Sintering and Densification of Particulate Composites: Inclusion Size and Clustering

M.W. Weiser
(Ph.D. Thesis)

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Inclusion Size and Clustering

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Ph.D. Thesis

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Abstract

Previously, attempts have been made to explain the lower densification rates observed in ceramic bodies containing inclusions in terms of hydrostatic back stresses that arise out of the matrix shrinking around the inclusion. These models can account for the observed dependence of the densification on the volume fraction of inclusions. However, they fail to account for the observed large differences in densification for inclusions of different sizes. It is proposed that the lower densification for smaller inclusions is a consequence of both a thin matrix layer at the inclusion's surface that densifies less readily than the bulk and the clustering that can occur more readily among smaller inclusions. The observed lower densification rates are a function of the volume fraction, size, degree of inclusion clustering, and the processing during powder mixing. These lower densification rates can be treated as the effective volume fraction of the second phase being greater than the volume fraction that is actually present.
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1. Introduction

During the past forty years great advances have been made in our understanding of the sintering phenomena. However, only in the past ten to fifteen years has the importance of inhomogeneities in the green compact been fully appreciated. Heterogeneities in the green compact can adversely affect the sinterability of the powder and leave an inhomogeneous final product that can have dramatically inferior properties compared to the homogeneous material. Recently, efforts have been made to produce two phase ceramics to take advantage of such properties as transformation toughening and whisker reinforcement as illustrated in figure 1.1. These materials are inhomogeneous by definition and considerable difficulties are often encountered in fabrication, as near theoretical density is nearly always required.

These two phase ceramic materials may be required to meet the demands of heat engines, turbines and other thermal systems operating at higher temperatures than high temperature metal alloys can withstand. Dispersed particulate composite ceramic systems are being investigated because most current single phase ceramics have low toughness and can not withstand the tensile stresses involved in these applications. It is possible to lower the required stresses, but this requires even higher operating temperatures to achieve the same efficiency. The use of even higher operating temperatures can cause high temperature creep. Although these materials have excellent high temperature creep resistance, they will be degraded if the temperatures are high enough.

Typically, for dispersed particulate composites, the matrix and inclusion have weak chemical interactions so that the composite will remain as two discrete phases
during use. The fabrication of these two phase materials is not easy, often requiring the addition of sintering aids or the use of techniques such as hot pressing\textsuperscript{1-3}. These methods will yield the required high final density, however, there are disadvantages; sintering aids often decrease the resistance to high temperature creep and only relatively simple shapes can be hot pressed. The optimal situation for the production of complex ceramic shapes is the ability to perform pressureless, or free, sintering.

This study is intended to investigate the effect of various sized inclusions at constant volume fraction on the sinterability of a ceramic matrix during pressureless sintering. A better understanding of the effect of inclusions on sintering will allow modification of the production procedure to attain near theoretical density. This result may be achieved by modifications of the starting powders, the consolidation procedure, or the heat treatment schedule.
2. Background

2.1 Experimental Studies

In the past few years a variety of studies have been conducted trying to understand the low sinterability of two-phase ceramic materials. The earliest of these were concerned with the effect of bimodal and agglomerated powders. These powders are similar to two phase systems because of the large difference in sintering behavior for the different size fractions. These investigations were motivated by the fact that most real powders are multimodal and agglomerated. Theoretically, a bimodal powder should pack to a higher initial density than a monomodal one. However, the improved sinterability due to this higher packing is rarely observed.

The addition of only a small volume fraction of inclusions has been shown to cause a large decrease in the densification of the compact in comparison to that of the pure matrix. In order to be able to densify fully compacts containing a high volume fraction of inclusions without resorting to hot pressing it will be necessary to understand the reasons for this large decrease in the densification. Once the mechanisms are understood it may then be possible to develop methods of processing in the green state, consolidation, and heat treatment that will allow the attainment of full density during sintering.

2.2 Models of the Effect

As pointed out above, there have been a number of studies done on the solid state sintering of two phase systems. However, only a few of them have made
serious attempts to understand the lowered sinterability based upon the presence of
the second phase.\textsuperscript{13-21} Rahaman and De Jonghe\textsuperscript{25,26} along with Raj et al.\textsuperscript{12} have
used a loading dilatometer to investigate the sintering stress in a fine grained
matrix containing various volume fractions of coarse inclusions. Both of these
studies show that the decreased sinterability is directly related to the volume
fraction of the inclusions and agree qualitatively with the theoretical analysis of
Hsueh et al.\textsuperscript{15,16}, Raj et al.\textsuperscript{12,21}, and De Jonghe et al.\textsuperscript{13} All of these studies have
determined that a hydrostatic back stress is developed in the matrix that opposes
the sintering. This back stress is a result of the matrix shrinking around the
inclusion and the inclusion being virtually incompressible. The stresses that arise
around a single, spherical inclusion are illustrated in figure 2.1.

The hydrostatic back stress model states that the back stress should only be a
function of the inclusion volume fraction, $f$. The change in the matrix density,$\Delta \rho$, is predicted to depend upon the the inclusion volume fraction as in equation
2.1.

$$\Delta \rho \propto \frac{f}{(1 - f)}$$

This model states that the back stress and hence the matrix sinterability will be
independent of the size of the inclusions if the volume fraction remains constant.
The present study shows that for a fine grained, 0.25 $\mu$m diameter, ZnO matrix
containing different sizes, 0.5 to 75 $\mu$m diameter, SiC the matrix sinterability is
strongly dependent upon the inclusion size. For a given volume fraction of
inclusions it is found that that sinterability decreased as the inclusion size
decreased, figure 2.3. It is therefore proposed that the matrix shrinkage is
dependent upon both the size and volume fraction of inclusions.
2.3 Theory

The sintering of a powder compact is driven by the reduction in the free energy of the system that accompanies the replacement of the solid/vapor interface with a solid/solid interface. The sintering rate of a compact is dependent upon a large number of different factors including but not limited to the particle size and shape, sintering temperature, and the applied stress on the system. These factors are normally grouped into three primary parameters: \( \kappa \), containing the various kinetic parameters involving the diffusion mechanism and sintering temperature; \( \Sigma/\phi \), the sintering stress or pressure determined by the particle size and shape; and, \( \sigma_a \), the applied stress on the sintering necks. It has been assumed by many authors, that the sintering rate, \( \dot{\varepsilon} \), has the general form.

\[
\dot{\varepsilon} = \frac{\Sigma}{\phi} + \sigma_a
\]

2.2

The sintering stress, \( \Sigma/\phi \), is composed of the effective stress on the necks, \( \Sigma \), and a geometric factor, \( \phi \), which includes the matrix porosity. The sintering stress defined in this manner will have the same affect upon the densification as an externally applied hydrostatic stress of equal magnitude and sign. The exact form and values of the constants in this equation is strongly dependent upon the geometry and temperature of the system.

2.4 Theory of Sintering with Non-Sintering Inclusions

The general theory of the effect of inclusions upon the sintering of a fine grained matrix has been developed by Evans, Hsueh et al., Raj et al., and De Jonghe et al. as mentioned earlier. This body of theory is concerned with the
development of a stress field in and around the inclusion as originally described by Eshelby\textsuperscript{29} for the continuum case, and the effect of this stress field upon the sintering of the matrix. The situation is further complicated by the fact that the matrix can creep to relieve the stresses. This means that the stress state at a given time is, in principle, dependent upon the state of stress and strain at all previous times. This type of stress/strain relationship is most commonly referred to as viscoelasticity.

The theory will be described here following the methods outlined by De Jonghe and Rahaman,\textsuperscript{13} but, many of the details of the analysis will be omitted. In these theories the overall lineal strain rate is used to describe the shrinkage of the matrix and is defined as

\[ \dot{\varepsilon}_\rho = \frac{\dot{\rho}}{3\rho} = \frac{-\nu}{3\nu} \]

where \( \dot{\rho} \), the volumetric densification rate, denotes the derivative with respect to time of \( \rho \), the matrix density. \( \dot{\varepsilon}_\rho \) is found to be of the form of equation 2.2 where \( \Sigma \) is dependent upon the matrix grain size \( G \), the average pore radius \( \langle r \rangle \), and the geometric factor \( \phi \), is the stress intensification factor that was derived by Viera and Brook\textsuperscript{30} from the data of Beere.\textsuperscript{31,32} This factor is found to be of the form \( \phi = e^{aP} \), where \( a \) is a function of the grain boundary dihedral angle, \( \psi \), and, \( P \), the volume fraction of porosity. The sintering stress, \( \Sigma/\phi \), arises from the surface tension and is equivalent to externally applied hydrostatic stress which would lead to the same densification rate. The sintering rate is then given by

\[ \dot{\varepsilon}_\rho = \frac{1}{\eta_m} \left( \frac{\Sigma}{\phi} - \sigma_h \right) \]
where $\sigma_h$ is the hydrostatic back stress and $\eta_m$ is the matrix viscosity.

In the analysis of Raj et al.\textsuperscript{12,21}, Evans et al.\textsuperscript{15,16} an equivalent mechanical circuit based upon the Maxwell model of viscoelasticity is employed to describe the stresses that result from the shrinkage of the matrix around a virtually incompressible inclusion. De Jonghe et al.\textsuperscript{13,33} have modified this equivalent circuit to use both a Maxwell and a Voight circuit in series to model the response of the matrix to both the back stresses due to the inclusions and the sintering stress. This circuit is illustrated in figure 2.2 and is composed of two subcircuits with relaxation times $r_1$ and $r_2$. The first circuit accounts for the quasi steady state creep and the second for the transient recoverable strain found by De Jonghe et al.\textsuperscript{17}

The quasi steady state creep viscosity, $\eta_c$, can be determined from the experimental data by use of the equation

$$\eta_c = \frac{\dot{\epsilon}_c}{G_m}$$

where $G_m$ is the shear modulus of the porous matrix and $\dot{\epsilon}_c$ is the creep strain rate. The exact values of $G_m$ have not been determined but can be estimated to be about 10 GPa for 70% dense oxide such as ZnO. The viscosity, $\eta_c$, is then found to be approximately 2 GPa min. Therefore, $r_1$ is approximately 0.2 min and $r_2$ is approximately 3 to 5 minutes.\textsuperscript{13} The short relaxation time, $r_1$, of the Maxwell component of this circuit compared to the Voight component assures that it dominates the viscoelastic response of the system. The response function of the system to a unit step strain can then be represented as

$$k(t) = G_m e^{-G_m t / \eta_c}$$
The stresses around the inclusion are derived from the elastic misfit stresses. Use of the method of Laplace transforms leads to a convolution integral of the form

\[ \sigma_i(t) = 4 \int_0^t \dot{\epsilon} \rho \ k(t-\tau) \ d\tau \]

where \( \sigma_i(t) \) is the radial misfit stress as a function of time at the inclusion/matrix interface the factor of 4 arises from the spherical geometry of the inclusion and the matrix surrounding it. The relaxation time associated with the response function is on the order of a few minutes in conflict with the analysis of both Evans and Raj. Since the shrinkage rate, \( \dot{\epsilon} \rho \), varies slowly with time compared to the relaxation time the shrinkage rate may be removed from the integral in equation 2.7. Substitution and integration gives

\[ \sigma_i(t) = 4 \eta_c \dot{\epsilon} \rho \left( 1 - e^{-G_m t/\eta_c} \right) \]

From the values given earlier it is found that the term \( G_m/\eta_c \) has a value of approximately 5 min\(^{-1}\). Therefore, the exponential term will become negligible compared to the first term after a very short time and will be neglected from this point onward.

For an infinite matrix there is no hydrostatic component to this stress field. In a finite matrix there is a mean hydrostatic stress component due to the inability of the free surface to support a normal stress. The stresses for both of these cases are shown in figure 2.3 as a function of the normalized distance from the interface for a spherical inclusion in a spherical domain. Integration of of both the radial and tangential stresses over the matrix volume leads to
2.9

\[ \sigma_h(t) = \sigma_i(t) \frac{f}{(1-f)} \]

where \( f \) is the volume fraction of inclusions. Since the matrix is shrinking around the inclusion the radial interfacial stress will be compressive and the tangential hoop stress will be tensile. The presence of only the hoop stress at the free surface results in the tensile nature of the overall hydrostatic stress component. Since the hydrostatic stress is tensile this will act to slow the sintering of the matrix.

Combination of the above equations gives the shrinkage rate for a matrix with a volume fraction \( f \) of non-sintering inclusions.

\[ \dot{\rho} = \frac{\Sigma_o/\phi}{\eta_m \left( 1 + 4 \frac{\eta_c f}{\eta_m (1-f)} \right)} \]

where \( \Sigma_o \) is the sintering stress when there are no inclusions present. The effect of the inclusions on the sintering is strongly dependent upon the ratio of the creep viscosity, \( \eta_c \), to the matrix viscosity, \( \eta_m \). This ratio has been assumed to be equal to one due to difficulty in measuring these two different viscosities. This probably a good assumption for glass and accounts for the small effect that inclusions have on the sintering. However, there are indications that \( \eta_c \) may be larger than \( \eta_m \) for crystalline materials which would partially account for the significant effect that the inclusions have upon the sintering of crystalline materials. However, the observed decreases in the sintering rate are still larger than would be predicted from equation 2.10 using the measured values of the viscosity.
In order to account fully for the observed large decreases in matrix sinterability it is necessary to find other mechanisms which lead to lower densification rates. It is proposed that a layer of matrix particles can form at the inclusion/matrix interface resulting in an increase in the effective volume fraction of inclusions. Clustering of the inclusions particles is also observed, especially among the finer inclusions, and it is proposed that this can have a significant effect on the matrix sinterability. Both of these ideas will be further explored and developed later in the section on the theory.
3.0 Experimental Procedure

This study is composed of two principal parts; an experimental investigation utilizing a ZnO/SiC composite, and a computer simulation of the effect of clustering. A wide variety of SiC inclusion sizes and volume fractions in identical ZnO matrices were used to determine the effect of inclusion size on the matrix sinterability. During the initial portions of this study it was found that the smaller inclusions tended to cluster so the simulation of clustering was added.

3.1 Sintering of Powder Compacts

A ZnO/SiC composite was prepared with a fine grained, 0.25 μm ZnO matrix and 2.5 to 20 volume percent of non-sintering coarse, 0.5 to 75 μm SiC inclusions. The different size fractions of SiC were prepared by air classifying various commercial SiC powders, the particle sizes were determined using scanning electron microscopy (SEM). Two different sets of compacts were made using the same starting powders and similar volume fractions of inclusions. Once the compacts were made, they were sintered in the dilatometer shown schematically in figure 3.1, at 1000K in flowing dry air.

The first set of compacts were prepared in acetone with 5 volume percent carbowax§ as a binder. The composite powders were made by combining the measured quantities of ZnO, SiC, and carbowax, and stirring for a half hour in an excess of acetone. They were air dried, and drying was completed by heating in a vacuum oven for an additional hour at 323K. The powders were gently ground

§ Polyethylene Glycol 3350, Union Carbide
and passed through a 32 mesh sieve to break up any large agglomerates. The resulting powders were pressed in a uniaxial punch and die, to produce compacts which were approximately 6.35mm in diameter by 6.35mm long with the ZnO matrix at 50% of the theoretical density of 5.606 g/cm³. The carbowax was burned out in flowing dry air during the initial half hour heat up to a constant temperature of 673K in the dilatometer. The compacts displayed a consistent axial shrinkage of 0.25% during this heating. The procedure from this point is identical for both powder preparation methods and is described later.

The second set of compacts were prepared in hexane with 0.5 volume percent Oloa 1200† added as both a dispersant and binder. The SiC powder was first dispersed ultrasonically in the hexane/oioa solution, then the ZnO was added and the mixture was stirred for a half hour and dried as above. These powders were much less weakly agglomerated so grinding and sieving was not needed. The resulting powders were pressed in a uniaxial punch and die yielding compacts which were approximately 9.53mm in diameter by 6.71mm long and 50% of the theoretical matrix density. The Oloa was burned out by heating in air for one hour at 723K after a one hour heating ramp from room temperature. The samples were sintered in the dilatometer as above except that the initial heat up was to 723K, and a 0.25% expansion was observed.

After the initial preheat, the dilatometer containing the sample was slid into the hot zone of the tube furnace which had been heated to 1050K. The furnace controller was then turned down to the sintering temperature of 1000K and the sample reached this temperature in approximately 5 minutes with little overshoot. The samples were sintered for times ranging up to 24 hours with most of the

† Chevron Chemical Corporation
experimental runs of 2 to 6 hours duration. The length of the sample was recorded every 2 seconds on a Bascom-Turner storage recorder and the data were transferred to a PC/AT for compression and analysis.

The length which was observed to vary approximately linearly with log time, as is shown in figure 3.2, so time was replaced as the independent variable by a new function \( z \), defined as

\[
z = \alpha e^{-\beta t}
\]

where \( \alpha = 59.02 \text{s} \) and \( \beta = 0.0165 \text{s}^{-1} \). This resulted in the compression of the 43,000 raw data points taken in a 12 hour experimental run to 400 data points upon which all subsequent calculations were performed. This made the calculations and data storage much simpler for the approximately 100 experimental runs and 8 different sets of derived data for each run.

The sample length as a function of time, in the above storage format, was used to calculate a variety of parameters to describe the sample matrix. The specific matrix volume was computed for each sample as a function of time using the assumption that the sample diameter was a linear function of the length. This assumption agreed with data from this study and has been shown to be fairly accurate for a variety of systems, including this one.\(^{11,25-27}\) The specific volume data were then smoothed and 3 to 6 experimental runs with compacts made from the same powder were averaged. The density, densification rate and volumetric strain rate were then calculated from the average specific volume. These sets of data were then analyzed to determine the relationship between the matrix sinterability and inclusion size and volume fraction.

Microstructural analysis was done on a portion of the samples in the scanning electron microscope (SEM) using both fracture and polished surfaces. The
contrast between ZnO and SiC on a fracture surface is not very strong in SEM, so energy dispersive X-ray analysis (EDAX) was used to map the location of the SiC inclusions at low, 200 to 800X, magnification. These low magnification maps were used to determine the extent of inclusion clustering for the various sizes and volume fractions of SiC inclusions.

3.2 Simulation of Clustering

The effect of clustering was simulated in two dimensions by using a computer model to fill a rectangular area of an infinite plane with a minimum of 1,000 circular particles. The area to be filled was scaled to the size and volume fraction of the particles and could be considered to be just one cell of an infinite lattice, thus avoiding edge effects. The coordinates of the particles were selected using a pseudo-random number generator and were prohibited from overlapping. A biasing function, which could either encourage or discourage clustering was used to simulate clustering. This biasing function was chosen to simulate the effect of having either an attractive or repulsive interaction between the particles.
4. Theory

4.1 Effect of Non-Sintering Inclusions

The general theory of the effect of inclusions upon the sintering of a fine-grained matrix has been developed by Evans, Hsueh et al., Raj et al., and De Jonghe et al.\textsuperscript{12-16} and was reviewed in the background section. The predictions of this theory can be summarized in the following equation which is a simplification of equation 2.10.

\[
\dot{\varepsilon}_\rho = \frac{\Sigma_o/\phi}{\eta_m (1 + 4f/(1-f))}
\]

where the creep viscosity, \(\eta_c\), and the matrix viscosity, \(\eta_m\), are assumed to have the same value. If the matrix viscosity, \(\eta_m\), is large equation 4.1 predicts that the shrinkage rate \(\dot{\varepsilon}_\rho\) is very strongly dependent upon the volume fraction of inclusions. For many ceramics \(\eta_m\) is found to be in the range of 5 - 10 MPa indicating that the hydrostatic backstress can have a significant effect on the sintering of composites, particularly at higher volume fractions of inclusions.

4.2 Modifications to Account for the Inclusion Size

The theory presented above does not predict any difference in the sintering behavior for different sized inclusions at constant inclusion volume fraction. The observed change in the sintering behavior is proposed to be a result of a change in the effective volume fraction of the inclusions. This change in the effective volume fraction is a result of the formation of a zone of unidirectionally densified particles around the inclusions. The thin matrix layer leaves a zone of relatively
low density that is unable to densify further in the later stages of sintering. This is illustrated in figure 4.1. Notice that the grain size has remained constant near the inclusion while it has increased in the bulk. This poorly densified zone is proposed to arise from two primary sources, first the combination of radial compressive and tangential tensile stresses around the particles, and secondly the adherence of the matrix particles to the surface of the inclusion.

The stress field that occurs around a non-sintering inclusion in a sintering matrix was shown figure 2.1. The radial compressive stress increases the sintering rate in any necks that are aligned with this stress. The tangential tensile stress decreases the sintering rate in any necks that are aligned with this stress. The effect of these stresses upon a commonly modeled neck geometry is shown in figure 4.2. This combination of higher radial and lower tangential sintering will prevent the formation of sintering necks tangential to the interface. There will be little densification in this region due to the lack of sintering neck formation during the initial stages of sintering. The result is the creation of a zone of relatively low density. This will increase the effective radius of the inclusion. Since the number of inclusions is fixed this is equivalent to an increase in the effective volume fraction of the inclusions.

\[
f_e = f (1 + x/r)^{-3}
\]

where \( x \) is the thickness of the layer and \( r \) is inclusion radius.

This effective volume fraction of inclusions can be used to modify the volumetric strain rate of equation 4.1 to give equation 4.3.
The term containing the volume fraction, \( f/(1-f) \), will increase faster with increasing volume fraction of inclusions in equation 4.3 than in equation 4.1 due to the presence of the surface layer. The result is that the volumetric strain rate, \( \dot{\varepsilon}_\rho \), will be lower for smaller inclusions at the same inclusion volume fraction and surface layer thickness. Even a small decrease in \( \dot{\varepsilon}_\rho \) will result in a significant decrease in the final density of the composite since the sintering takes place over an extended period of time.

The formation of this region of low density is further enhanced if the matrix grains adhere to the surface of the inclusion. If matrix grains adhere to the surface of the inclusions, they are not able to approach each other. As a result, neither densification nor coalescence can occur. This agrees well with the conclusions of Lange,35 Weiser and De Jonghe,36 and others that consider rearrangement and particle coalescence necessary for densification. The adherence of the ZnO matrix particles to the SiC inclusions is enhanced by the presence of a thin surface layer of SiO₂ on the SiC as found by Rahaman et al.37

4.3 Effect of Inclusion Clustering

Clustering of the inclusions can cause the matrix sinterability to either increase or decrease, depending upon the extent of clustering and the inclusion/matrix interactions at the interface. If there are no interface effects and the inclusion clusters are fully dense, the clusters are equivalent to larger inclusions of the same
volume fraction, figure 4.3a. Then, there will be no effect upon the sinterability, since there has been no change in the effective volume fraction of inclusions. However, the inclusions will probably form clusters of 35 to 60% of theoretical density resulting in an increase in the effective volume fraction of inclusions and a resultant decrease in the sinterability, figure 4.3b. A strong matrix/inclusion interaction will result in a portion of the matrix at the interface being associated with the inclusion, as described in the section above. In this case, clustering can result in a decrease in the effective volume fraction since there will be less inclusion/matrix interface, figure 4.3c. The combination of these two effects will be difficult to describe without a very detailed picture of the cluster density, extent of clustering, and interfacial effects.

The simple description of the possible effects of clustering are further complicated by the various stress/strain relationships that constrain the system. The first of these is that there can be no normal stresses at the surface of the compact in the case of pressureless sintering, figure 4.4a. The second is that the shrinkage rate, $\dot{\varepsilon}_\rho$, at any point in the matrix must either be the same as that at any other or large scale shear processes must occur to accommodate the mismatch, figure 4.4b. As the system becomes more clustered it becomes more heterogeneous and the shrinkage mismatch can become extreme, even resulting in the formation of cracks in the matrix, figure 4.4c. This result has been described by Evans et al. 14, and Kellet et al. 19.
5.0 Results and Discussion

It was found that matrix sinterability of a ZnO/SiC composite was strongly dependent upon size, volume fraction, and degree of clustering of the SiC inclusions. The matrix density after a given heat treatment decreases as the inclusion size is decreased, the volume fraction is increased, or the degree of clustering is increased; this is illustrated schematically in figure 5.1. The effect of changing the volume fraction of inclusions has been shown previously by other authors\textsuperscript{17,24}, therefore the results of this study will be discussed only briefly. The effect of changing the size of the inclusions has not been described before, and will be covered in some detail. The effect of inclusion clustering has not been described before and will be covered in a qualitative manner. The coverage is qualitative because of the difficulty in describing the degree of clustering and of approaching the subject from a theoretical standpoint.

5.1 Inclusion Volume Fraction

The effect of adding non sintering inclusions to a sintering matrix is to decrease the final density of the matrix after a given heat treatment. Increased fractions of inclusions cause the densification to be decreased further as shown in figure 5.2. This study investigated the effect of the volume fraction of inclusions using three different sizes and five different volume fractions of inclusions. The matrix densities after four hours of sintering are summarized in table 5.1 and figure 5.3 for the powders prepared in hexane/Oloa.

Figure 5.3 shows that the matrix density decreases with either an increase in the volume fraction of inclusions or a decrease in the size of the inclusions. This
trend is described fairly well for the larger volume fractions, 0.10 to 0.20, by equation 5.1

\[ \rho \propto c f \]  

where the constant c is an increasing function of the inclusion size.

<table>
<thead>
<tr>
<th>Volume Fraction</th>
<th>0.000</th>
<th>0.025</th>
<th>0.050</th>
<th>0.100</th>
<th>0.150</th>
<th>0.200</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Matrix Density</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75 ( \mu \text{m} )</td>
<td>88.04</td>
<td>76.76</td>
<td>76.26</td>
<td>77.55</td>
<td>68.16</td>
<td>65.38</td>
</tr>
<tr>
<td>10 ( \mu \text{m} )</td>
<td>88.04</td>
<td>75.48</td>
<td>77.01</td>
<td>74.61</td>
<td>64.16</td>
<td>62.85</td>
</tr>
<tr>
<td>2 ( \mu \text{m} )</td>
<td>88.04</td>
<td>79.33</td>
<td>78.36</td>
<td>65.72</td>
<td>59.15</td>
<td>58.25</td>
</tr>
</tbody>
</table>

The densities for the lower volume fractions of inclusions, 0.025 and 0.05, are less consistent and lower than would be predicted by equation 5.1. This effect is probably the result of two different mechanisms. First the back stress is probably less linear as a function of the volume fraction than is assumed in the theory due to the overlap of the stress fields of nearby particles. Secondly, heterogeneities other than the inclusions can play a significant role in the matrix sinterability and may be the major cause of the lower densification rate at these low volume fractions of inclusions. It may be that small amounts of matrix agglomeration may be catalyzed by these small volume fractions of inclusions.

5.2 Inclusion Size

The density at a given sintering time is very strongly dependent upon the inclusion size for compacts of the same initial density and inclusion volume
fraction as shown in figure 5.4. For the largest inclusions, 45 \mu m and 75 \mu m, there is little difference in the matrix densities. The largest effects are seen for the smallest inclusions, 0.5 \mu m to 3 \mu m. Except for the longest sintering times these inclusions are larger than the matrix grains in the bulk.

Figure 4.1 showed a fracture surface illustrating that the matrix particles near the surface of the inclusion do not grow while the particles in the bulk have grown and densified. The primary mechanism of particle growth in porous compacts has been shown to be coalescence. Therefore, the lack of grain growth indicates that the particle centers have not approached, and densification has been prevented in this surface layer.

The volumetric strain rate \( \dot{\epsilon}_p \) is found to be a very strong function of time, figure 5.5, varying by over three orders of magnitude during the experiment. The ratio of \( \dot{\epsilon}_p \) for the different inclusion sizes is seen to remain nearly constant during the experiment. The constant ratio is particularly noticeable after the initial temperature transient of 5 minutes is over. The lower final density of the compacts containing smaller inclusions appears to arise from a lower densification rate throughout the sintering rather than a change in the densification behavior at some point.

Equation 4.1 states that the volumetric strain rate, \( \dot{\epsilon}_p \), can be expressed as a function of the effective volume fraction of inclusions, \( f_e \)

\[
\dot{\epsilon}_p = \kappa \left( 1 + 4f_e / (1-f_e) \right)^{-1}.
\]

where \( \kappa = \Sigma / \phi_m \). For the diffusion mechanisms that are active in ZnO at 1000K the proportionality should scale as \((G/G_0)^2\). This is plotted in figure 5.6 for a
variety of inclusion sizes and volume fractions at three different densities. The effective volume fraction was computed using a surface layer composed of a single layer of matrix particles. As the inclusion size decreases or the volume fraction increases the value of \( (1 + 4f_e/ (1-f_e))^{-1} \) decreases from one for the pure material. A portion of the scatter in the data for \( \rho = 0.55 \) can be attributed to the fact that most of these data are from first 5 minutes of sintering, which is during the thermal transient. It is proposed that the reason for the lack of agreement for this portion of the data is that the establishment of the full hydrostatic back stress state requires a period of time.

The regression analysis of these data does not pass through the origin as is expected. This underestimate of the effect of the inclusions is a very good indication that the backstress model does not completely describe the effect of the inclusions on the matrix sinterability. Therefore, surface layers, clustering, and chemical effects must play a fairly important role in the decrease of the matrix sinterability caused by the addition of inclusions.

5.2.1 Powders Dispersed in Acetone

The data discussed at the beginning of this section are from powders which were dispersed in acetone. The results from these powders were not as reproducible as was desired. The reproducibility of the results decreased as the powders aged even though they were all stored in a desiccator under dry nitrogen. Upon drying, these powders were rather strongly agglomerated and it was necessary to grind and sieve them prior to die pressing. These agglomerates were not completely broken up as can be seen in figure 5.7. There were also indications that SiC tends to cluster in acetone.
5.2.2 Powders Dispersed in Hexane

The powder preparation method was changed to increase the reproducibility of the results and decrease the potential for inclusion clustering. A solution of 0.5 volume percent Oloa 1200 in hexane was used to mix the powders. The powders prepared in hexane were much less agglomerated than those prepared in acetone and there was no need for grinding prior to die pressing. The SiC was also observed to settle out of suspension more slowly in this solution than in acetone indicating that less clustering and flocculation was occurring.

The matrix density for composites containing 5% SiC is observed to decrease as the inclusion size decreases. However, a very dramatic shift in behavior is seen for inclusions which were approximately 5 μm in diameter. The matrix density is seen to decrease much more rapidly for larger inclusions than for smaller inclusions, figures 5.8 and 5.9. This result was verified in several cases by using two different powder samples prepared using the same amounts of all components. The only difference between samples of the same composition was the order in which the ZnO and SiC were added to the hexane/Oloa solution. In all but one case, samples of the same composition sintered to the same density.

The samples containing 5% 5μm SiC sintered to dramatically different densities, ≈ 55% and ≈ 83% of theoretical ZnO density. The lower density pellets were made by adding the ZnO to the hexane/Oloa first and the higher density pellets were made by adding the SiC first. The difference in the sintering behavior is proposed to be a result of the adsorption of Oloa on the surface of the first particles added to the solution. It is proposed that this layer is strongly adsorbed on the SiC and weakly adsorbed on the ZnO.
When the SiC is the first set of particles added to the solution it is coated with a thin layer of Oloa. After the Oloa is burnt off the inclusion is located in an oversize hole preventing the buildup of the backstress in the matrix until some of the densification has occurred. This results in the SiC inclusions having a slightly smaller effect than would be predicted based upon the volume fraction and size of the inclusions. The microstructure of a 5% 5μm SiC composite is shown in figures 5.10a and 5.11a. These figures show nearly full densification of the bulk with areas of somewhat lower density around the inclusions. The low density areas are located between SiC particles, and the ZnO grains are nearly the same size as the ZnO grains in the bulk. The areas of low density are associated with the SiC particles indicating that the lack of complete densification is a result of the back stresses since these stresses are higher near the matrix/inclusion interface.

When the ZnO is the first set of particles added to the solution the Oloa weakly adsorbs on to the ZnO surface. Upon addition of the SiC the Oloa is strongly attracted to the SiC and causes a layer of ZnO particles to bond to the SiC particles, figures 5.10b and 5.11b. The ZnO particles in this layer can not easily move as indicated by the lack of grain growth. As a result this layer is effectively a portion of the inclusion resulting in an increase in the effective volume fraction of inclusions.

A very thin layer of ZnO particles was observed to cover the surface of the larger inclusions as shown in figure 5.12. The extent of this affected layer was observed to decrease as the size of the inclusion increased. This causes the ratio of the effective radius to the actual radius of the inclusion, $R_e/R$, to increase as the inclusion size decreases and figure 5.13.
5.3 Clustering

As was discussed in section 4.3 the inclusions can cluster in a variety of different manners with various expected effects on the matrix sinterability. The larger inclusions were found to form loose clusters containing up to a dozen SiC particles with the most common clusters containing two or three, figure 5.14. The most obvious form of clustering in these compacts were the areas that seemed to contain fewer inclusions than would be expected based upon the overall volume fraction of inclusions, figures 5.14 and 5.15. The clustering observed in these composites is felt to be the result of random fluctuations of the number density of inclusions during the green processing rather than attractive interactions between inclusions.

A simulation of inclusion clustering was done in two dimensions to compare with the actual micrographs of the composites. The degree of clustering could be varied by use of a parameter to simulate inter inclusion forces, both in magnitude and sign. Plots of these simulations are shown in figure 5.16. In the upper plot the inclusions have been biased to decluster, the middle has had no bias, and the lower has been biased to cluster. Comparison of figures 5.14a and 5.16b shows that the types of inclusions are very similar. This leads to the conclusion that there must be relatively little clustering among the larger inclusions contrary to conclusion reached from simple visual inspection.

The fact that the inclusions are not homogeneously distributed will cause problems with the correlation of the experimental results and the theory. Problems arise because the theory is based upon an extremely homogeneous system, composed of equal sized spherical inclusions at the center of equal sized spherical domains.
A real composite will have a distribution of inclusion sizes, domain sizes, and domain shapes, the latter is illustrated in figure 5.17. It is felt that the related problems of domain size and shape will have significant effects on the matrix sinterability. This is because the stress field is proportional to $r^{-3}$, where $r$ is the distance from the center of the inclusion and the distance to and stress state at the edge of the domain will not be the same as in the spherical case. It is felt that any perturbation from the homogeneous case will result in higher back stresses and lower sintering rates. Future studies are intended in this area.

The clusters in the compacts containing inclusions 2µm in diameter and smaller were observed to be much more compact and contain more SiC particles than those of the larger inclusions. Only a portion of the SiC particles were observed to be contained in these large clusters containing hundreds of particles. Two slightly different types of clusters were seen in different samples. The first were composed primarily of SiC particles, contained only a small portion of the total SiC, and were very poorly adhered after sintering, figure 5.18a. The SiC particles on the surface are a result of dusting the sample with compressed air. The second were composed of a mixture of SiC and ZnO particles, contained a larger fraction of the total inclusions, and were well adhered, figure 5.18b.

The composites containing the pure SiC clusters also exhibited a nice even distribution of inclusions throughout the matrix. The clusters were easily seen as a very rough area with distinct SiC particles, figure 5.19a. The interface between the cluster and the matrix displays a thin layer of small matrix particles, figure 5.19b. There is also a small cluster of five particles at the right hand side of this figure. The large cluster is nearly pure SiC but there are a few isolated ZnO particles distributed among the SiC particles in the cluster, figure 5.20a. The small
cluster is shown in detail in figure 5.20b and the SiC/ZnO interface appears to be very similar to the clusters of larger particles in figure 5.12. This indicates that the actual interaction between the matrix and inclusion particles is not dependent upon the inclusion size.

The composites containing the mixed SiC/ZnO clusters appeared to have a large portion of the SiC contained in the clusters. These clusters had a slightly darker contrast in the SEM, figure 5.21a, but it was necessary to use higher magnifications to confirm that these dark areas were indeed SiC clusters. The reason for this lack of strong contrast is evident in figure 5.21b, the SiC is only about 30% of the cluster, the remainder is ZnO. The clusters in these composites were smaller and more numerous than those of the composites which contained pure SiC clusters. The clusters are a mixture of both SiC and ZnO as can be seen in figure 5.22a. The main matrix of these composites contains very few inclusions, figure 5.22b, indicating that most of the SiC particles are clustered.

These two different types of clustering are predicted to have different effects on the matrix sinterability. The pure SiC clusters in the 5% 2μm SiC composites only contain a small fraction of the total inclusions. The effective volume fraction is only increased slightly over the actual volume fraction since only a portion of the inclusions are contained in the inclusions and there is not a strong interface interaction. The mixed SiC/ZnO clusters of the 5% 0.5μm SiC composites contain nearly all of the inclusions. These clusters contain approximately 30% SiC, resulting in an increase in the effective volume fraction by a factor of approximately three. The composite containing the pure clusters sintered to ≈ 78% matrix density and the mixed clusters sintered to ≈ 63% matrix density. The lower density of the composites containing mixed clusters indicates that it is the
effective volume fraction and not the actual volume fraction of inclusions which affects the matrix sintering rate.

In some cases there is a surface layer of ZnO at the SiC/ZnO interface which does not densify. This is much more prevalent in the composites containing larger SiC inclusions, > 5μm, figure 5.23a. It is felt to be a result of the processing in the green state rather than chemical interactions during the sintering. There should be very little chemical interaction between the SiC and ZnO at the sintering temperature of 1000K used in this study. This is supported by the clean ZnO/SiC interfaces seen in the fracture surfaces, the minimal neck formation at the interface, figure 5.23b, and chemical analysis using scanning auger microscopy which indicated no Si on the matrix of a fracture and only low concentrations of Zn in a 0.02 nm thick layer on the SiC surface.

The total surface area of the inclusions is proportional to \( r^{-1} \), where \( r \) is the inclusion radius. As the inclusion radius increases there is less SiC surface for adsorption of Oloa, resulting in a portion of the Oloa binding to the ZnO particles. As the solvent is evaporated these Oloa coated ZnO particles are attracted to the SiC surface resulting in the adherence of a layer of ZnO particles to the inclusion surface. This hypothesis is supported by the strong dependence of the final density upon the order of addition of the ZnO and SiC to the solution for the 5% 5μ SiC composite. This indicates that it is not only necessary to have a solvent system that will disperse the second phase, but that it is necessary to make sure that there are no adverse effects of having more dispersant than can be adsorbed upon the inclusion surface.
6.0 Conclusions

It is seen that the effective volume fraction of the inclusions is a function of the actual volume fraction, the size of the inclusions, the extent of inclusion clustering, and the green body preparation. Experimental evidence is presented that the matrix densification is strongly dependent upon the inclusion size. At a constant volume fraction of inclusions the matrix sinterability decreases with decreasing inclusion radius. The extent and type of inclusion clustering was found to be dependent upon the green body processing and have a variety of effects upon the matrix sinterability.

A layer of matrix particles is found at the inclusion/matrix interface does not densify due to lack of particle coalescence. This zone of matrix particles at the interface is prevented from densifying fully and has two major effects on the matrix sinterability; it is a low density region which prevents the attainment of full density, and it acts to increase the effective radius and volume fraction of inclusions. The incorporation of this observation as an increase in the effective volume fraction of the inclusions allows the current theory to be extended to explain the lower matrix sinterability seen in composites containing smaller inclusions.

Three different types of clustering were found to occur in composites of different inclusion sizes. The larger inclusions, > 5μm, ended to form clusters of a few inclusions which were probably the result of random fluctuations in the number density of inclusions. The smaller inclusions formed two types of clusters containing up to a few hundred inclusions. In the first case the clusters were nearly pure SiC and contained only a portion of the total number of inclusions, the
remainder were distributed throughout the matrix. The clusters in the second case
were a mixture of SiC and ZnO and contained nearly all of the inclusions. It was
felt the second, mixed type cluster would decrease the matrix sinterability the most
since it results in the largest increase in the effective volume fraction of
inclusions.

The method of green body preparation was found to have a very significant
effect upon the matrix sinterability even when identical powders and solutions
were used. It was found that the order of addition of the matrix and inclusion
particles to a dispersant solution changed the matrix density from 83 to 55 percent
of theoretical. The dispersant used in this study is good for dispersing the SiC
inclusions. Addition of the ZnO first resulted in the formation of a very complete
coating of non-sintering ZnO on the inclusion surface causing an increase in the
effective volume fraction of inclusions and lower sintered density.

Unless the inclusions are very strongly dispersed they will be located rather
inhomogeneously as was shown in both the simulations and the experiments. The
degree of inhomogeneity can have rather strong effects upon the sintering rate of
the matrix as was pointed out earlier. The naturally occurring packing
inhomogeneities can possibly account for the observed lower sintering rates than
the theory would predict. The current theories do not account for any
inhomogeneities in the inclusion packing. Modifications to the theory will have to
be made to account for the effects of inclusion clustering on the sintering rate.
References


33 L. C. De Jonghe, M. N. Rahaman, and M. W. Weiser, "Densification of Particulate Composites", unpublished work


59 M. W. Weiser, "Rearrangement During Sintering of Two Dimensional Arrays of Spheres", M. S. Thesis, University of California, Berkeley (1985)

60 Rowland Cannon, private communication.

Figure 1.1 Schematic drawing showing the inclusions used in transformation toughening and whisker reinforcement.
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Figure 5.13 The normalized effective inclusion radius, $R_e$, versus log (inclusion radius).
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Figure 5.22 Micrograph of a 63% dense composite containing 5% 0.5\(\mu\)m SiC, (a) high magnification image of the cluster showing approximately 30% large SiC particles in a ZnO matrix, (b) high magnification image of the main ZnO matrix showing the lack of SiC in this area.
Figure 5.23 Micrographs of the ZnO/SiC interface, (a) the layer of ZnO adhered to the SiC surface, (b) high magnification of the interface showing the lack of chemical interaction between the two powders.