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and C.H. Hsueh

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TRANSIENT STRESSES IN BIMODAL COMPACTS DURING SINTERING

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ABSTRACT

A method is described and used to evaluate the transient stresses in a sintering compact of ZnO containing a hard, dense dispersion of SiC. A hard second phase can severely limit densification rates by generating a mean hydrostatic stress, σ_h , which opposes the compressive sintering stress of the matrix. σ_h rapidly increases with increasing volume fraction, f , of the second phase. The interface stress, σ_i , at the ZnO/SiC boundary increases with decreasing f . σ_i can attain large values, especially in the intermediate stage of sintering. The effect of these stresses on microstructural development is considered.

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INTRODUCTION

Powder characteristics and compacting procedures can cause inhomogeneities such as agglomerates and non-uniform particle packing within a green compact. It is now widely recognized that these inhomogeneities induce differential sintering rates which in turn produce transient (and sometimes residual) stresses within the sintering compact. These stresses influence particle rearrangement, resulting in the development and enlargement of void space. They may also influence creep processes within the porous sintering compact and induce creep damage by generation of crack-like voids.

Theoretical methods for the computation of these stresses resulting from non-uniform sintering rates have been recently considered by Evans (1) and by Raj and Bordia (2). Evans considered a model consisting of an inner fine-grained zone surrounded by a coarse-grained matrix. The stresses arise when the fine-grained inner zone attempts to densify more rapidly than the coarse-grained matrix. The problem was solved by a procedure similar to the "Eshelby technique" for the determination of the elastic field of an inclusion and by extending the solutions from the elastic to the viscoelastic case (3,4). Raj and Bordia considered a spherical domain which can shrink faster or slower than the surrounding, spherical matrix. The densification and viscoelastic creep processes were represented by Kelvin-Voigt and Maxwell elements, respectively. The transient stresses were then calculated using linear viscoelastic analysis and a

Laplace transform method (5) to obtain the time-dependent solutions. A major limitation of Raj and Bordia's analysis, however, is that the elastic modulus and the viscosity of the sintering compact were assumed to remain constant throughout sintering. Both theory and experimental evidence suggest a strong porosity dependence of these two quantities. Furthermore, the simple Kelvin - Voigt element is not adequate to fully represent the densification behaviour of the sintering compact. Recently, constitutive laws were developed by Hsueh et al (6) and by Hsueh and Evans (7) to describe densification and deformation and to predict the transient stresses in bimodal compacts during sintering. The solutions, however, involve complicated numerical analysis.

Experimental observations of internal cracks due to non-uniform sintering have been made by Lange and Metcalf (8), who deliberately introduced hard agglomerates into the powder compact, by Reeve (9), Vasilos and Rhodes (10), and by Spriggs et al (11). Rhodes (12) found that agglomerates impeded the densification kinetics of yttria-stabilized zirconia and interfered with the development of the microstructure.

The main purpose of this paper is to describe a procedure for evaluating the transient stresses in a sintering compact containing a uniform dispersion of a hard, dense second phase. The procedure utilizes the sintering kinetics and relatively uncomplicated theory, documented earlier for CdO (13), which does not require detailed

numerical analysis for the solutions. The system studied is fine-grained ZnO containing a dispersion of coarse SiC particles. Sintering was performed in air at 700°C, at which temperature the SiC particles are hard and inert towards ZnO.

II. EXPERIMENTAL

A fine-grained ZnO powder^{*}, average grain size ~ 0.4 μm , was used as the matrix material and SiC powder^{**}, classified to a narrow size range about an average of 12 μm , was used as the dispersion. The powders were mixed in a rotary mixer for one day, then hand-ground lightly using a mortar and pestle and finally die-pressed to give compacts of green density, ρ_0 , of $(3.18 \pm 0.04) \times 10^3 \text{ kg m}^{-3}$. This value is almost equal to the theoretical density of SiC ($3.22 \times 10^3 \text{ kg m}^{-3}$) and is 57% of the theoretical density of pure ZnO.

The compacts were sintered for 2 hours at 700°C, in flowing air (~50cc/min), using a dilatometer (14) that allowed the sintering kinetics to be monitored continuously. The density of the compacts at any time was determined from ρ_0 and from the measured shrinkage. The final density was also measured using Archimedes' Principle. The microstructure of the fracture surface of the sintered samples was examined in a scanning electron microscope.

* Reagent grade, Mallinckrodt Inc., Paris, Kentucky.

** 1000 Mesh, Geoscience Corp., New York.

III. THEORY

Consider a powder compact (e.g. ZnO), initial volume V_0 and initial density ρ_0 , containing no second phase particles (fig. 1), then the densification rate during sintering may be expressed as (13)

$$\dot{\rho}_b = K_1 \Sigma_b \phi_b^{n/2} G_b^{-n} \quad \text{Eqn. (1)}$$

where K_1 is a kinetic constant, Σ_b is the sintering stress, ϕ_b is the stress intensification factor, equal to the ratio of the cross-sectional area of the specimen over its actual internal load-bearing area, n is a number determined by the sintering mechanism, and G_b is the grain size.

Now, for a compact of initial volume V_0 , containing a volume fraction, f , of a hard dispersion of second phase particles (e.g. SiC), the densification rate of the matrix is given by

$$\dot{\rho}_m = K_2 (\Sigma_m - \sigma_h) \phi_m^{n/2} G_m^{-n} \quad \text{Eqn. (2)}$$

where Σ_m and ϕ_m are the sintering stress and the stress intensification factor respectively, of the matrix. σ_h is the mean hydrostatic stress exerted by the dispersion on the matrix (7, 15). It is noted that in the case of a tensile hydrostatic stress, σ_h opposes the sintering stress of the matrix and decreases the densification rate.

Then at any given time $K_1 = K_2$ and $G_b = G_m$, since the large - sized, second phase should not affect the grain growth kinetics, so that

$$\dot{\rho}_m / \dot{\rho}_b = (\Sigma_m/\Sigma_b - \sigma_h/\Sigma_b)(\phi_m/\phi_b)^{n/2} \quad \text{Eqn. (3)}$$

Now

$$\dot{\rho}_m = m_m d(1/V_m)/dt \quad \text{Eqn. (4)}$$

where m_m is the mass and V_m the volume of the matrix, given by

$$V_m = V - fV_o \quad \text{Eqn. (5)}$$

where V is the instantaneous volume of the bimodal compact.

Then
$$\dot{\rho}_m = [1 + f\rho_s/(\rho_o - \rho_o f)]^{-1} [1 - f\rho/(\rho_o - \rho_o f + f\rho_s)]^{-2} \dot{\rho} \quad \text{Eqn. (6)}$$

where $\dot{\rho}$ is the densification rate of the ZnO/SiC compact, and ρ_s is the density of the dispersed particles. For these experiments $\rho_s \sim \rho_o$,

Using equations (3) and (6) and putting $\rho_s = \rho_o$,

$$\dot{\rho} = \dot{\rho}_b (1 - f)^{-1} (1 - f\rho/\rho_o)^2 (\phi_m/\phi_b)^{n/2} (\Sigma_m/\Sigma_b - \sigma_h/\Sigma_b) \quad \text{Eqn. (7)}$$

For some oxides (12, 14), it has been observed that ϕ has an exponential dependence on porosity, P , of the form similar to that due to Beere (15, 16), i.e.

$$\phi = \exp(\alpha P) \quad \text{Eqn. (8)}$$

where α is a constant that depends on the equilibrium dihedral angle.

Hence

$$\phi_m = \exp \{ \alpha [1 - \rho(1 - f)/(1 - f\rho/\rho_0)] \} \quad \text{Eqn. (9)}$$

$$\phi_b = \exp [\alpha(1 - \rho_b)] \quad \text{Eqn. (10)}$$

The sintering stress is given by the equation

$$\Sigma = \gamma/r \quad \text{Eqn. (11)}$$

where γ is the surface tension and r the mean pore radius of the compact. Over a wide range of density, it has been observed that (13, 19)

$$r \sim GP \quad \text{Eqn. (12)}$$

where G is the average grain size. Therefore

$$\Sigma_m/\Sigma_b = (1 - \rho_b)/[1 - \rho(1 - f)/(1 - f\rho/\rho_0)] \quad \text{Eqn. (13)}$$

σ_h/Σ_b can then be determined experimentally as a function of time if the constants n and α for the matrix are known.

The interface stress, σ_i , at the ZnO/SiC boundary is given by an equation of the form (7, 15)

$$\sigma_i = -\sigma_h(1 - f)/f \quad \text{Eqn. (14)}$$

σ_i can then be determined from σ_h . In the case of non-sinterable heterogeneities, a compressive stress develops at the interface which in turn gives a tensile hydrostatic stress in the matrix, as seen from eq. (14).

IV. RESULTS AND DISCUSSION

Fig. 2 shows the density, ρ versus time, t , for compacts containing different volume fraction, f , of SiC and sintered at 700°C. Each curve is the average of two runs under the same conditions. Time $t = 0$ represents the beginning of shrinkage (for ZnO) and the sintering temperature was reached after $t = 6$ min. ρ is drastically reduced by the addition of the hard dispersion of coarse-grained SiC. Above $f \sim 0.25$, there is almost no change in the density of the compact during sintering. For $f = 0.27$, the compact shows a small expansion up to the sintering temperature ($t = 6$ min) before densifying slightly after 2 hours.

It is interesting to compare the experimental results with those predicted by the classical rule of mixtures. In Fig. 3 the change in density normalized to the change in density of the ZnO powder compact, $\Delta\rho/\Delta\rho_{f=0}$ is plotted versus f after $t = 10$ and $t = 100$ min. According to the rule of mixtures, this plot should be a straight line intersecting the ordinate and abscissa at 1.0. However, for a hard dispersion $\Delta\rho/\Delta\rho_{f=0}$ equals zero when the dispersed particles begin to touch. For the coarse dispersion used, this should occur at $f \sim 0.5$. Even with this adjustment to a simple rule of mixtures, the deviations of the experimental results would still be very large. These deviations can be explained by the tensile hydrostatic stresses developed in the matrix which opposes the sintering stress and reduces

the densification rate. A detailed numerical analysis (7), which takes this hydrostatic stress into consideration, gives a good fit to the present results. Also, there does not appear to be any significant difference between the results at $t = 10$ and $t = 100$ min.

The variation of the densification rate, $\dot{\rho}$, with time is shown in Fig. 4. $\dot{\rho}$ decreases somewhat less steeply with t as f increases. At any t , the decrease in $\dot{\rho}$ with increasing f is more pronounced above $f \sim 0.13$.

The microstructure of a compact having $f = 0.06$ and sintered for 2 hours is shown in fig. 5. The SiC particles are seen to be angular and well dispersed. SEM micrographs at higher magnification show no reaction at the ZnO/SiC interface.

As shown in section III, σ_h may be deduced from the sintering kinetics if the constants n and a in equation (1) and (8) are known. Published results for ZnO support both $n = 2$ (20) and $n = 3$ (21). These values were deduced by comparing diffusion coefficients measured in sintering and grain growth with those obtained from ionic diffusion experiments. The experimental determination of these two constants for ZnO, using a loading dilatometer, are currently in progress in our laboratory. Results for CdO (13) using the same technique yield $n = 3$ and $a = 1.6$. For the present paper the exact values of n and a are not required. Values similar to those obtained for CdO will be used, i.e. $n \sim 3$, $a \sim 2$, since our current work indicates that CdO and ZnO behave

similarly. Also, the determination of σ_h (equation 7) is not very sensitive to changes in n or α . The maximum difference in $(\phi_m/\phi_b)^{n/2}$ for $n = 3$ and $n = 2$ is about ten percent.

Fig. 6 shows σ_h/Σ_b versus t for compacts containing volume fractions, f , of 0.03, 0.06 and 0.13 SiC. Σ_b is the sintering stress for the ZnO compact and may be found experimentally by a method similar to that used for CdO (13). σ_h/Σ_b can be quite large at early sintering times and at any time t , it increases with increasing f . These results are consistent with the recent theoretical analysis of Hsueh and Evans (7, 15).

The ratio σ_i/Σ_b , where σ_i is the ZnO/SiC interface stress, is plotted versus t in fig. 7 for $f = 0.03, 0.06$ and 0.13 . Over most of the time scale, σ_i/Σ_b increases as f decreases and can attain large values for small f . This is also consistent with the theory of Hsueh and Evans (7, 15). The dependence of σ_i on f is quite the opposite of that of σ_h and this arises because these stresses are interrelated through f (eqn. 14). A recent theoretical analysis (15) predicts that σ_h (and hence σ_i) depends strongly on f , especially for small f , but is quite insensitive to the number (or size) of the second phase particles.

It is worth considering the importance of the results in figs. 6 and 7 on the microstructural development of the bimodal compact. While

a very small value of f may not severely restrict the "effective" sintering stress of the matrix, it can nevertheless lead to very large interface stresses which may cause microstructural cracks in the compact. Larger values of f do not lead to high interface stresses but they severely reduce the "effective" sintering stress of the matrix leading to a weak, porous matrix.

It should be pointed out that the system used, i.e. a coarse dispersion in a fine-grained matrix, may be relevant to the understanding of various aspects of the sintering behaviour of powder compacts containing inhomogeneities. Practical examples of systems that experience the effects studied in this paper are, for example, a compact containing hard, dense agglomerates, a coarse-grained region surrounded by a fine-grained zone, and a compact containing coarse precipitates. Fig. 8 is a scanning electron micrograph of a polished surface of an alumina compact sintered to a relative density of ~70%. Dense areas surrounded by an outer, fine-grained, porous region are clearly evident.

V. CONCLUSIONS

A procedure has been described and used to evaluate the transient stresses within a sintering compact of ZnO containing a uniform dispersion of inert, large SiC particles. The procedure utilizes the

sintering kinetics and relatively uncomplicated theory that does not require detailed numerical analysis.

The dispersion can severely limit densification rates by exerting a significant tensile hydrostatic stress, σ_h , which opposes the compressive sintering stress of the matrix. σ_h increases with increasing volume fraction, f , of the dispersion.

The interface stress, σ_i , at the ZnO/SiC boundary increases with decreasing f . It can attain large values at low f , and may lead to the creation of microstructural cracks in the compact.

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LIST OF FIGURES

- Fig. 1. Sketch of system used in the derivation of the equations in Section III.
- Fig. 2. Density as a function of time for ZnO containing different volume fractions of SiC.
- Fig. 3. The normalized change in density versus volume fraction of SiC compared to the prediction of the rule of mixtures.
- Fig. 4. The variation of densification rate with time for different volume fractions of SiC.
- Fig. 5. Scanning electron micrograph of a fracture surface of a ZnO compact containing 6 vol. % SiC.
- Fig. 6. The ratio of the hydrostatic stress (exerted by the dispersion) to the sintering stress versus time.
- Fig. 7. The ratio of the interface stress to the sintering stress versus time.
- Fig. 8. Hard agglomerates surrounded by a porous outer zone in an alumina powder (sintered to ~ 70% relative density).

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Figure 1

Figure 2

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XBL 852-1280

Figure 3

XBL 852-1281

Figure 4

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Figure 5

XBL 852-1282

Figure 6

XBL 852-1283

Figure 7

XBB 852-1419

Figure 8

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