamma_s}f_2\right) \quad (32)$$

$$\Delta\mu_L = -\Omega\phi\frac{\gamma_s}{R_L}\left(f_3 - N\frac{\gamma_b}{\gamma_s}f_4\right) \quad (33)$$

When a quasi steady-state prevails, matter should be removed uniformly from all boundaries. This will require the generation of a compressive stress on the segment X_1 compensated by a tensile stress on the load bearing boundaries, compared to their unconstrained state. For the geometry shown, this leads immediately to

$$\Delta\mu = \Delta\mu_o - \Delta\mu_L = \left(\sigma_c + \sigma_t\right)\Omega \quad (34)$$

where σ_t and σ_c are the absolute values of the effective stresses on the boundaries.

The force balance requires that

$$\sigma_t n = 2\sigma_c \quad (35)$$

where n is the number of boundary segments of length S_1 in the cell shown in Fig. 2.

If the large pore has a high grain coordination number, then it will be approximately spherical, so that one might write:

$$\phi = \phi_m / (1 - P_L) \quad (36)$$

where P_L = volume fraction of the large pores, and where the stress intensification factor for the fine-pore matrix, ϕ_m , is

$$\phi_m = \exp(a(P - P_L)) \quad (37)$$

The total sintering stress, Σ , when referred to the sintering stress, Σ_o , of the unconstrained fine pore matrix and when it is assumed that the large pores are inactive so that $\Delta\mu_L = 0$, then becomes

$$\Sigma = \Sigma_o (1 - \sigma_t / \Sigma_o) \quad (38)$$

where

$$\sigma_t / \Sigma_o = 1 / \phi (1 + \frac{n}{2}) = (1 - P_L) / (1 + \frac{n}{2}) \exp(a(P - P_L)) \quad (39)$$

and $n \approx D/G$ = the ratio of the large-pore spacing over the grain size. Eqn. 41 describes the sintering stress for a bimodal pore system where the coordination of the large pores, N , is such that

$$N = \gamma_s f_3 / \gamma_b f_4 \quad (40)$$

An estimate of Σ/Σ_o for $D/G = 10$ and $P_L = 0.3$, with $\Delta\mu_L = 0$ would give $1 > \Sigma/\Sigma_o > \approx 0.9$. Thus, it would appear that the presence of even a sizeable volume fraction of large, inactive pores does not affect the sintering stress significantly except for the effect on ϕ . The effect of a bimodal porosity on ϕ might be assessed approximately if

the densification process can be described by two separable branches: a first branch in which only the small pores are active, and the large ones remain essentially inactive; and a second branch in which a now uniform matrix densifies. This second branch could be reached either by elimination of all small pores, or by pore development in the matrix leading to pores approaching the size of the inactive large pores so that homogeneity results. This latter case was recently found for heterogenous MgO densification.¹² While the large pores are inactive one might describe the overall factor ϕ by:

$$\phi_a = \frac{1}{(1-P_L)} \phi_m = \frac{1}{(1-P_L)} \exp(a_a(P-P_L)) \quad (41)$$

where P_L is the inactive volume fraction of large pores and ϕ_m is the stress intensification factor belonging to the small-pore homogeneous part of the matrix. After the sample has become homogeneous, either through small-pore elimination or through other homogenization processes, one should have

$$\phi_b = \exp(a_b P) \quad (42)$$

Thus, significant changes in ϕ , observable as creep rate or densification rate anomalies, could occur for compacts in which the microstructure evolves as considered here. Such changes, consistent with the above analysis, have been found for heterogeneous MgO compacts.¹² A schematic representation of the expected evolution of ϕ is shown in Fig. 3. The two branches of ϕ are shown in this figure corresponding to the bimodal case (ϕ_a) at high porosity and the monomodel case at low porosity (ϕ_b). Extrapolation of ϕ_b to $P = 0$ gives $\ln \phi_b = 0$. Extrapolation of ϕ_a to $P = P_L$, ie. $P_m = 0$, should give $\phi_a = 1/(1-P_L)$. Thus, $1/(1-P)$ should intersect ϕ_a at $P = P_L$ as shown. Remarkably good agreement with this analysis was indeed found for the heterogeneous MgO studied recently.¹²

Transport Coefficients and Pore Spacing

Difficulties in interpretation of the data may also arise if some diffusion rate changes would occur that made the transport coefficient, K , time dependent. Time dependence of K could be evaluated by considering the densification of homogeneously evolving compacts starting at different green densities. For such samples, the graingrowth compensated creep should no longer be proportional to $\exp(aP)$. Significant deviation from this relationship would strongly suggest transport rate anomalies, since they would not be attributable to microstructural evolution.

Another factor to be considered in the comparison of creep and densification is the relationship between pore spacing, X_o , and grainsize, G . It is possible that preferential pore elimination or rapid local densification could lead to a pore spacing that is larger than the grain size. Thus, Eqn. 25 should be written as:

$$X_o^2 = \phi^{-1} D^2 \alpha_1 / \beta_1 \quad (43)$$

where D is the pore spacing. One may put

$$D^2 = F G^2 \beta_1 / \alpha_1 \quad (44)$$

where F can be a function of time, density, etc. The creep rate, $\dot{\epsilon}_c$, should then be written as :

$$\dot{\epsilon}_c = -K \sigma_a \phi^{(m+1)/2} F^{m/2} / G^m \quad (45)$$

F can be found from polished cross-sections of the sintered compact at various densities, by determining the ratio of the number of pores, N_p , per the number of grains, N_g , per area. Then:

$$F = N_p / N_g \quad (46)$$

The ratio of the densification strain rate over the creep strain rate

$$\dot{\epsilon}_p / \dot{\epsilon}_c(\sigma_a) = \Sigma / \sigma_a \phi \quad (47)$$

remains, however, unaffected by this. Further, since Eqns. 38 and 39 indicate that the most significant dependence of Σ on microstructural heterogeneity is contained in ϕ , the ratio $\dot{\epsilon}_p \sigma_a / \dot{\epsilon}_c(\sigma_a)$ should be expected to be fairly constant at constant σ_a . This has indeed been observed for a wide variety of compacts studied to date, as is evident from Fig. 4.

Particulate Composites

Stresses arising during densification of particulate composites may also be considered. The evaluation of the accommodation stresses around inert second phase particles starts with an analysis of elastic misfit stresses, and derives the viscoelastic stresses using the correspondence principle and Laplace transformations.^{14,3*} The radial viscoelastic misfit stress, $\sigma(t)$, at an isolated, undeformable particle in an infinite, shrinking matrix can then be described by a convolution integral¹⁴

$$\sigma(t) = 4 \int_0^t \dot{\epsilon}_p(\tau) k(t-\tau) d\tau \quad (48)$$

where $\dot{\epsilon}_p$ = radial strain rate, ie. the linear densification strain rate of the matrix of the composite, and $\sigma(t)$ = radial stress at the particle/matrix interface. $k(t)$ is the relaxation function, ie. the stress response of the matrix to a unit step displacement, $\mathbf{e}_1$. The relaxation function can be obtained from an equivalent spring and dashpot network that properly describes the response of the sintering compact to the displacement $\mathbf{e}_1$. Bordia and Raj² have considered such equivalent networks. Important in the development of the equivalent mechanical network is the distinction between the long-range response of

* In Ref. 3, the elastic solution was directly transformed assuming both the shear modulus, G , and the viscosity, η , to be constant, and time dependences were inserted after transformation. This can lead to some errors in the form of $k(t-\tau)$.

the system, ie. the quasi-steady state densification and creep as expressed by Eqns. 29 and 34, and the strain. Fig. 5a shows the response of a CdO powder compact to a loading and unloading stress step, clearly indicating that the stored anelastic strain has a relaxation time on the order of a few minutes. The quasi-steady state deformation due to the densification or creep is **not** recoverable. Thus, the appropriate equivalent circuit is shown in Fig. 5b. The relevant ^{**} response of this system, $k(t)$ to be used in Eqn. 48 is then:

$$k(t) = G \exp(-t/\tau_2) e_1 \quad (49)$$

where τ_2 is the relaxation time associated with the recoverable strain. G is the shear modulus of the porous compact. Since $\dot{\epsilon}_p$ varies very slowly with time compared to $k(t)$, ie. $\tau_1 \gg \tau_2$, $\dot{\epsilon}_p$ may be put outside the integral in Eqn. 48, leading to a very simple result if G is assumed to be approximately constant. Thus:

$$\sigma(t) = 4G\tau_2\dot{\epsilon}_p(\exp(-t/\tau_2) - 1) \quad (50)$$

For a particulate composite containing a dispersion of an undeformable second phase the densification rate of the matrix may be written as¹⁵

$$\dot{\epsilon}_p = \frac{1}{\eta} \left(\frac{\Sigma_o}{\phi} - \sigma_h \right) \quad (51)$$

where Σ_o/ϕ refers to the *unconstrained* matrix of the composite, and σ_h is the hydrostatic backstress generated by the incompatibilities with the dispersed phase. Also^{2,3}

$$\sigma_h(t) = \sigma(t)f/(1-f) \quad (52)$$

^{**} In both the treatments of Raj et al^{2,17} and of Hsueh et al³, the relaxation times used for $k(t)$ are those of the quasi-steady state creep, instead of those of the recoverable strain. Use of these relaxation times in the treatment presented here would give only a simple viscous stress for $\sigma(t)$, and lead to the erroneous result that this stress would be insignificant. In the work of Refs. 2, 3, and 17 the relaxation parameters of the recoverable strain process were not determined or not available. The apparent agreement with the experimental data of Rahaman and De Jonghe¹⁶ was then reached with an analysis that is inconsistent with the one presented here.

where f is the volume fraction of the second phase. Eqns. 50-52 thus give for the composite, when $t \gg \tau_2$

$$\sigma_h(t) = \frac{\Sigma_o}{\phi} \frac{f}{1-f} / \left(\frac{\eta}{4G\tau_2} + \frac{f}{1-f} \right) \quad (53)$$

and finally

$$\dot{\epsilon}_\rho = \frac{\Sigma_o/\phi}{\eta \left(1 + \frac{4G\tau_2}{\eta} \frac{f}{1-f} \right)} \quad (54)$$

The important variable may thus be expressed as $4G\tau_2/\eta$. Eqn. 54 predicts a very strong dependence on volume fraction of the second phase if $4G\tau_2/\eta$ is much larger than 1. Such is the case for ZnO and for the other ceramic materials examined so far for which data have been shown in Fig. 4. For ZnO^{1,24} the shear modulus, G , is estimated to be about 10 GPa, and η , for the experimental conditions for which the particulate composite of SiC dispersed in ZnO was studied, was about 625 MPa.min at a density of 0.70. With τ_2 about 2 min, $4G\tau_2/\eta$ is about 150. Thus, Eqn. 54 would predict a strong dependence of the matrix densification rate on the volume fraction of the dispersed inert phase. At constant matrix density Eqn. 54 then gives

$$G^m \dot{\epsilon}_\rho \propto \left(1 + \frac{4G\tau_2}{\eta} \right)^{-1} \quad (54)$$

since for $\rho = \text{constant}$ Eqns. 29 and 34 show that η is proportional to G^m , and from Fig. 4 Σ_o/ϕ is nearly constant

A plot of the grain size compensated linear densification rate of the matrix for ZnO/SiC composite studied earlier versus $(1 + (4G\tau_2/\eta)(f/(1-f)))^{-1}$ is shown in Fig. 6. The agreement is excellent.

It is, at present not clear how the anelastic relaxation time, τ_2 , depends on materials

parameters such as density and grain size. The indications from a very limited amount of transient loading experiments^{1,8,9,15} would indicate that τ_2 is not strongly density dependent. This would suggest that the hydrostatic backstress would decrease with respect to Σ_o/ϕ with increasing ρ , since η increases strongly with density; such behavior is consistent with observations.¹⁶ Eqn. 54 implies that the densification of the matrix of a particulate composite may be thought of as that of a same, single phase material at strongly reduced sintering stress. Thus, one should expect that efforts used in improving the densification behavior of single phase ceramics are equally useful for particulate composites. For glasses or for liquid phase containing ceramics, the ratio of the shear modulus over the steady state creep viscosity G/η can be very significantly lower. While the values of the anelastic relaxation time of these systems needs yet to be studied, we do expect that $4G\tau_2/\eta$ will be considerably lower than for the ceramic systems, which would straightforwardly explain the rule of mixtures behavior observed in those cases.²

It should be noted that the analysis is limited to volume fractions of the second phase below 15 - 20%, otherwise the probability of forming particle strings increases strongly, eventually leading to a hard skeleton structure that densifies with great difficulty. For those high volume fractions particle impingement effects, rather than the hydrostatic backstresses, can dominate densification behaviour.

CONCLUSIONS:

The sintering stress for a densifying powder compact can be considered as an equivalent applied, stress Σ_o/ϕ , that would produce the same densification rate for the system, at identical geometry, but with surface tension effects absent. The sintering stress contains a structure insensitive part, and a structure sensitive factor, ϕ . The ratio $\dot{\epsilon}_p/\dot{\epsilon}_c(\sigma_a)$, is found to be nearly constant for a particular system at constant σ_a , but depends on green density and other materials parameters.

For particulate composites with inert spherical inclusions, matrix radial stresses at the particle/matrix interface can be described simply by $\sigma(t) = 4G\tau_2\dot{\epsilon}_p$, where τ_2 is the relaxation time of the stored strain. τ_2 can be determined from the strain response to an applied stress step during densification of the single phase matrix. The analysis then leads to a matrix densification rate $\dot{\epsilon}_p = (\Sigma_o/\phi)/\eta (1 + \frac{4G\tau_2}{\eta} \frac{f}{1-f})$. The important parameter for densification of a particulate composite is thus the ratio of the shear modulus over the creep viscosity, times the relaxation time of the recoverable strain. The measurement of the transient creep response, especially the short time response, is thus an important factor in the study of densification of particulate composites with ceramic or glass matrix.

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FIGURE CAPTIONS:

- Figure 1 a) Space-filling cell for the 2-dimensional sintering problem
 b) Triple junction geometry
- Figure 2 Space-filling cell for a bimodal pore distribution
- Figure 3 Expected branches for the geometrical stress intensification factor ϕ , for a shift from a bimodal to a monomodal pore distribution.
- Figure 4 $\dot{\rho}/3\rho\epsilon_c(\sigma_a)$ versus density for various ceramics and for glass, at a constant $\sigma_a = 0.2$ MPa.
- Figure 5 a) Response of a CdO powder compact to transient loads during sintering, showing a relaxation time at about 2 mins for the recoverable strain, (from Ref. 2).
 b) Equivalent spring dashpot model for the densification - deformation process. G = shear modulus of porous compact; τ_1 = relaxation time of the densification process; τ_2 = relaxation time of the recoverable strain.
- Figure 6 Grainsize corrected matrix densification rate, $\dot{\epsilon}_p G^2/G_0^2$ for a ZnO matrix/SiC composite/data (from Ref. 16) at the indicated matrix densities versus the functions of the volume fractions, f , of SiC. G_0 is the initial grainsize.

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XBL 867-2710

Figure 1

XBL 867-2713

Figure 2

XBL 867-2712

Figure 3

XBL 867-2711

Figure 4

XBL 848-3388

Figure 5a

XBL 8611-4715

Figure 5b

Figure 6

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