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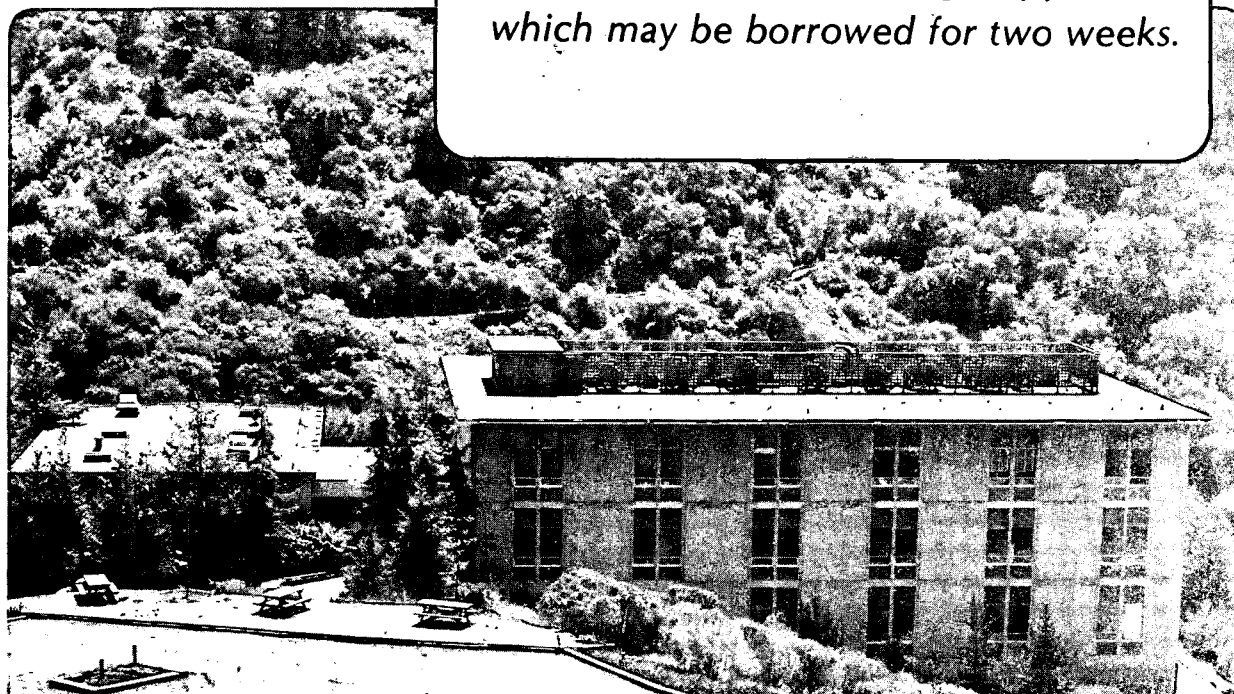
Effect of Rigid Inclusions on Sintering

M.N. Rahaman and L.C. De Jonghe

December 1987

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EFFECT OF RIGID INCLUSIONS ON SINTERING

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ABSTRACT

The predictions of recent theoretical studies on the effect of inert, rigid inclusions on the sintering of ceramic powder matrices are examined and compared with experimental data. The densification of glass matrix composites with inclusion volume fractions of ≤ 0.15 can be adequately explained by Scherer's theory for viscous sintering with rigid inclusions. Inclusions cause a vast reduction in the densification rates of polycrystalline matrix composites even at low inclusion volume fractions. Models put forward to explain the sintering of polycrystalline matrix composites are discussed.

INTRODUCTION

Ceramic matrix composites are required to meet the demands of many advanced technological applications. They include structural composites for heat engines or aerospace components and electronic composites for dielectric applications. The presence of second phase inclusions, such as particles, whiskers or fibers, however, lead to a vast reduction in the densification rate of the matrix. Thus considerable difficulties are often encountered in the fabrication of ceramic matrix composites by conventional, pressureless sintering. Although techniques such as hot-pressing, or liquid phase sintering will yield the required high density, there are a number of disadvantages involved in their use. Hot-pressing can be used to fabricate relatively simple shapes only, and sintering aids lead to a deterioration of high temperature mechanical properties. The large-scale application of ceramic matrix composites in advanced applications requires the fabrication of complex shapes by conventional, pressureless sintering.

Over the past twenty years a number of studies have been made to understand the sintering of bimodal and agglomerated powders (1-10). However it is only within the past five years that progress has been made

to understand the effects of heterogeneities and inclusions on the densification of ceramic powder compacts. The system of interest for ceramic matrix composites generally consists of a rigid, non-sinterable, inert phase (e.g. particles, whiskers or fibers) dispersed in a porous powder matrix.

In the following sections, the predictions of recent theoretical studies on the effect of inclusions on sintering are first examined, and then compared with experimental data. Finally, possible explanations for the deviations between theory and experimental data are discussed.

RECENT THEORETICAL STUDIES

Transient stresses are developed during sintering when one region of the powder compact shrinks differently from its surroundings. Deviatoric creep will always seek to relieve the stresses. The calculation of the stresses therefore requires a viscoelastic solution to the problem where differential shrinkage generates internal stresses in the body and the internal stresses are relaxed by creep.

Several authors (11-18) have attempted to determine analytically the transient stresses and their effect on densification. Raj and Bordia (12) and Hsueh et al. (13-15) considered a "composite sphere" model consisting of a spherical domain (i.e. the inclusion) which can shrink faster or slower than the surrounding spherical cladding (i.e. the matrix). The viscoelastic stresses developed during sintering were calculated by first assessing the elastic stresses and then applying Laplace transforms to the solutions. For the case where the domain does not sinter as fast as the matrix (e.g. inert, rigid inclusion), a compressive stress, σ_i , arises within the inclusion, and radial compressive and tangential tensile stresses arise within the matrix. Raj and Bordia (12) and Hsueh et al (13-15) showed that the stresses within the matrix could be resolved into a shear stress, dependent on the distance from the inclusion/matrix boundary, and a hydrostatic tensile stress, σ_m , independent of position but dependent on the volume fraction of inclusion, v_i . The stresses σ_i and σ_m , shown in Fig. 1, satisfy a "force balance" condition and are related by the equation

$$\sigma_m = -v_i \sigma_i (1 - v_i) \quad (1)$$

The equations for the viscoelastic stresses exhibit the general form

$$\sigma_m(t) = \alpha \dot{\epsilon}_{mp}(\tau) \cdot k(t-\tau) d\tau \quad (2)$$

where $\dot{\epsilon}_{mp}$ is the linear densification rate of the matrix of the composite, $k(t)$ is a relaxation function (i.e. the stress response of the matrix to a unit displacement) and α is a constant that is defined by the geometry of the model. For the composite sphere model, $\alpha=4$. The ease with which the explicit value for the magnitude of $\sigma_m(t)$ can be obtained will depend on the complexity of $k(t)$ and how rapidly $\dot{\epsilon}_{mp}$ varies with respect to $k(t)$. In the analysis of Raj and Bordia (12) and Hsueh et al (13-15) an equivalent mechanical model based on the Maxwell model was employed to describe the viscoelastic deformation of the matrix. The material parameters that define $\dot{\epsilon}_{mp}$ and $k(t)$ then need to be determined from experiment. Gross errors can be introduced in the evaluation of the viscoelastic stresses if, for example, the equivalent mechanical circuit is not chosen correctly, or the

parameters that determine $\dot{\epsilon}_{mp}$ and $k(t)$ are collected from the literature on porous materials that are not identical in every respect.

An important aspect of the theories of Raj and Bordia (12) and Hsueh et al. (13-15) is that they predict large stresses within the matrix. Scherer (18) has shown that the large stresses predicted by these authors result from incompatible expressions for the shear and bulk viscosities of the matrix. In Scherer's theory, two models were considered: a "composite sphere" model, similar to the one considered by Raj and Bordia and by Hsueh et al, and a "self-consistent model" which is related to one used previously by Scherer (19) to analyze the sintering of a body containing a bimodal pore size distribution. From an analysis of the "effective moduli" of the composite sphere model, Scherer showed that the hydrostatic component of the stress in the matrix can be expressed as

$$\sigma_m = -\Sigma v_i [v_i + 3\eta_{mb}/(4\eta_{ms})]^{-1} \quad (3)$$

where Σ is the sintering stress (but see eqn. (10) for differences in symbolism), and η_{mb} and η_{ms} are the bulk and shear viscosities of the matrix, respectively. The linear densification rate of the matrix, $\dot{\epsilon}_{mp}$, defined according to the equation

$$\dot{\epsilon}_{mp} = (\Sigma - \sigma_m)/\eta_{mb} \quad (4)$$

can be expressed as

$$\dot{\epsilon}_{mp} = \Sigma / \{ \eta_{mb} [1 + 4v_i \eta_{ms}/(3\eta_{mb})] \} \quad (5)$$

Thus the stresses and strain rates depend only on η_{ms}/η_{mb} . The stress in an inclusion, σ_i , can be expressed as

$$\sigma_i/\Sigma = 2(1 - 2v_m)/(1 + v_m) \quad (6)$$

where v_m is the Poisson's ratio of the matrix. It is seen that σ_i cannot be greater than twice the sintering stress unless $v_m < 0$. For the self-consistent model considered by Scherer, the stresses and strain rates obey equations similar to eqns. (3)-(6), except that η_{ms} is replaced by η_{cs} , the shear viscosity of the composite.

De Jonghe and Rahaman (17) have reconsidered the equivalent spring and dashpot network used by Raj and Bordia (12) to define the relaxation function $k(t)$ of eqn. (2). Important in the development of the equivalent mechanical network is the distinction between the densification of the system and the recoverable, stored strain. The response of a powder compact to a loading and unloading stress step (Rahaman et al (20)), has clearly shown that the stored anelastic strain has a relaxation time of the order of a few minutes. The quasi-steady state deformation due to densification is not recoverable. Thus the appropriate equivalent circuit used by De Jonghe and Rahaman consists of a Maxwell and a Voigt element in series (Fig. 2). The Maxwell element has a relaxation time τ_1 and accounts for the steady state creep, while the Voigt element has a relaxation time τ_2 and represents the transient recoverable strain found by Rahaman et al (20). The quasi-steady state creep rate of the matrix, $\dot{\epsilon}_{mc}$, can be defined in terms of the "creep viscosity", η_{mc} , by the equation

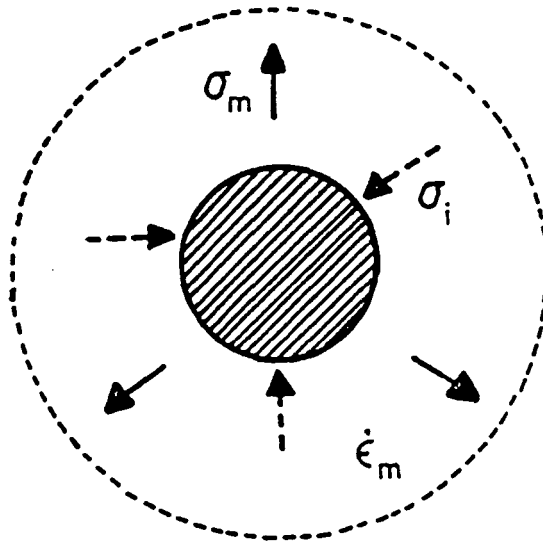


Fig. 1. The stresses around a rigid inclusion in a sintering matrix.

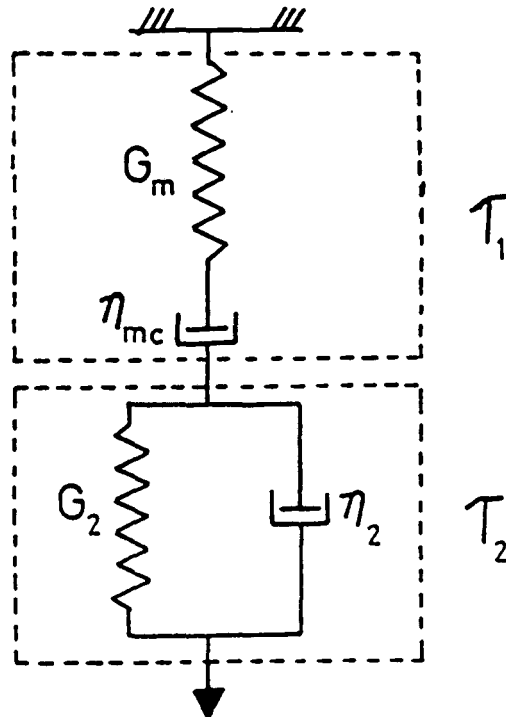


Fig. 2. Equivalent mechanical model for the densification-deformation process during sintering.

$$\dot{\epsilon}_{mc} = \sigma_a / \eta_{mc} \quad (7)$$

where σ_a is the uniaxial, applied stress. The relaxation time, τ_1 , is, at most, of the order of seconds, and thus much shorter than τ_2 . Thus the relaxation function to be used in eqn. (2) is

$$k(t) = G_m \cdot \exp(-G_m t / \eta_{mc}) \quad (8)$$

Since $\dot{\epsilon}_{mp}$ varies very slowly with time, compared with $k(t)$, it may be put outside the integral of eqn. (2), leading to a relatively simple result if G_m is assumed to be approximately constant. Thus

$$\sigma_m(t) = 4\eta_{mc} \cdot \dot{\epsilon}_{mp} \quad (9)$$

where the factor 4 arises from the spherical geometry of the model. The analysis therefore shows that the stresses due to the inclusions are only viscous in nature. Combining eqns. (1), (4) and (9) gives

$$\dot{\epsilon}_{mp} = (\Sigma/\phi) / \left\{ \eta_{mp} \left[1 + 4(\eta_{mc}/\eta_{mp}) v_i / (1 - v_i) \right] \right\} \quad (10)$$

In eqn. (10), the sintering stress was defined as an equivalent applied stress, Σ/ϕ , that would produce the same densification rate for the system, at identical geometry, but with surface tension effects absent (17). The term ϕ is a structure sensitive factor, usually called the "stress intensification factor", and is of the form (21-23)

$$\phi = \exp(aP) \quad (11)$$

where a is a constant that depends on the dihedral angle and P is the porosity. Thus Σ in eqn. (3) is equivalent to Σ/ϕ defined here. Equation (10) predicts that the matrix densification rates depend only on η_{mc}/η_{mp} .

COMPARISON OF THEORY WITH EXPERIMENTAL DATA

Glass Matrix Composites

Rahaman and De Jonghe (24) recently reported data for the densification of soda-lime glass powder compacts containing different volume fractions of inert SiC inclusions. The average size of the glass and SiC particles was 4 and 35 μm respectively. After mixing, the composite powders were consolidated by die-pressing to give compacts having approximately the same matrix density (~0.55 of the theoretical density of the glass). Shrinkage was recorded continuously at 605°C using a dilatometer. Figure (3) shows data for the density of the composite vs time for different volume fractions of inclusions, v_f . The quantity v_f was calculated on the basis of the fully dense composite, and is related to v_i by the equation

$$v_i = \rho_m \left[\rho_m + (1 - v_f)/v_f \right]^{-1} \quad (12)$$

In Fig. (4) data for the densification rate of the composite, $\dot{\epsilon}_c$, relative to the value calculated on the basis of the rule of mixtures, $\dot{\epsilon}_c^{(rm)}$, are

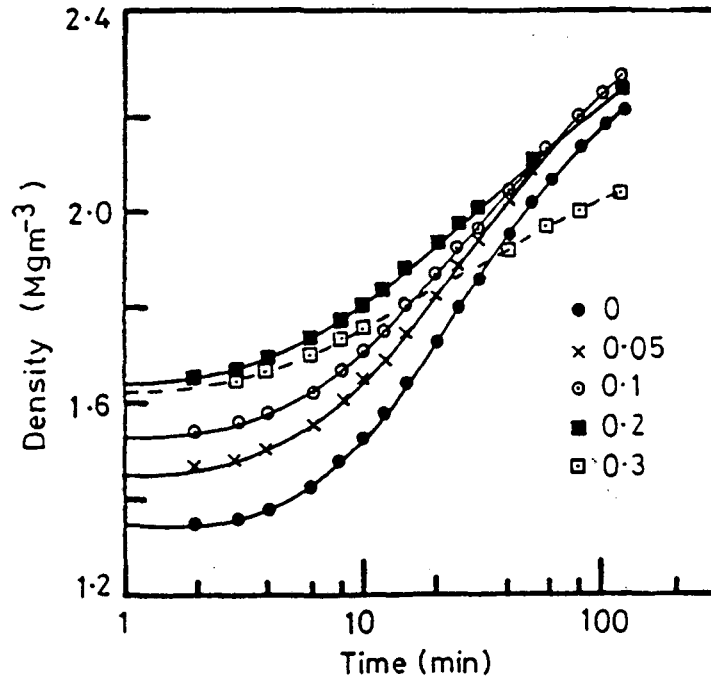


Fig. 3. Density of the glass matrix composite vs time for indicated volume fractions of SiC inclusions

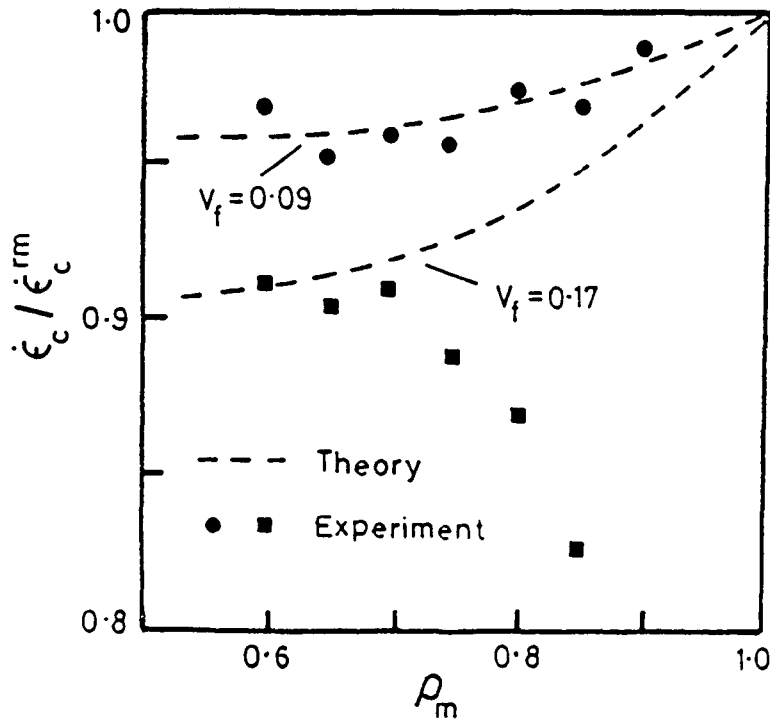


Fig. 4. Comparison of experimental data for the densification rate of the glass matrix composite normalized to the densification rate from the rule of mixtures vs relative density of the matrix with the predictions of Scherer's model.

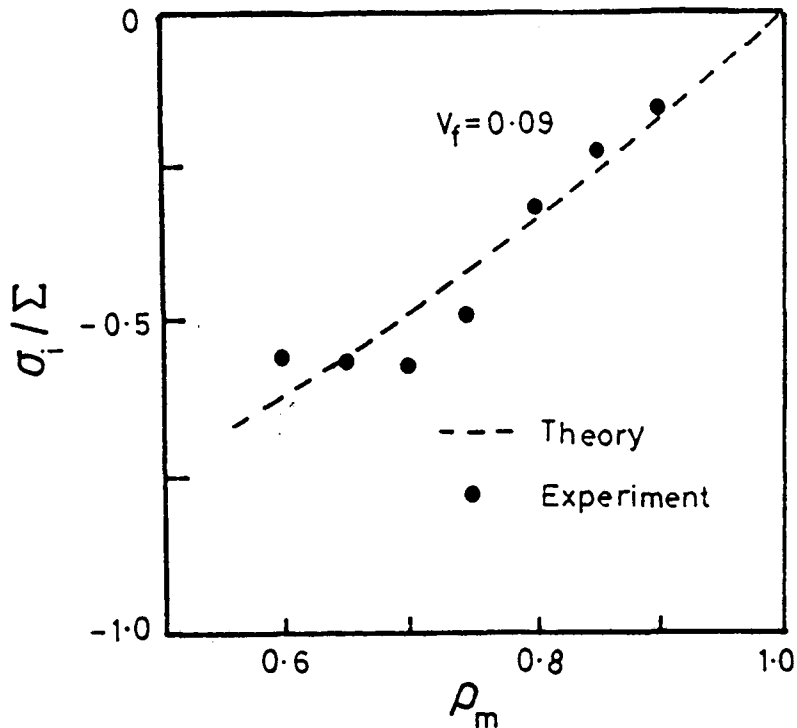


Fig. 5. Stress in the inclusion of the glass matrix composite, normalized to the sintering stress vs relative density of the matrix.

compared with the predictions of Scherer's theory (eqn. (5)) for values of v_f of 0.09 and 0.17. It is seen that the data are in excellent agreement with Scherer's theory for $v_f=0.09$. For $v_f=0.17$, there is initially good agreement, but significant deviations are evident above $\rho_m=0.7$. At this value of ρ_m , the inclusion volume fraction, $v_i=0.12$. Figure (5) shows data for σ_i/Σ for $v_f=0.09$. It is seen that there is excellent agreement with Scherer's theory (eqns. (1) and (3)), and that σ_i/Σ is much smaller than the theoretical predictions of Raj and Bordia (12) and Hsueh et al (13-15). As for Fig. 4, deviations from the theory become significant for $v_i>0.12$. Deviations from the theory above $v_i=0.12$ might be due to interactions between the inclusion particles. Scherer's model does not allow for the fact that the inclusions will initially interfere, and later will come into contact, eventually leading to a hard skeleton structure that densifies with difficulty. Thus for $v_i>0.12$, impingement effects rather than the viscoelastic backstresses can dominate the behavior.

Polycrystalline Matrix Composites

De Jonghe and Rahaman (25) have also reported data for the densification of polycrystalline ZnO powder compacts containing different volume fractions of inert SiC inclusions. In these experiments the average size of the ZnO and SiC particles was 0.4 and 12 μ m respectively. The method of fabricating the green composite bodies was similar to that used for the glass/SiC composites. Shrinkage was recorded continuously at 725°C using a dilatometer. The data for the density of the composite vs time for different v_f are shown in Fig. 6. The inclusions cause a dramatic reduction

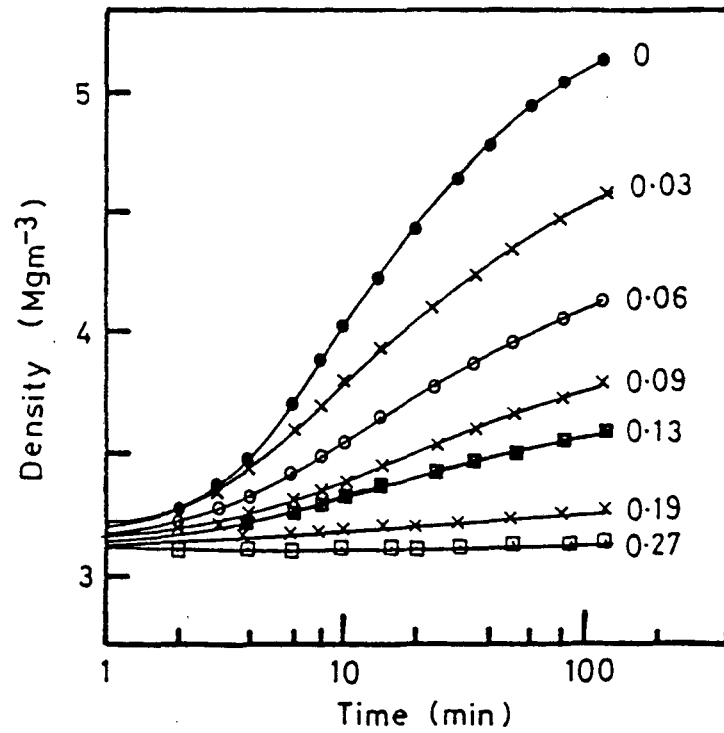


Fig. 6. Density of the ZnO matrix composite vs time for indicated volume fractions of SiC inclusions.

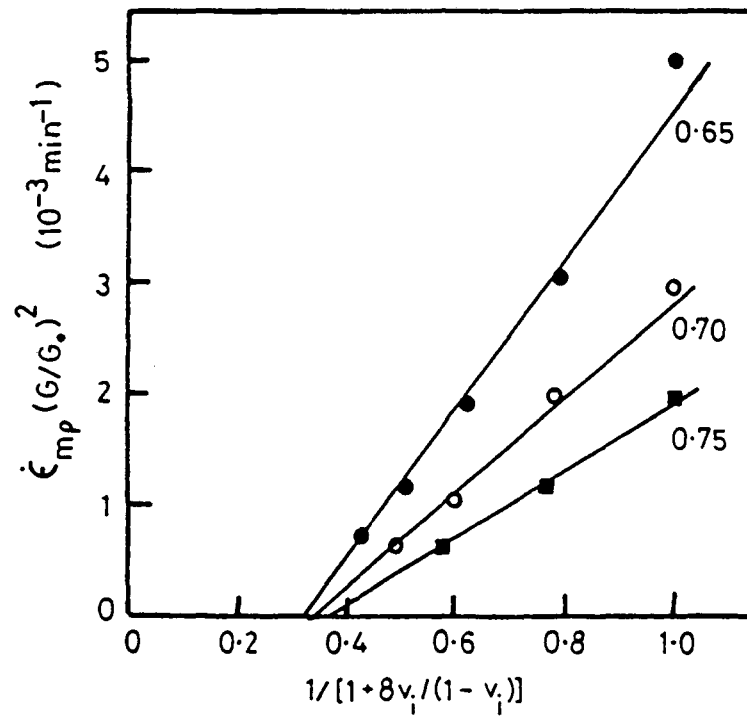


Fig. 7. Grain size compensated densification rate of the matrix of the ZnO matrix composite vs the function of the inclusion volume fraction, [eqn. (10)].

in densification, compared with the glass/SiC composites, and it is seen that above $v_i \sim 0.3$, densification is almost totally inhibited.

The vast reduction in the densification rates of the ZnO/SiC composites might, at first sight, be viewed as a confirmation of the large viscoelastic backstresses predicted by the theories of Raj and Bordia (12) and Hsueh et al (13-15), in contrast to Scherer's analysis, which predicts considerably lower stresses.

Lange (16) has proposed a constrained network model to describe the densification of composites in which the inclusion particles form a sparse, contiguous network. The model contains one adjustable parameter, the inclusion spacing, and by varying this, Lange was able to obtain a good fit to the data of De Jonghe and Rahaman for the ZnO/SiC composites. Lange's model is, however, purely geometric and does not make any distinction between polycrystalline and amorphous matrices. In addition, it appears unlikely that nearly spherical inclusions would form a contiguous network below $v_i \approx 0.1$.

The analysis of De Jonghe and Rahaman (17) gives eqn. (10) as the important relation between the matrix densification rate and the properties of the matrix. The quantity η_{mc}/η_{mo} has not been measured for ZnO, but preliminary data on an MgO/Bi₂O₃ system in which sintering occurs by a liquid phase mechanism (De Jonghe and Srikant (26)), indicate that it is ≈ 2 . Assuming the same value for ZnO, then a plot of $\dot{\epsilon}_{mo}$, corrected for grain growth, vs $1/[1 + 8v_i/(1 - v_i)]$ should yield a straight line that extrapolates through the origin. This plot has been done in Fig.7. A linear relationship is obeyed, but considerable deviations from the theory are apparent, even for low inclusion contents. A number of suggestions have been put forward recently to explain these deviations; these range, for example, from the effects of inclusion size and inclusion clustering (Weiser and De Jonghe (27)), to the formation of a skeletal network of the inclusions (Lange (16)), to microstructural anisotropy due to the viscoelastic stress field (Bordia and Scherer (28)).

CONCLUDING REMARKS

For glass matrix composites, Scherer's theory provides an excellent explanation of the experimental data for inclusion volume fractions, v_i , below $\sim 15\%$. At higher values of v_i , deviations from the theory might be due to impingement effects between the inclusion particles.

Data for the densification of polycrystalline ceramic matrix composites show considerable deviations from theory even at low inclusion contents, and a number of suggestions have been put forward recently to explain these deviations. Considerable work involving both theoretical modelling and experimental investigations of sintering and microstructure development is needed to extend the present understanding of the densification of polycrystalline ceramic matrix composites at high inclusion contents.

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