CO-SINTERING OF INTEGRATED CERAMICS:
FUNDAMENTALS, OBSERVATIONS AND DESIGN GUIDELINES

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by

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ABSTRACT

There is considerable interest in developing a comprehensive and robust model for simulating sintering behavior of co-fired systems. The development of a reliable modeling tool entails knowledge of measured thermo-mechanical properties such as viscosity and viscous Poisson’s ratio. To measure the viscosity of densifying materials as a function of both porosity and temperature, isothermal cyclic loading dilatometry (ICLD) is proposed as a convenient technique. We demonstrate its merit relative to constant load techniques in minimizing the stress history effects (changes in shrinkage anisotropy and sample microstructure) that arise due to the application of an external load. A constant load test overestimates the viscosity by an order of magnitude compared to a cyclic load test. To obtain accurate viscosity data, maximum loading rates and longer unloading periods are desirable as they reduce effects of shrinkage anisotropy on viscosity values.

A novel technique, based on the concept of pressureless constrained sintering and the viscous analogy, for determining the viscous Poisson’s ratio of sintering materials is proposed. The method involves measuring the sintering rate of a free-sintered specimen, and a specimen constrained by two non-sintering layers. The viscous Poisson’s ratio varied from 0.25 at ~ 74% density to about 0.45 at ~ 93%, which agreed well with model
predictions. The method applies only during the intermediate stage of densification, because the material is viscous during this period of sintering.

The uniaxial viscosity data of three commercial LTCC systems i.e. DuPont 951Tape (DU), Heraeus CT2000 (CT), and Ferro A6 (FE) were measured by cyclic loading dilatometry. The viscosity initially decreases with temperature, changes little during the intermediate stage and increases towards the end of densification. The viscosity increased sharply beyond the onset of crystallization. At slower heating rates, the viscosity increased at lower temperature, because of densification and crystallization. The isothermal viscosity data range from 0.1 to 100 GPa.s between 73% and 95% density. Ceramic particle-filled glasses, DU and CT systems showed a higher isothermal viscosity compared to pure glass system i.e FE. From master viscosity curves based on isothermal data, the activation energies for viscous flow were \( \sim 375 \pm 30 \text{ kJ/mol} \), \( 450 \pm 10 \text{ kJ/mol} \) for DU and FE, respectively. These energies were comparable to values obtained from the master sintering curve approach.

Predicting the sintering viscosity accurately is key to developing reliable sintering models. A theoretical understanding for the observed viscosity of LTCC materials, and a framework for predicting the evolution of their viscous behavior during sintering was developed. The complex viscosity of these materials is affected by a host of interdependent factors such as the base glass composition, temperature, porosity, particle size and distribution, contact area, volume fraction of filler particles, phase separation, crystallization and heating rate. A model based on the simplifying assumption that these
variables are mutually exclusive is presented. The model predictions were in reasonable agreement with measured data.

The concept of constrained sintering has attracted a lot of attention as it offers the advantages of tight dimensional tolerances and minimal distortion. The effect of an external constraint (uniaxial compression and pressure-less constraint) on the microstructure, density and shrinkage anisotropy during the sintering of CT and DU were studied. The difference in the viscous behavior of the two materials led to significantly different microstructures, density and shrinkage anisotropy. The shrinkage anisotropy constant of DU was significantly higher than that of CT and non-linear under uniaxial compression. A combination of higher viscosity, lower viscous Poisson’s ratio, and higher constraining stresses led to lower densities for CT compared to DU. The maximum tensile stress due to a pressure-less constraint, assuming the viscous model, was in the range of \(~10-100\) kPa. The calculated uniaxial compressive stress required for zero radial shrinkage in the perpendicular plane was in the range of \(~10 – 180\) kPa.

To evaluate the shrinkage compatibility of different components and validate the measured thermo-mechanical properties, we used in-situ observations of curvature during co-sintering of bilayers of materials including LTCC, silver and alumina, and the bilayer strip model. There was good agreement between the measured viscosity data and model predictions. The rate of curvature follows the differential sintering kinetics between the two layers and is modulated by changes in their viscosity. The viscosities were used to calculate viscous stresses in the bilayers. For silver-LTCC bilayer, the maximum tensile
stress in the silver and LTCC layers are \(~\text{100 kPa}\) and \(\text{25 kPa}\), respectively. The bilayer strip model provides useful guidelines for designing co-fired systems. For a given differential sintering rate, the model predicts maximum warpage for \(m^2n=1\), where \(m\) and \(n\) are the relative thickness and viscosity, respectively.
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yasya sarve samārambhāḥ
kāma-saṅkalpa-varjītāḥ
jñānāgni-dagdha-karmānaṁ
tam āhuḥ paṇḍitaṁ budhāḥ

One is understood to be in full knowledge whose every endeavor is devoid of desire for sense gratification. He is said by sages to be a worker for whom the reactions of work have been burned up by the fire of perfect knowledge.

- Bhagavad-Gita 4.19, Lord Krishna to Arjuna
Dedicated to

My guru, God and my late mother
Chapter 1

INTRODUCTION

Integrated ceramics are everywhere. In microelectronics, integrated ceramic packaging is increasingly needed to limit the number of surface mounted components and provide greater functionality. The next generation of packages will integrate the functionality of capacitors, inductors, resistors and/or mechatronic, biological, photonic and chemical functions. Low Temperature Co-fired Ceramic (LTCC) technology has led the so-called ‘microsystems’ revolution, and is considered key to future size reduction and passive component integration. Other important co-fired technologies such as multilayer ceramic capacitors, solid oxide fuel cells, and functionally graded materials have revolutionized the way we design materials and have spawned innumerable applications. However, two main issues that confront the integration include sintering mismatch and the chemical/physical incompatibility between the different components, and these remain largely unaddressed.

Monolithic bodies usually sinter to uniform shrinkage and homogenous microstructures. The sintering of integrated ceramics, however involves non-uniform shrinkage because of the constraints imposed by constituent materials as different materials have different shrinkage behavior. The constraint prevents the shrinkage of a sintering body by inducing a tensile stress that counteracts the hydrostatic sintering stress. This has been shown to result in inhomogenous microstructures, lower fired densities,
and even defects such as cracks, porosity and distortion. It is thus important to understand the origin of these co-sintering stresses and tailor material properties so as to minimize them and prevent defects.

There is a growing interest in the development of a comprehensive modeling tool for prediction of dimensional and shape changes during co-sintering. Knowledge of material properties such as uniaxial viscosity and viscous Poisson’s ratio, and how they evolve during the sintering process, is essential for optimal sintering of co-fired systems and for use in continuum sintering models. Little is known about how these properties evolve during sintering, and how they change with firing conditions. Different models have been proposed to predict the evolution of these properties with densification, but these disagree in their predictions. Thus, there is a clear need to measure these properties for developing reliable models.
1.1 OBJECTIVE OF RESEARCH

The main focus of this research is to develop a fundamental understanding of the processing of co-sintered systems that will enable the development of sintering models which would allow predictions of stresses, shrinkage and deformation during device production. The key objectives of this research, therefore, include,

- Establish testing protocols to determine the viscosity and viscous Poisson’s ratio of the constituent materials
- Establish testing protocols to evaluate shrinkage compatibility of co-fired systems.
- Test and further develop models for the evaluation of stress and damage evolution in co-fired systems.
- Investigate the problem of constrained sintering with attention to microstructure, shrinkage anisotropy and physical properties
- Develop guidelines for optimal co-sintering of integrated ceramics
Chapter 2

LITERATURE SURVEY

This chapter reviews the recent literature on co-sintering (or constrained sintering) with relevance to LTCC technology. The chapter is divided into three sections: 1) a brief discussion of sintering theory with emphasis on viscous sintering, 2) a detailed review of constrained sintering and continuum sintering models that have been developed to describe the viscous behavior of glass-based and polycrystalline systems, and 3) a review of the historical development of LTCC technology and key studies on co-sintering problems such as distortion and zero-shrinkage.

2.1 SOLID-STATE SINTERING

Frenkel [1] assumed solid state sintering occurred by the deformation of crystalline particles under the influence of surface tension as would occur for amorphous materials. However, predictions of his model did not agree with experimental results. Kuczynski [2] demonstrated that sintering occurs by diffusive processes and proposed models to describe the early stages of sintering for different transport mechanisms and diffusion paths. Coble [3] developed models for later stages of sintering for lattice or GB diffusion. Although, later studies [4-8] have refined these basic ideas, the early models describe the sintering processes reasonably well.
2.1.1 Stages of Sintering

The sintering process is typically divided into three stages based on the connectivity of the microstructure: initial, intermediate and final. In the initial stage there is growth of the necks between individual powder particles with the radius of neck ~0 - 0.2 of the particle radius. In the intermediate stage, the pores approximate to continuous pore channels coincident with the three-particle junctions. And, in the final stage, the pore channels break up into isolated pores located at four-grain junctions, which occurs at ~92% relative density. The driving force for sintering is reduction in surface energy. In case of coarsening, there is no pore removal and shrinkage, while densification results in both. To determine which dominates (coarsening or densification), it is necessary to determine the rates of surface area change.

2.1.2 Initial stage

The simplest initial stage sintering model is the two-particle model. A basic premise of the model is that matter is transported from high chemical potential surface to low chemical potential. Convex surfaces and grain-boundaries (GBs) are regions of high chemical potential. Evaporation and condensation and surface diffusion result in coarsening, while GB diffusion results in densification and lattice diffusion can result in either, depending on the source of matter (convex surface or GB).

Driving force for transport is the difference in concentrations arising from difference in chemical potential that results from curvature differences. Positive curvature surfaces (convex) correspond to compressive stresses and have a higher vapor than a flat
surface. And, the converse is true for negative surfaces. Vapor pressure difference leads to transport through the vapor phase to the neck, while stress difference leads to transport by diffusion to the neck. Both mechanisms will be active and the neck growth is the sum of the two processes.

The rate of neck growth rate during the initial stage of sintering, assuming that all the transport processes are independent and additive, can be expressed as [9],

\[
\frac{dx}{dt} = \frac{C_1 \gamma D_{l} R}{x^3} + \frac{C_2 \gamma D_{n} R^2}{x^5} + \frac{C_3 \gamma D_{g} R^2}{x^5} + \frac{C_4 \gamma p_o R}{x} \quad (2.1)
\]

where \(x\) is the radius of the neck, \(\gamma\) is the surface energy, \(R\) is the particle radius, \(C_i\) is a constant which takes into account the specific diffusion path and the geometry of the model, \(p_o\) is the vapor pressure, and \(D_i\) is the diffusion coefficient for lattice (\(l\)), grain boundary (\(b\)), or surface (\(s\)) diffusion.

### 2.1.3 Intermediate stage

During the intermediate stage of sintering, the pore structure transitions to tubular pores lying along particle junctions. The pore channels shrink in diameter until the geometry becomes unstable to fluctuations of the surface (Rayleigh Instability). While pore channels can shrink by surface diffusion, the path length for transport becomes very large and this shrinkage is controlled by lattice or GB diffusion [6].
2.1.4 Final stage

The final stage is the most crucial for most applications. The final properties of sintered materials are largely decided by final stage sintering. During this stage, the tubular pores shrink to the point of becoming unstable and break to form isolated pores. While surface diffusion can change the shape of the pores, shrinkage of the pores is controlled by GB or lattice diffusion. For nearly spherical pores, the flux of matter, $J$, to the pore is approximately given by,

$$J = K_1 D_1 \Delta c \left( \frac{r R_m}{R_m - r} \right)$$

(2.2)

where $K$ is a geometric constant, $D_1$ is either the lattice or GB diffusion coefficient, $\Delta c$ is the concentration difference, $r$ is the radius of the pore, and $R_m$ is the effective matter source radius.

2.1.5 Rate of sintering

Temperature (which controls the rate of diffusion) and particle size (which controls the length scale of diffusion) are the two most important factors that determine the rate of sintering. Reduction in particle size results in increase in sintering rate. The size dependence is due to both increase in the driving force (curvature changes) and the kinetics (diffusion length changes). Decrease in sintering temperature can be beneficial in preventing decomposition or evaporation of a material, reducing energy use and inhibiting grain growth. Changes in sintering temperature can also lead to changes in
dominant sintering mechanism leading to different microstructures with different properties.

**2.1.6 Dihedral angle effect**

The dihedral angle, $\psi$ for a pore on a grain boundary, is defined by the ratio of the grain boundary energy, $\gamma_b$ to the surface energy, $\gamma_s$, such that

$$\frac{\gamma_b}{\gamma_s} = 2 \cos \left( \frac{\psi}{2} \right)$$

(2.3)

The curvature of the pore surface increases as the dihedral angle increases and so the driving force increases. When a pore is located on the junction of 3 or more grains, the curvature of the pore is determined by both the dihedral angle and no. of grains the pore contacts. When the dihedral angle is too low, pores will be stable in the structure and there will be a limiting density even though removal of pores would lower the energy of the system. As grain growth occurs, the number of grains intersecting the pore will decrease so that the pores will become unstable and shrink. However, as the grain size increases, the diffusion distances increase and the shrinkage rate slows down, making pore removal a relatively slow process.

**2.2 LIQUID-PHASE SINTERING (LPS)**

For LPS, liquid must be present at sintering temperature, there should be good wetting (low contact angle), and appreciable solubility of solid in liquid [10, 11]. Three stages densification during LPS include, 1) rearrangement, 2) solution-precipitation to 3) final pore (or vapor-phase) removal stage. There exists significant overlapping in
connecting stages in actual powder compacts. Kwon and Messing [12] developed a ternary LPS diagram. In this, stages of LPS and dominant sintering mechanisms are mapped as a function of relative volume fractions of solid, liquid, and pores. Densification by LPS is driven by the thermodynamic driving force to minimize interfacial free energy of the system. If good wetting and no grain growth are assumed, then the liquid-vapor interface is most important in determining the driving force.

### 2.2.1 Rearrangement

Earlier models on axial symmetry do not adequately explain the driving force. In this stage, both solids and liquid particles rearrange, because of unbalanced capillary forces around solid particles as dictated by particle contact and liquid meniscus geometries that result in shearing and rotational movements of particles. As density increases, particles experience increasing resistance to rearrangement due to crowding by neighboring particles until the formation of a closed packing structure.

The driving force for rearrangement arises because of an imbalance in capillary pressure as a result of,

- Particle size distribution
- Irregular particle shape
- Local density fluctuation in powder compact
- Anisotropic material properties

If the geometry of the particle contact is known, the driving force can be calculated for various particle shapes and contact geometries. Kwon's model [13] is based on the theory
that the viscous flow of a liquid sandwiched between solid particles limits the rearrangement process. The densification rate, assuming a Newtonian liquid is given by,

\[
\frac{d(\Delta \rho / \rho_s)}{dt} = A(g) \frac{\gamma_{lv}}{\eta r_s}
\]  

(2.4)

where \(\rho\) is the relative density, \(t\) is the time, \(A(g)\) is the geometrical constant, \(\gamma_{lv}\) is the surface tension, \(\eta\) is the viscosity of liquid, and \(r_s\) is the radius of the solid particle. The volume fraction of liquid is an important factor in determining the extent of rearrangement. At approximately 30-35 vol% liquid, full densification can be achieved by rearrangement alone [10, 11]. The sintering of powder compacts with excessive liquid is quite different from LPS [14]. This will be discussed under viscous sintering below.

### 2.2.2. Solution-precipitation

When rearrangement is insignificant, dissolution of the solid at grain contacts results in center-center approach of particles. The solubility is proportional to the normal traction at grain contacts from the capillary forces (Laplacian forces) that draw the particles together. The dissolution rate of the solid decreases as the contact area increases due to simultaneous reduction of effective stress at the contact area. Accordingly, densification rate decreases as density increases. The densification rate can be controlled (or rate-limited) by either diffusion or interface reaction [13],


Diffusion-controlled rate:

$$\frac{d(\Delta \rho / \rho_0)}{dt} = B(g) \gamma_{lv} \delta D_v c \Omega r_s^{-4}$$  \hspace{1cm} (2.5)

Interface reaction-controlled rate:

$$\frac{d(\Delta \rho / \rho_0)}{dt} = C(g) \gamma_{lv} K c \Omega r_s^{-2}$$  \hspace{1cm} (2.6)

where, $B(g)$ and $C(g)$ are the geometrical constants depending on $V_s$, $V_l$ (volume fraction of solid and liquid, respectively), $\rho$, and the dihedral angle, $\delta$ is the thickness of liquid boundary, $c$ is the solubility of solute, $\Omega$ is the molecular volume of the solute, $k$ is the Boltzmann constant, $K$ is the interface reaction constant, and $T$ is the absolute temperature. In both cases, the rate strongly depends on the particle size. Interface reaction is more likely with smaller particles. This is consistent with a simple geometrical analysis, in that the larger grain requires a longer diffusion distance from the grain contact to pore sites for densification. If grain-growth occurs rapidly, the rate limiting step may shift from interface-reaction to diffusion.

2.2.3 Pore removal

During intermediate stage of sintering, interconnected pore channels pinch off to form closed pores in the density range from 0.9-0.95 depending on the material. After pore closure, the driving force for densification is given as,
\[
DF_{\text{final}} = \frac{2\gamma_{lv}}{r} - \sigma_p
\]

where \(\sigma_p\) is the vapor pressure inside the pore. If there is growth and coalescence of pores, and increase in internal gas evolution, then, de-densification can occur (i.e. pore growth and bloating). Pressure assisted sintering helps achieve lower sintering temperatures, higher final density, and a more homogeneous microstructure [15].

### 2.2.4 LPS issues

In real compacts, key issues include liquid penetration into aggregates/agglomerates limiting densification, formation of liquid pools due to heterogeneous liquid redistribution and liquid-pore filling processes, and influence of sintering atmosphere on final stage densification. Optimum sintering temperature can be estimated using phase equilibria and viscosity. Compositions for LPS could be chosen away from eutectics such that volume fraction of liquid increases slowly with temperature. This can help minimize warpage and migration of liquid associated with temperature gradients during heating.

### 2.3 VISCOUS SINTERING

Noncrystalline materials sinter by viscous flow, which reduces their surface area and thus the free energy. This is in contrast to crystalline materials, where sintering involves diffusion of atoms or vacancies in the crystal lattice. For the case where there
are no constraints, the rate of densification during viscous sintering can be estimated if the viscosity, surface tension and pore size are known. In practice, however, materials are often constrained either internally or externally. For example, a material maybe attached to a substrate that either does not shrink or has a different sintering behavior. Another important type of constraint is the presence of crystals or rigid inclusions that retard the shrinkage of the matrix. In such cases, the sintering rate can be calculated if the mechanical properties of the porous material are known. This is separately discussed in the section on constrained sintering.

Frenkel [1] was the first to establish a theoretical basis for viscous sintering. He suggested that the energy needed to drive viscous flow is provided by reducing the surface area of the body. The rate of sintering is determined by equating these two energies. He analyzed the coalescence of two spherical particles. The distance, \( L \), between the centers of the spheres was found to decrease linearly with time, \( t \), according to,

\[
\frac{L(0) - L(t)}{L(0)} = \frac{3\gamma t}{8\eta a} \tag{2.8}
\]

where \( \gamma \) is the surface tension, \( \eta \) is the viscosity, and \( a \) is the initial radius of the spheres. The linear shrinkage rate has been verified experimentally. Jagota and Dawson [16, 17] showed through numerical simulations of the same problem that Frenkel’s [1] assumptions were incorrect, although his results were close to exact solution, probably due to compensating errors.
Mackenzie and Shuttleworth (M-S) [18] proposed a spherical shell model, which is a good representation of the final stage of sintering, when the pores become isolated. In comparison to Frenkel’s [1] two-sphere geometry, the analysis of M-S model [18] is mathematically easy as the spherical shape is preserved as the shell contracts. The relative density was given as,

\[
\frac{m^{1/3}}{\eta} = f(\rho(t) - f(\rho(0)) \tag{2.9}
\]

where,

\[
f(\rho) = -\frac{2}{3} \left( \frac{3}{4\pi} \right)^{1/3} \sqrt{3} \tan^{-1} \left( \frac{2(1/\rho - 1)^{1/3} - 1}{\sqrt{3}} \right) + \frac{3}{2} \log[(1 - \rho)^{1/3} + \rho^{1/3}] \tag{2.10}
\]

Scherer [19] proposed the cylinder model for sintering bodies with low initial densities, such as gels and soot performs used for optical waveguides. The rate of densification was given by,

\[
\frac{1}{\rho} \frac{d\rho}{dt} = \frac{\gamma S \rho_s}{2\eta} \tag{2.11}
\]

where S is the specific surface area and \( \rho \) is the density of the solid phase. The predictions of all three models are shown in Fig. 2.1. Interestingly, there is good agreement between the models inspite of the different microstructural geometries used. Later, experimental studies verified that the sintering rate of noncrystalline particles follows the curves predicted by the models.
Fig. 2-1 Relative density vs. time for spheres (Frenkel), spherical shell (M-S), and cubic network (Scherer) calculated assuming an initial density, $\rho = 0.52$ as for a simple cubic packing of spheres. Frenkel’s model applies to the early stage of sintering, Scherer’s model upto $\rho = 0.52$, and M-S’s model beyond that.
2.3.1 Factors affecting sintering rate

The time required for complete sintering for a simple cubic packing of spheres is approximately,

\[ t_s \approx \frac{\eta}{\gamma n^{1/3}} \approx \frac{1.6\eta a}{\gamma} \]  

(2.12)

As indicated by the equation, smaller particle size and lower viscosities lead to faster sintering times. For crystalline materials, \( t \) is proportional to \( a^3 \) or \( a^4 \) and thus, more sensitive to particle size. The rate of sintering increases as the surface energy increases, as the surface energy drives the sintering process. However, the dependence of the surface tension on temperature and composition is weak. In contrast, the viscosity is extremely sensitive to both temperature and composition. Thus, the time for sintering can be drastically reduced by raising the temperature. The viscosity of oxide glasses is strongly influenced by the presence of hydroxyl (OH) groups [20]. For example, the sintering rate for silica is an order of magnitude faster in air than in dry gas. Similarly, the loss of hydroxyl during sintering of gels results in an increasing viscosity and decreasing densification rate.

2.3.2 Ceramic-filled Glass Sintering

A detailed study on the sintering of ceramic particle-filled glasses was done by Ewsuk et al. [14]. This section summarizes the key findings from this study, because of its relevance to this work. Experiments were conducted on alkaline earth borosilicate glass and either 50, 60 or 65 vol% of a commercial 1.5 \( \mu \text{m} \) alumina powder. To evaluate the effect of filler particle size on densification, experiments were conducted on
composites composed of 40 vol% of the borosilicate glass and 60 vol% of a 0.4, 1.5 or 6.3 micron-sized alumina powder. To evaluate the effect of glass physical properties, experiments were conducted on 60 vol% alumina and 40 vol% of one of three different glass compositions. In addition to the borosilicate glass, two lab-prepared silica-modified alkaline earth borate glasses. The physical properties were measured at 750 and 900°C; Glass wetting angles were measured using the sessile drop method.

Ewsuk et al. [14] proposed a non-reactive liquid phase sintering (NLPS) model, in which densification occurs by a combination of glass redistribution, grain rearrangement and viscous flow. It was found that the composite densification improved with decreasing filler content and increasing filler particle size. While decreasing the filler content reduces the viscosity of the composite and thus aids in densification, increasing the particle size improves the glass redistribution kinetics, because larger particles tend to have larger pores, through which the glass can penetrate. Ewsuk et al. [14] also observed that good wetting between the glass and ceramic, and a moderately high viscosity resulted in improved densification behavior. Although low viscosity increases the densification rate, a more viscous mass provides greater time for grain rearrangement leading to better intermediate stage sintering.

The driving force for glass distribution is given by,

\[ DF_{\text{distribution}} = \frac{\gamma_{lv} \cos \theta}{r} \]  \hspace{1cm} (2.13)

where \( \gamma_{lv} \) is the glass surface tension, \( \theta \), the wetting angle and \( r \), the radius of cylindrical pore channel. The time required for a glass of viscosity \( \eta \), to infiltrate the cylindrical pore by a distance \( h \) is given as,
\[ t = \left( \frac{h \pi}{2} \right)^2 \left( \frac{2\eta}{r \gamma_{lv} \cos \theta} \right) \]  \hspace{1cm} (2.14)

The driving force for grain rearrangement comes from the presence of both solid-liquid and solid-vapor interfaces leading to a force imbalance, given by,

\[ DF_{gr.} = 2\pi \gamma_{lv} R \sin(\phi + \theta) - 2\pi \gamma_{lv} \frac{R^2}{r} \sin \phi \]  \hspace{1cm} (2.15)

where \( R \) is the particle diameter, and \( \phi \) is a geometric factor related to the solid-vapor-liquid intersect. The driving force for final stage viscous flow is defined by the Laplace equation;

\[ DF_{final} = \frac{2\gamma_{lv}}{r} \]  \hspace{1cm} (2.16)

The time required to eliminate a pore of radius \( r \) during final stage viscous sintering is directly proportional to the viscosity of the glass.

\[ t = \frac{2r \eta}{\gamma_{lv}} \]  \hspace{1cm} (2.17)

For ceramic particle-filled glasses, the viscosity in the above equation is the viscosity of the composite rather than that of the pure glass.

The difference in densification kinetics between coarser and finer particles was attributed by Ewsuk et al. [14] to,
1) Difference in infiltration kinetics: The smaller the pore size, which is the case for fine filler particles, the greater is the time for glass infiltration into pore channels. However, the effect of filler particle size and size distribution become less significant as the glass volume fraction increases and/or the sintering temperature increases.

2) Particle rearrangement: This occurs during intermediate non-reactive LPS. This would further decrease the pore size, as well as the pore area available for glass infiltration. The combined effect, they noted would produce a 20-30X difference in infiltration time between the coarse and fine composites. The rearrangement effect is presumed to be more prevalent in fine composites where, in order to achieve the same depth of infiltration, the glass would have to infiltrate a pore channel several filler particle diameters long as compared to one ~ 1 particle dia long for the coarse composite.

3) Changes in Viscosity: In the fine-particle composite, it is possible that high viscosity CFG dispersion is created during sintering. If this factored into the infiltration equation, orders of magnitude changes in infiltration time was found. The relative viscosity of composite increases with decreasing particle size.

4) High surface area: A smaller particle has higher surface area and thus more glass can adsorb on to its surface leaving less glass for glass redistribution.

Higher filler loading is necessary for high thermal conductivity. High-filler loaded, ceramic particle-filled glass composites, Ewsuk et al. [14] reasoned can be produced by enhancing grain rearrangement during the intermediate stage of NLPS by hot pressing. This is also possible tailoring the physical properties - wetting angle, viscosity and surface tension. For example, a more viscous glass lengthens the time for glass redistribution, and thus grain rearrangement, which increases the amount of
densification during intermediate stage sintering. Further, as noted by Ewsuk et al. [14] while it maybe important to minimize the composite viscosity to optimize the kinetics of densification during final stage NLPS, to optimize overall composite densification, it maybe more important to utilize a glass with a moderately high inherent viscosity to optimize the kinetics of densification during second stage NLPS.

2.4 CONSTRAINED SINTERING

The literature on constrained densification will be reviewed in this section. Both theoretical analyses and experimental observations are discussed. The viscous models, which form the basis for experimental studies on constrained sintering are discussed. Under experimental studies, observations of damage due to constrained densification and development of tools such as loading dilatometry to measure the thermo-mechanical properties of densifying materials are discussed. The correlation of material properties to microstructural and warpage observations and stress development is also highlighted.

2.4.1 Definition of Constrained Sintering

Constrained sintering is a common phenomenon observed in ceramic processing. Any external attempt to mechanically influence the shrinkage behavior of a material can be termed constrained sintering. Based on the effect of the constraint on the densification behavior of a material, which can be either negative or positive, constrained sintering can be broadly classified into two types [21]: 1) Retarding constraint, which results in retardation in densification of atleast one component, for example, a film on a rigid substrate or a matrix with rigid non-sintering inclusions; 2) Enhancing constraint which
results in enhancement of densification by application of pressure such as in sinter-forging or hot-pressing. In both cases, additional stresses develop that depend on the thermo-mechanical properties such as Young’s modulus, viscosity, Poisson’s ratio of the material concerned.

2.4.2 Constitutive models of viscous sintering

Porous materials sinter by mass flow due to capillary forces, but the kinetics are almost always influenced by external forces such as applied stresses as in the case of hot pressing, friction due to contact with external surfaces, and internal constraints due to microstructural inhomogenities and inclusions. The mechanical response of a material to a stress can be elastic, viscoelastic or viscous (Fig. 2.2). The ‘viscosity’ of sintering bodies is defined as the resistance to creep or densification of the material in the presence of an internal and/or external stress. Depending on the stress state i.e., shear, hydrostatic or uniaxial, the viscosity takes on different meanings. In fact, a sintering material cannot be fully described, unless the shear and hydrostatic (or bulk) viscosities, or the uniaxial viscosity and viscous Poisson’s ratio are known. This kind of description follows the elastic-viscous analogy, and has been found to be quite useful in developing sintering models based on the continuum sintering approach [22-24, 25].

Skorokhod [26] introduced a constitutive equation to predict the influence of applied stresses on densification kinetics of porous materials,

\[
\sigma_{ij} = 2G \left( \dot{\epsilon}_{ij} - \frac{1}{3} \delta_{ij} \dot{\epsilon}_{ii} \right) + K \delta_{ij} \dot{\epsilon}_{ii}
\]  

(2.18)
Fig. 2-2 Schematic showing elastic, viscous and viscoelastic responses to an applied stress
where \( \epsilon_g \) and \( \sigma_g \) are the strain and stress tensors, \( \delta_g \) is Kronecker’s delta, and \( G \) and \( K \) are respectively the shear and bulk viscosities of the porous body given by,

\[
G = \rho^2 G_f
\]

\[
K = \frac{4}{3} \left( \frac{\rho^3}{1 - \rho} \right) G_f
\]

where \( \rho \) is the relative density and \( G_f \) is the viscosity of fully dense material.

Scherer [19] proposed an equation for viscous sintering of the form,

\[
\ddot{\epsilon}_x = \epsilon_f + \frac{1}{\eta} [\sigma_x - \nu (\sigma_y + \sigma_z)]
\]

Based on a cubic array of cylinders, the expressions for the uniaxial viscosity and viscous Poisson’s ratio were,

\[
\eta = \left( \frac{3 \rho}{3 - 2 \rho} \right) G_f
\]

\[
\nu = \frac{1}{2} \left( \frac{\rho}{3 - 2 \rho} \right)^{1/2}
\]
Although the above equations are over-simplistic considering the fact that actual microstructures do not resemble the cylinder model, still they give fundamental ideas about mechanical behavior of porous materials. For example, viscosity decreases with increase in porosity, since the effective load-bearing area decreases which imply that a given load on a porous sample would result in a higher internal stress than same load on a dense sample (see Fig. 2.3).

Bordia and Scherer [22] have suggested that a porous glass undergoing sintering can be treated as a linear viscous material instead of a viscoelastic body, as the elastic component during sintering is negligible. The use of viscoelastic analysis for sintering and its difficulties are discussed below. According to the linear viscous model for materials that sinter under the influence of an external uniaxial stress ($\sigma_z$), the axial strain rate ($\dot{\varepsilon}_z$), and the viscosity ($\eta$) are related as follows,

$$\dot{\varepsilon}_z = \dot{\varepsilon}'_{/z} + \frac{\sigma_z}{\eta}$$  \hspace{1cm} (2.24)

where, $\dot{\varepsilon}'_{/z}$ is the axial strain rate of the free-sintered specimen. The viscosity is calculated by applying an external load, and measuring the strain response. Equation (2.24) is the basis of sinter-forging and cyclic loading dilatometry studies used to measure the uniaxial viscosity of sintering materials [27-32].
Fig. 2-3 Stress intensification due to reduced load-bearing area in a porous material with the same dimensions as a fully dense sample; in actual particulate compacts, the load-bearing area is not a linear function of pore volume (after Ref. [21])
2.4.3 Application of Viscoelastic Analysis

Although, the viscous analysis has been adopted after the simplification proposed by Bordia and Scherer [22], some earlier studies [33, 34] used the viscoelastic analysis. The sintering matrix was assumed to be linearly viscoelastic.

To perform the viscoelastic analysis, the following steps are followed:

1) The relaxation moduli are represented by using the spring and dashpot models.

2) Laplace transformation is performed on relevant stress equations

3) The elastic solution is adopted since step (2) leads to equations analogous to the elastic equations.

4) The stresses are then obtained using the viscoelastic analogy.

In their work on bi-modal powder compacts, Bordia and Raj [33] used viscoelastic analysis. They assumed viscosities and moduli to be constant during densification. A parameter called, \( \beta \), which is the ratio of creep to densification rates was used to characterize stress relaxation. But, Bordia and Scherer [22-24] later pointed out basic problems with the analyses of Bordia and Raj. Firstly, the assumption that a porous sintering material can be considered linearly viscoelastic is wrong as the viscosities and moduli are not constant but time-dependent. As porosity increases, the relaxation moduli decrease. Let’s consider the Maxwell model (see Fig. 2.4a). The shear stress is given by,
\[ S_{ij} = 2G_o e_{ij} \exp\left(-\frac{G_o t}{h}\right) \]  
(2.25)

\[ G_i(t) = 2G_o \exp\left(-\frac{G_o t}{h}\right) \]  
(2.26)

For which the Laplace transform is,

\[ G_1^*(s) = \frac{2G_o}{S + \frac{G_o}{h}} \]  
(2.27)

However, if \( G \) and \( \eta \) are functions of time, no simple laplace transform can be done and thus the viscoelastic analogy fails. Although the assumption that a sintering body is viscoelastic is reasonable, since the densification strains are enormous compared to elastic strains, the sintering body could be adequately described as a viscous material. Thus, viscoelastic analogy is unnecessary and its failure is not important.

Secondly, in Bordia and Raj’s model, the Kelvin-Voigt element (Fig. 2.4a) was used to represent the densification behavior of the sintering compact. But, unlike the recoverable strain in the Kelvin-Voigt element (i.e., delayed elasticity), the densification strain in a viscous material is permanent. Thirdly, the equations which estimated large transient stresses were those for which the viscous Poisson’s ratio was negative. Experimental results show otherwise. Despite these apparent problems, the Bordia-Raj model works well for case of a glass matrix constrained by rigid inclusions. This is due to the reason that \( \beta \) is constant with density when creep and densification follow the same mechanism, which is viscous flow for glass systems.
Fig. 2-4a Linear viscoelastic models; R is spring constant and \( \eta \) is the viscosity of dashpot (after Ref. [21])

Fig. 2-4b Stress relaxation for the Maxwell model; The axes are in arbitrary units (after Ref. [21])
2.4.4 Experimental Investigations

In order to determine the mechanical response of a sintering compact and to validate the theoretical results, experimental investigations of constrained sintering are essential. Scherer [35] proposed sinter-creep experiments as a means to measuring the viscosity of porous materials. A sinter-creep experiment involves applying a uniaxial load and measuring the axial and radial shrinkages of powder compacts. The equipment typically used is the loading dilatometer (see fig. 2.5).

Rahaman et al. [27] used small loads (\(\sigma << P\)) and found that the applied loads did not affect the densification much, while Venkatachari and Raj [28] used larger loads (\(\sigma \geq P\)) and found a strong influence of stress on densification. They used creep and densification rates determined by Raj’s methodology [36] and calculated the viscosities. In case of polycrystalline materials, for isothermal experiments, the viscosity depends only on \(\phi\) and grain-size, where \(\phi\) is the stress concentration factor and is given by,

\[
\phi = \alpha \exp(\alpha P)
\]

where \(\alpha\) is a parameter that describes pore shape and \(P\) is the fractional porosity. Low \(\alpha\) indicates a high load-bearing area. For glass powder compacts, Scherer’s theory gave an \(\alpha\) value of 2.4, whereas Rahaman et al.’s experiments gave a value of 11.5. Some possible reasons for disagreement between theory and experiment are; Scherer’s cylinder model over-estimates load-bearing area (see Fig. 2.6). It can be seen from Fig 2.5 that the area of contact approaches the area of cylinder only at high densities.
Fig. 2-5 Sinter-creep experiments: a) Rahaman and DeJonghe (σ << Σ) [27]; b) Venkatachali and Raj (σ ~ Σ) [28]. LVDT = Linear Variable Differential Transformer (after Ref. [21])

Fig. 2-6 Load bearing area of two spheres compared to a cylinder model; the contact area approaches that of the cylinder as the density increases (after Ref. [21])
Rahaman et al. [27] attributed the disagreement between theory and experiment to difference in pore morphology. While they observed lenticular pore morphology, Scherer’s model [19] assumes cylindrical pores. The viscosity of a sintering compact depends not only on the amount of porosity but also on pore shape and orientation. Interestingly, in contrast to their earlier work, in their study on borosilicate glass powders, Rahaman et al. [29] showed very good agreement with predictions of Scherer [19]. This was attributed to reduced shrinkage anisotropy and use of much broader particle size distribution compared to earlier work.

2.4.5 Sintering with Rigid Inclusions

In their work on SiC inclusions in glass powder compacts, Rahaman and De Jonghe [37], found that the transient stresses in the matrix due to presence of nonsintering inclusions were much less than the sintering stress ($\sigma_1 \sim (0.1-0.2)P$, where $P$ is the sintering stress). Also, the densification rates from experimental data matched well with Scherer’s theory [38] up to ~17% inclusions (percolation threshold). The deviation observed they reasoned could be due to the following reasons:

- Elastic analysis is only valid for non-interacting stress fields, which implies that analogous viscous analysis is expected to diverge from reality above percolation threshold.
- As Scherer himself pointed out the use of Hashin-Shtrikman’s [39] equation for shear viscosity could have led to deviation.
It was suggested by Scherer that the use of numerical simulation values or measured values could give better agreement between theory and experiment.

In their work on SiC inclusions in ZnO matrix, Rahaman and co-workers [40, 41] observed that the densification was severely retarded by even small volume fractions (~5%) of inclusions. The transient stresses were too small to account for the retardation in densification rate. The reduction in densification rate was attributed to powder processing-induced causes. Bordia and Raj worked on TiO$_2$ and Al$_2$O$_3$ composites [42] and used linear viscoleelastic models to describe the sintering behavior. They observed very large transient stresses much greater than the sintering stresses, but as pointed out by Bordia and Scherer [22-24], transient stresses were large for those cases for which the viscous Poisson’s ratio was negative, and thus the Bordia-Raj analysis was found to be incorrect.

Numerical tools such as finite element method are being used to precisely model the viscous sintering material [25, 17, 43]. In their work on the two-sphere particle model, Jagota et al. [17] showed that Frenkel’s assumptions were poor. They also noted that earlier models such as those of Scherer and Mackenzie-Shuttleworth are insufficient in that they do not take into account the effect of contact area on the viscosity of sintering materials. This is discussed in more detail below. Jagota and Scherer [43] used the truss and beam models to study the problem of sintering with rigid inclusions. The effect of percolation on viscosity was found to be sensitive to the wetting and the degree of slip between inclusions. They noted that the traditional self-consistent and Hashin-Shtrikman models failed to predict the composite viscosity, especially beyond the percolation
threshold at which the individual particles connect to form a rigid network. As Scherer rightly notes [44],

“Unfortunately, there are presently no accurate models for predicting the rheology of percolating systems, and this must be the goal of future research. Numerical simulations of the type discussed here will be invaluable tools in the search for such models.”

2.4.6 Damage due to Constrained Sintering

Constrained sintering has profound effects on the microstructure of densifying materials. It can lead to sintering damage which can be defined as any detrimental effect on final microstructure. Cai et al. [45] studied constrained sintering of alumina-zirconia composites and observed different kinds of defects in case of symmetric and asymmetric laminates. The cause of the defects was attributed to the transient stresses (in-plane tensile stresses) due to mismatch in sintering rates of the constituent materials. The mismatch was reduced by doping ZrO₂ with Al₂O₃. Fig. 2.7 shows common defects observed in symmetric and asymmetric laminates and micrographs of doped defect free Al₂O₃- ZrO₂ composites. In order to make a good estimation of the in-plane stresses that led to camber or microstructural defects, knowledge of the mechanical responses of the sintering materials is of absolute necessity. Thermo-mechanical properties such as
Fig. 2-7 Defects in a, b) asymmetric and symmetric alumina-zirconia laminates and c) effect of doping [44];
viscosity, Poisson’s ratio need to be determined in order to make any kind of useful estimation of the transient stresses. As described earlier, as suggested by Scherer, Rahaman et al. [27] used loading dilatometry to determine the thermo-mechanical properties. But, in their experiments they used a constant loading profile, i.e., they applied a constant uniaxial load over the entire heating period. The thermo-mechanical properties depend on the stress history (i.e. changes in microstructure, density and shrinkage anisotropy due to the load) of the sample and use of a constant load would not allow correct estimation of these properties. Cai et al. [45] proposed cyclic loading dilatometry as a technique to measure the viscosities at different temperatures and densities and to eliminate the stress history effects. Also, Cai et al. [43] represented the sintering compact by viscoelastic models, but later found out that the elastic strains were minimal compared to the viscous strains supporting Bordia and Scherer’s argument that the sintering compact could be adequately described by viscous models.

Damage is expected to occur through creep since materials are viscous or viscoelastic (Fig. 2.8). Also, cracks could be generated due to differential densification
Fig. 2-8 Sintering damage resulting from differential densification a) radial cracking and interfacial debonding in agglomerated powders and b) cracking and distortion in bilayers (after Ref. [21])

Fig. 2-9 Ceramic-metal and Glass-metal symmetric bilayers; Notice the cracking in the ceramic layer [50]
between regions of different packing densities or between the matrix and an inclusion phase. One of the best examples of deleterious effects of constrained sintering is curvature development, particularly in asymmetric structures [46-53]. Earlier works by Lu et al. [46] and Jean et al. [47] analyzed stress development and distortion during cofiring of LTCC-metal systems based on theoretical models for describing the viscous behavior of the materials. We [48] recently reported observations and model predictions of curvature in LTCC-silver bilayers based on measured viscosities using cyclic loading dilatometry. Similarly, Garino [49] reported curvature analysis in LTCC and silver-palladium systems. Cheng and Raj [50] (Fig. 2.9) studied multilayers with axial symmetry observed cracks and void formation for ceramic/metal and glass/metal co-sintered systems. Transient stresses are relieved either through [54-58],

- Induced shrinkage anisotropy (constant volume creep), or
- Defect generation in the form of cracks.

In real cases, both effects are seen. However, distortion is more important in cases where multilayers have no axial symmetry. Also, more defects are observed when the one of the component materials is a ceramic rather than a glass. Cheng and Raj [50] observed cracks in ceramic layers while no defect was observed in glass layers (Fig. 2.9b). This is due to good shear relaxation of glasses compared to polycrystalline materials. Glasses have the tendency to relax transient stresses and are often responsible for defect-free specimens. Thus, having glass as a component would be quite useful in preventing defect-formation.
2.4.7 Practical solutions

The most direct solution to the problem of constrained sintering is to try match the sintering behavior of component materials. Although, it’s not possible to completely match the sintering rates of two dissimilar materials, it helps to reduce defects by preferentially doping one component with another as shown by Cai et al. A common industrial approach is to employ techniques such as applying an external load, designing symmetric structures, and using sacrificial or self-constraining techniques are used to minimize or eliminate curvature [59-61]. However, these methods often involve additional costs and materials and add further steps to the manufacturing process. Figure 2-10 below shows the effect of an applied load on a viscous sintering material. This recent work by Lee et al. [62] utilizes the viscous nature of the specimen to deform the material. The presence of the loading plate on the specimen leads to zero distortion. The use of a glassy phase as a component in the system also helps in achieving defect-free products. As demonstrated by Cheng and Raj [50], glass has better stress relaxation capabilities than a ceramic and thus helps relieve transient stresses which are responsible for defects. LTCC materials are glass-based systems. The glass helps not only in improving the mechanical response of the sintering compacts but also has low-dielectric constant which is an important requirement for these materials.
Fig. 2-10 Application of a small load on a viscous sintering body results in zero distortion [62]
2.4.8 Summary of constrained sintering

- Several studies, theoretical, experimental and numerical have focused on the problem of constrained sintering; These have helped us gain a deep understanding, but there is more work to be done, especially in the area of thermo-mechanical characterization of sintering materials.
- Viscoelastic treatments though reasonable are considered unnecessary; Moreover, sintering materials are not linearly viscoelastic; They can be considered viscous with a porosity dependent viscosity
- Sinter-creep experiments could provide useful data for dependence of viscosity on porosity, temperature, and possibly stress or strain; Cyclic loading dilatometry is a viable alternative as it reduces stress-history effects.
- Model predictions for densification with rigid inclusions match reasonably well with experimental results below the percolation threshold; above threshold, large deviations are observed; precise viscosity values are necessary for better predictions
- Transient stresses are too low to explain significant retardation observed in densification rate in ceramic matrix composites
- Constrained sintering leads to either curvature or defect generation; Defect generation is less in glass compared to ceramic matrix due to good shear relaxation of the former.
2.5 MODELS OF VISCOSITY

Constitutive laws that are used to model the sintering process entail knowledge of constitutive parameters such as viscosity and Poisson’s ratio. Many theoretical and empirical models have been proposed to describe the viscous behavior of sintering systems [23, 63] (see Fig. 2.11). These can be broadly classified into micromechanical and phenomenological models.

Micro-mechanical models have been developed based on a two-sphere geometry, spherical pores, and cylindrical networks [1, 18, 19]. As noted before, these agree well with each other. Mackenzie and Shuttleworth [18] derived expressions for shear ($G_p$) and bulk viscosities ($K_p$), based on a spherical shell model. Scherer [19] proposed expressions for $\eta$ and $\nu$ as functions of relative density for low-density glasses based on a microstructural model consisting of cubic unit cells of cylindrical particles. The model does not take into account grain growth and assumes particular pore morphology. Skorokhod [26] suggested expressions for effective shear and bulk viscosities, based on irreversible thermodynamic principles and Bassani [64] has proposed constitutive equations for densifying compacts that contain microcracks, based on the differential self-consistent model.

Scherer’s [19] model, as noted above, was developed for viscous systems, but for very low-density glasses, such as gels and waveguide performs. As noted by Scherer, the cylinder network is not a good representation of powder packed structures. This is because a cylinder network has a much larger load-bearing cross-sectional area compared to a powder packed structure at the green density state. For a powder packed structure, at the green density state, the viscosity, which depends on the load-bearing area, is expected
Fig. 2-11 Empirical and theoretical models for viscosity as a function of density (source: Ref [63]); note, the viscosity is normalized to the value at 75% density
to be low for small contact areas. Thus, as noted by Scherer and demonstrated by Jagota et al. [65], density alone, as used in several previous models [18, 19], is not a precise indicator of the load-bearing fraction of the cross-sectional area, and thus the constitutive parameters. Thus, in their work, Jagota et al. [65] succinctly note,

“The actual variation of effective viscosities with, for example, relative density requires an integration of the evolution equations along a particular deformation history. It is not possible to present the constitutive parameters as unique functions of the porosity. This is particularly true when both sintering and external tractions contribute to the evolution of the state. This is simply a statement of the fact that sintering and external tractions change the contact area and relative density differently.”

Other micromechanical models, such as those of McMeeking and Kuhn [66], Cocks [67], Swinkels and Ashby [68], Helle et al. [69] and Svoboda et al. [70] consider different stages of sintering, such as the initial, intermediate and final stages, and take into account the interaction between grain growth and densification. For example, Svoboda et al. [70] derived expressions for the intermediate and final stages of sintering based on an analysis for simple cubic grain arrangements assuming grain-boundary diffusion as the predominant creep mechanism. Du and Cocks [71] developed a general constitutive model for different stages of sintering, based on the grain-growth studies of Brook [72] and Swinkels [68], and the creep and densification models of Hsueh et al. [73], McMeeking and Kuhn [66], Cocks [67], and Helle et al. [69] with the material constants determined from Coble’s [74] experimental data. Like the phenomenological models, this model assumes a linear viscous response but takes into account the effect of grain growth similar to Hsueh et al. [73]. However, separate evolution laws for
densification and grain-growth were developed unlike Hsueh et al.’s model, in which the grain size was expressed as a unique function of relative density based on experimental observations of Coble and Coble and Kingery [75]. It is worth noting that inconsistencies in Hseuh et al.’s [73] model have been pointed out that question the validity of their model [23].

In addition to these micromechanical models, a number of phenomenological models have been used to surmount the difficulties with the former. In the phenomenological models, reviewed by Bordin and Scherer [23], a linear-viscous response is assumed and the shear ($G_p$) and bulk viscosities ($K_p$) or the uniaxial viscosity ($\eta$) and viscous Poisson’s ratio ($\nu$) are expressed as functions of relative density. The same equation is applied to all stages of sintering with no identification of different stages. Among the phenomenological models reviewed by Bordin and Scherer are those developed based on sinter-forging tests. These tests have been used to determine how viscosity as a function of relative density for glasses, ceramic-filled glasses and polycrystalline ceramics. In these studies, a loading dilatometer [76] was used to study simultaneously the creep and densification of a porous sample and thus calculate the shear and bulk viscosities. For example, Rahaman et al. [27] and Ducamp and Raj [30] reported non-linear variation of shear viscosity with porosity for soda-lime silica glass and borosilicate glass, respectively. In both studies, empirical functions were used to fit the experimental data.
The empirical relation of Rahaman et al., for the shear viscosity, $G_p$, was given by,

$$\frac{G_p}{G_o} = \exp[-\alpha(1 - \rho)]$$

(2.28)

where $\alpha$ is an adjustable empirical parameter, $G_o$ is the intrinsic shear viscosity of fully dense glass, and $\rho$ is the relative density. Their experimental viscosities were fitted to the above relation with $\alpha = 11.2$. The empirical fit of Rahaman et al. [27] showed poor agreement with Scherer’s theoretical model [19] and this discrepancy was attributed to a difference in pore shape. Interestingly, in contrast to their earlier work [27], in their study on borosilicate glass powders, Rahaman et al. [29] showed very good agreement with predictions of Scherer [19]. This was attributed to reduced shrinkage anisotropy and use of much broader particle size distribution compared to earlier work. The expression for the bulk viscosity is not known. However, they reported similar empirical relations for $G_p$ and $K_p$ for CdO [77]. They are given as,

$$\frac{AG_p}{d^3} = \rho \exp[-2a_o(1 - \rho)]$$

(2.29)

$$\frac{AK_p}{d^3} = \rho \exp[-a_o(1 - \rho)]$$

(2.30)

where $d$ is the grain size, $A$ and $a_o$ are empirical parameters.
The empirical relation of Ducamp and Raj for $G_p$ has the form,

$$\frac{G_p}{G_o} = \exp[-\alpha \left(1 - \frac{\rho}{\rho_0}\right)]$$  \hspace{1cm} (2.31)

and $\alpha = 2.4$ to 4.0. For the bulk viscosity, $K_p$, a theoretical expression based on the analysis by Mackenzie and Shuttleworth [18],

$$K_p = \frac{4}{3} G_p \frac{\rho}{1 - \rho}$$  \hspace{1cm} (2.32)

was shown to have quite a good agreement between theory and experiment. Sura and Panda [31] performed isothermal constant loading experiments on cordierite-glass powders and showed reasonable agreement between their theory and the experimental data of Rahaman et al. [27] and Ducamp and Raj [30] for the shear viscosity. Sura and Panada’s model based on Nielsen’s analysis [78] for two-phase elastic materials takes into account the effect of pore geometry on the viscosity.

Sinter-forging tests are typically done under a constant load. The main weakness of a constant load technique is the irreversible effect of the applied load on the sample microstructure and consequent stress history effects. Because the application of an external load enhances densification and can affect grain growth, the microstructure of a specimen under load can be very different from that of a pressureless sintered specimen. On the other hand, as described in previous reports a cyclic load with alternating loading and unloading regimes alleviates the stress history effects since the specimen is allowed to relax towards its original stress-free state after each loading step [45, 79]. Cai et al.
[45] reported the successful use of cyclic loading dilatometry for measuring the uniaxial viscosities of Al₂O₃ and ZrO₂ and their use in predicting camber and stresses in Al₂O₃/ZrO₂ laminates [44, 51]. Similarly, Gillia et al., recently reported viscosities of WC-Co compacts and their use in phenomenological modeling [80, 81].

2.6 LTCC TECHNOLOGY: CO-SINTERING STUDIES

Low Temperature Co-fired Ceramic (LTCC) materials after their commercialization in the early 1980s, have offered new opportunities for advanced electronic packaging. The use of LTCC dielectric tape systems with thick film metallization combines the processing advantages of high temperature co-fired ceramic (HTCC) tape technology with the materials advantages of thick-film technology [82]. The LTCC systems co-fired with high-conductivity metallurgies provide functionally denser and electrically faster systems. However, co-sintering of the metal/ceramic multilayer structure, one of the most important steps in manufacturing Multi-Layer Ceramic Packaging (MLCP) is acknowledged to be a crucial technical hurdle in the development of LTCC packaging technology (see schematic in Fig. 2.12a). Also, the ever-increasing demand for increased circuit densities has fueled efforts to incorporate passive devices including capacitors, varistors, resistors and inductors within co-fired packages (see schematic in Fig. 2.12b). The inclusion of buried passives adds a level of complexity to the control of co-sintering in these MLCPs. Co-sintering the various materials incorporated in an integrated ceramics package requires that the materials be chemically, mechanically and process compatible.
Fig. 2-12a Processing flowchart for LTCC manufacturing; the co-sintering step is considered the key challenge.  
[Courtesy: D. Wilcox, Motorola]
Fig. 2-12b Schematic of an LTCC package for a) wireless and b) fuel-cell applications [Courtesy: D. Wilcox, Motorola]
2.6.1 Mismatched sintering kinetics

In the past decade or two, as noted before, a few studies have examined the effect of mismatched sintering kinetics on curvature and stress development in an LTCC package. Lu et al. [46] co-fired gold/LTCC composites and observed the curvature evolution during the co-sintering process due to the development of in-plane stresses which arise, because of mismatch in the sintering kinetics of the two materials. They used optical-scanning equipment for in-situ measurements of linear shrinkage profiles of tape-cast samples. Significant curvature was observed due to differential sintering of the materials. Not surprisingly, no chemical interactions were found between gold and LTCC, given the chemical inertness of gold. Therefore, the bonding was primarily due to mechanical interlock at the interface enabling them to examine the problem using the various constrained sintering models that had been widely studied.

One way to approach the sintering problems is to adopt the viscoelastic (VE) analogy. But, as noted earlier, Bordia and Scherer [23] recognized the inadequacy of applying the VE analogy. Scherer developed the viscous analogy to explain the sintering of porous materials. Though, developed for materials that sinter by viscous flow, the viscous analogy has also been applied to materials that sinter by solid-state diffusion. By using the viscous model for an isotropic porous body, Lu et al. [46] were able to derive equations for the in-plane tensile stress that led to development of curvature. The stress analysis entails knowledge of densification kinetics of the constrained and unconstrained materials. Since the densification rate is related to the shear and bulk viscosities, knowledge of the density dependence of these parameters is essential. The densities of
constrained gold specimens were obtained based on Skorokhod’s [26] model for the shear and bulk viscosities. As expected, the densification kinetics of the constrained gold lagged behind that of a free gold film.

For the purpose of stress calculations, Lu et al. [46] assumed the deformation in gold to be controlled by grain-boundary diffusion (Coble creep). Jean et al. [47] also noted in their study on Ag-LTCC system that the rheological behavior of Ag during co-firing was best accessed by boundary diffusion controlled creep. In case of LTCC, a simple relation between viscosity and density was not known because of the complexity of viscous sintering process in the composite (glass + ceramics) sintering. Lu et al. noted that creep studies similar to the one carried out by Rahaman et al. [27] were essential to get accurate data on the stresses. Jean et al. [47] used the glass sintering models of Mackenzie and Shuttleworth [18] and Scherer [19] to arrive at equations for the shear viscosities using the softening point and activation energy of viscous flow, and thus were able to determine the curvature rates. However, the agreement between observed and calculated curvature rates was poor.

2.6.2 Physical-Chemical Interactions

The drive toward further miniaturization and increased complexity in integrated circuits in response to the expanding needs of the electronic industry has fueled efforts to embed passive devices within the multilayer LTCC substrate architecture. There are few detailed and systematic studies on the problem of co-sintering passive devices with LTCC materials. The inclusion of passive functions within the multilayer ceramic package adds a level of complexity to the control of co-sintering in these packages. Two
major issues confront the co-sintering problem. First, the stress development that lead to
defects in the system and second, the chemical and physical interactions between the
different components that affect the functional properties of the passive devices. These
issues must be understood and controlled to produce reliable electronic packages.

In the mid 1980s, H.T Sawhill et al. [83] studied the problem of co-sintering of
tape dielectric with buried passive components like resistors and capacitors. In the case of
thick film resistors, the sintering rates were adjusted to match those of tape dielectric and
metal conductor to prevent the formation of defects. Changes in the chemistry or physical
characteristics of the components were deemed necessary to match sintering rates. Buried
capacitors were found to have co-sintering and compatible requirements similar to those
for buried resistors. Sutterlin et al. [84] studied the effects of resistor/dielectric
interactions on the electrical performance of the resistors. They observed three types of
resistor/dielectric interfaces corresponding to three different resistor compositions:
abrupt, broad and diffuse interfaces, which represented increasing interactions in that
order. Extensive (diffuse interface) interaction highly compromised sheet resistance and
the temperature co-efficient of resistance (TCR) of the resistor. It was evident that the
chemical and physical properties of the glass used in various components to be co-fired in
an integrated ceramic package should be compatible. Sutterlin et al. believed that
limited, well-behaved interactions might actually be desirable as long as the interactions
didn’t affect electrical or mechanical performance.

Differential shrinkage rates were found to be the main cause of defects in the fired
structure. Hackenberger [21] proposed Rate Controlled Sintering (RCS) as an alternative
route to reduce defects in co-fired LTCC/ conductor systems. High heating rates were
used that caused the conductor films to come under transient compression at lower densities than they did for slower heating rates. They reasoned that compressive stresses would have helped heal defects that formed before the onset of LTCC sintering. Control of shrinkage rate using a RCS dilatometer (designed for the purpose) was found to result in multilayer with fewer conductor film discontinuities and insulator-conductor delaminations. However, the origin of delamination was left unanswered though a possible cause was attributed to interfacial porosity. It was believed that RCS could be easily applied to industrial multi-layer processing and could help increase yield without having to use expensive powder processing techniques.

Hackenberger et al. [85] used environmental scanning electron microscope (ESEM) to observe microstructural development of an LTCC Three main stages of microstructural development were observed in LTCC. In the first stage, the sintering was found to be controlled by simple viscous flow of glass leading to neck formation between particles. After neck formation, the sintering was limited by glass spreading over crystalline particles. In the final stages, glass wetting and solution/precipitation of the crystallites were found to lead to final densification and particle rearrangement.

Defects may also be generated due to physical interaction across the interface between the co-fired components resulting in differential sintering and stress mismatch between regions. Twiname [86] investigated physical redistribution of glass in to ferrite inductor layer that lead to defects (Fig. 2.13). The main reason behind this was the large difference in sintering temperatures of the industrial LTCC system and ferrite inductor. Delaminations were observed perpendicular to the interface between the LTCC and
Fig. 2-13 Physical redistribution of glass from LTCC layer into the ferrite leads to defects [86]
ferrite. However, the addition of sintering aids to match the sintering rates of LTCC and ferrites resulted in defect-free fired samples. Since the ferrites densified almost at the same rate as the glass + ceramic system, physical redistribution of the glass was prevented and thus defects reduced. The sintering aids were also found to reduce both permeability and loss thus increasing the quality factor of ferrite layers.

2.6.3 Zero-shrinkage Technology

The concept of constrained sintering (also called “zero shrinkage” technology) has gained increasing attention in the low temperature co-fired ceramic (LTCC) industry, for the precise control and maintenance of sintering shrinkage and tight dimensional tolerances [59-61, 87-89]. During co-firing, stresses develop, because of mismatch in sintering behavior of different components [47-48]. These co-firing stresses can lead to curvature, and non-uniform shrinkage resulting in poor dimensional tolerances. Zero shrinkage technology is thus an attractive option as it completely inhibits the in-plane (tranverse) shrinkage, and allows only out-of-plane (longitudinal) shrinkage, resulting in extremely small dimensional changes in the plane of the structure, thus maintaining tight tolerances. The technique involves the use of non-sintering layers, either porous or fully dense, to constrain the densifying material. Variants of this technique used in the LTCC industry include pressure-assisted sintering (PAS), pressure-less assisted sintering (PLAS), self-constrained sintering, and the LTCC-M approach (see schematic in Fig.)
Fig. 2-14 Schematic of different variants of constrained sintering technique
2.14). Except for the PAS technique, all use either an internal or external non-sintering material to constrain in-plane shrinkage of the LTCC.

Tzeng and Jean [90] studied stress development in a Ca-borosilicate glass constrained by alumina layers. They adopted the viscoelastic theory to map the stress distribution using finite element analysis, and correlated it to the porosity distribution in the LTCC layer. The residual porosity was found to increase from the free edge towards the middle in the x-y (in-plane) direction and decrease from the interface to the middle in the z (thickness) direction.

Our work [91] studied the effect of constraint on two commercial LTCC systems DuPont 951Tape™ (DU) and Heraeus CT2000™ (CT) with different viscous behavior. The observed difference in the shrinkage, microstructure and fired densities were correlated to the viscous behavior of the systems. The DU showed significant deformation under an external load compared to CT. Based on the viscous model, a higher value of the viscous Poisson’s ratio was speculated to be the cause for higher z-shrinkage. For CT, the fired densities were found to be lower for constrained specimens compared to free-sintered specimens.

2.6.4 Mechanical Strength

The strength of a ceramic material is adversely affected by flaws such as pores, inclusions, cracks due to its brittle nature. The presence of vias has a significant effect on the mechanical properties of co-fired ceramics and more when the number of vias is considerably large. Design features such as vias, cavities and metal layers may be
considered as flaws if a solid ceramic with no flaws is taken to be the ideal case. Kellerman [92] studied the effect of these design features on the strength of co-sintered ceramic package. He performed four point bend flexure tests on ceramic multilayer substrates with and without vias. The strength data that he presented were based on Weibull statistics analysis technique. A high Weibull modulus indicated a homogeneous material. He found that the addition of vias had a significant effect on the ceramic strength and that the via acted as a strength limiting flaw. This was found to be truer in case of stacked and staggered vias in tension. Although, there was little structural strength difference observed between stacked and staggered vias, however the Weibull Modulus was seen to be higher for staggered vias. Vias tested in compression were found to have a lesser weakening effect than those in tension. Kellerman Suggested that vias should be connected to compressive surfaces whenever possible. In case of a via that must be connected to a tensile surface placing a ceramic layer was found to help increase the structural integrity of the ceramic package. The addition of cavities was found to cause significant weakening of the package structure. Minimization of cavity sizes was proposed as a solution for achieving increased structural strength. The addition of metal layers seemed to strengthen the package structure. By successful use of flexure tests to understand the effects of design features Kellerman showed that these were viable techniques for determining design rules for structural integrity of ceramic packages.

Hines et al., [93] evaluated the increased stress concentrations due to the presence of vias in ceramic printed wiring boards and correlated this increase to the choice of the via and ceramic board materials. They modeled the via as a cylindrical inclusion and used 2-D elastic models that had been solved and verified by many authors like Goodier [94]
and Muskheilishvili [95]. Several assumptions were made including that of an infinite ceramic matrix, vias that are significantly far from any edge, and a perfectly bonded via/matrix system. They analysed the stresses acting on an element at the via-matrix boundary including radial stress, hoop stress and shear stress. The presence of via (inclusion) increases the local stresses by a factor of magnitude given by the stress concentration factor (SCF). Thus, the maximum allowable applied stress decreases by a factor given by SCF. By analyzing the stresses acting on boundary elements, Hines et al. [93] were able to evaluate the SCFs due to vias in ceramic boards. For a rigid inclusion (via) i.e., when the via was much stiffer than the matrix, the radial stress was found to be the largest. And, when the matrix was stiffer than the via the hoop stress was found to be the largest. The magnitude of SCF and where the maximum stress occurs were found to depend on the relative material properties. The effect of different via materials including gold, silver, copper, tungsten and molybdenum on commercial ceramic tapes, Dupont 951Tape, Ferro A6, 90% HTCC, and 92% Al₂O₃ HTCC were evaluated. The SCFs for typical material systems, for e.g., heavy metals in HTCC or noble metal vias in LTCC were found to be less than 1.2. Hines et al. [93] reasoned that if the assumptions made were true, then their model for the calculation of the effects of vias on the strength of a ceramic PWB was of correct order of magnitude and that it could be applied to typical material systems. The results obtained based on the above theoretical approach were found to match well with the experimental results published by Kellerman [92]. In continuation of the above work, Hines and Barker [96] used 3-D and non linear finite element methods and evaluated the validity of the results and assumptions used in the 2-D analysis. They concluded that in order to validate the assumptions made in the 2-D
model, 3-D factors should be added to the stresses depending on the relative material properties.

2.6.5 Electrical Considerations

While we consider co-sintering problems, it is important keep in mind other functions of the device such as the electrical performance and vice versa. LTCC technology is being increasingly considered for high speed digital and RF applications. These applications require the use of transmission lines on the surface and in buried layers within the multilayer architecture. Vias are used to connect transmission lines in different layers. The ever-increasing working frequency of circuits demands better frequency behavior of the multilayer elements, especially the transmission lines. Vias have a frequency behavior different from that of transmission lines and thus present a discontinuity in the course of the transmission lines. The wave impedance (frequency behavior) of via depends on its geometry and does not correspond with wave impedance of the transmission line in most cases. Vias that are used to connect transmission lines have to cross through the ground plane and in some cases through a meshed ground plane. Various investigations have been carried out to optimize via connections between transmission lines. Coax via was proposed as a technique to reduce crosstalk and enhance impedance match at vias [97]. Thelemann et al. [98] used a meshed ground plane contrary to earlier investigations on via connections using ground planes. They found that the frequency behavior of vias crossing a meshed ground plane could be improved by a modification of meshed ground plane geometry and layout. They observed that improvement of the layout and use of additional vias led to better results i.e., lower
attenuation and thus a lower impact on the frequency behavior of the transmission line. Also, the additional attenuation due to vias was found to be small compared with the attenuation of the transmission line and it became important only in the case of a high number of vias.

Microstrip lines are used for final connections between multi-layered circuit boards and integrated circuits. However, microstrip transmission lines radiate energy which can couple to identical microstrip lines in its vicinity. Coupling between microstrip lines or crosstalk in dense RF packages is a common problem that degrades the circuit performance and must be reduced. G.E. Ponchak et al. [99,100] utilized a 3D-FEM electromagnetic simulation to evaluate the use of metal-filled via fences along microstrip lines for the purpose of reducing the radiation loss of isolated lines and the coupling between adjacent lines. Metal-filled via holes, being inexpensive in LTCC packages, are commonly used to create via fences to reduce coupling between circuits. In addition, via fences may be used to reduce coupling between striplines. But Ponchak et al., found that metal-filled via fences did not reduce the radiation loss of the lines or the coupling between lines. However, they observed that by connecting the top of the via posts with a continuous metal strip, the radiation loss of the microstrip line was reduced and the coupling between lines was reduced by 8-10dB. They inferred that the above method could be used to permit closer spacing between microstrip lines without increasing the crosstalk in the circuit. However, in other study on isolation between stripline circuits, Ponchak et al., observed that the radiation loss and the coupling between striplines increase if the metal-filled via hole fences were placed too close to the stripline. The
minimum separation between via fence and a stripline in order to prevent increased coupling, was found to be four times the ground plane separation away from the strip.

2.6.6 Other Considerations

A major advantage of LTCC technology is its ability to be co-fired with high-conductivity metallization such as Ag, Au, Cu, because of its lower sintering temperature. Much work has been done to find the most optimum metallization. Ag has increasingly replaced Au conductors as a low cost and high-performance metallization. But, widespread acceptance of Ag has been impaired due to its migration problems. Silver tends to diffuse easily causing electrical opens, which degrade the integrity of circuits. The use of silver as an inner layer conductor also demands that the top layer conductors be compatible with inner layer silver. Martin and Schroeder [101] investigated several top layer metallization for compatibility with inner layer silver under various test conditions like high operating temperature, high humidity, solderability etc. It was found that there was no silver migration to the dielectric. They observed that Cu and Ag/Pd surface conductors were migration resistant and capable of being interfaced with silver. The problem in using Au as a surface conductor was due to the concerns over voiding problems encountered when Au and Ag are in contact with each other. But, it was found that all conductors except Au either migrated or oxidized when exposed to biased environmental conditions. So, it was proposed that an LTCC system containing internal Ag and surface Au conductors would be the best alternative for low cost and high reliability LTCC MCMs.
The problem of Ag-Au interdiffusion was effectively addressed by Drozdyk et al. [102] who used a novel conductor for interconnecting Au inner layer and Au surface conductors. The novel conductor was tested for both thick film and LTCC processes. Direct connection of silver to gold results in voids called *kirkendall* voids near the interface due to difference in metal diffusion rates during firing. These voids lead to electrical opens thus causing obvious reliability problems. In addition, substantial silver diffusion leads to increased risk for environmental failure as shown by Needes et al.

Williams and Shaikh [103] studied Ag via fill ink formulations consisting of Ag powders, glasses and ceramic oxides and the compositions were adjusted to match the shrinkage and thermal expansion behavior of the LTCC. The glasses and ceramic oxides used in the via fill formulation were found to be chemically compatible with the tape. Electrical conductivity of the via material affects the signal propagation as well as microwave losses of the package. Thus, high electrical conductivity is desirable. Also, when thermal via arrays are used to conduct heat away from the device in to a heat sink, high thermal conductivity of the fired via material is desired. However, Williams and Shaikh observed decreases in both electrical and thermal conductivity values due to the use of ceramic oxides to modify the CTE or the shrinkage behavior of the via fill material. By optimizing the selection of via materials, they were able to achieve fired structures devoid of voids and cracks and flush via surfaces.

Kwang et al. [104] investigated LTCC-Ag electrode systems with regard to Ag diffusion and microstructure development in the fabrication of high-frequency couplers. To achieve the desired microstructure and to maintain interface integrity, care should be taken to control the two major steps, binder burnout and sintering during co-firing of
LTCC systems. Kwang et al. [104] used XRD, EPMA and SIMS techniques to carry out microstructural and microchemical analyses, for phase identification and Ag diffusion analysis. They also performed SEM experiments to determine the electrode line thickness and deformation. During the binder burnout process, it was found the decomposition of binders led to generation of pores due to rapid evolution of gases, which was detrimental to the electrode. Also, gases entrapped within pores due to incomplete decomposition were found to burst at high temperatures leading to glass infiltration from the substrate to the electrode which in turn led to Ag diffusion. Thus, it is very important to control the binder decomposition process. The key factors determining the microstructure are mainly governed by sintering behavior. At sintering temperatures below 875°C, no Ag diffusion was observed and Ag electrode reached its maximum density. But above 900°C, the increase of sintering temperature lowered the glass viscosity leading glass infiltration to the electrode and thus activating Ag diffusion to the substrate. The glass intrusion and Ag diffusion were found to cause severe deformation of the electrode line. Crystalline phases of Al2O3 and anorthite (Al-Ca-Si) were found to act as barriers against Ag diffusion.

2.6.7 NEMI (National electronics manufacturing initiative) Roadmaps [105]

Advancements in silicon technology are driving materials to lower dielectric constant, lower loss dielectrics with need for high conductivity conductors such as Cu and Ag. To meet ever-increasing customer demands of higher performance, higher functionality at a lower system cost, smaller vias on a finer pitch and integrated passive elements are desired. Some key suggestions from the most recent NEMI roadmaps are noted below,
• Smaller vias (< ~75 micron) could be achieved by utilizing advanced via formation techniques including mechanical, laser and photo via tools.

• Finer striplines and spacings should be made possible by using photo-imaging to pattern metallization.

• For embedded passive components, thick film resistor and high-K capacitor technology should be adopted for compatibility with LTCC tapes. For inductors photo-patterning to create high density spiral patterns could be applied.

• The need to improve analog functions has led to improved insulation materials with low dielectric loss (high Q) at microwave frequencies and combining conventional patterning with advanced patterning technologies.

• Device performance is the main driver for embedded passives while the lack of design and simulation tools, and test equipment is the primary hindrance to the technology development.

In this chapter, the problem of co-sintering (or constrained sintering) with relevance to LTCC technology was discussed. Modeling the co-sintering process, reducing sintering-related damage and improving device performance are key challenges facing the sintering community. The goal of this work is thus to develop a fundamental understanding of the processing of integrated ceramics (eg: LTCC, SOFC, MLCC etc.) to enable the development of a comprehensive sintering model.
Chapter 3

SCIENTIFIC APPROACH

In this research, we focused on three commercial LTCC systems i.e. DuPont 951Tape™, Heraeus CT2000™ and Ferro A6-M™ (hereon called DU, FE, and CT, respectively), since they illustrate the range of characteristics shown by ceramic particle-filled and crystallizable glass systems. The chemical composition data for the three materials determined by spectrochemical analysis are given in Appendix A. DU and CT tapes are ceramic particle-filled borosilicate glasses, while FE is a crystallizable Ca-borosilicate glass with no filler particles. DU is a Pb-borosilicate glass with alumina as the ceramic filler particle. To our knowledge, no detailed studies on the glass-filler interaction during heating in this system exist. In case of CT, the alkaline-silicate glass reacts with the alumina and titania filler particles to form high quality factor crystalline phases. The crystalline phases are designed to achieve low dielectric loss and high mechanical strength.

There are few detailed studies on understanding the fundamentals of the co-sintering problem and this work aims to fulfill this need. Three kinds of experiments will be done,

a. Thermo-mechanical characterization of LTCCs and silver metallization. This will include measurement of sintering kinetics, uniaxial viscosity and the
viscous Poisson’s ratio by development of new and improved tools and protocols.

b. Investigation of co-sintering phenomena such as warpage, and observation of microstructures and physical properties

c. Thermal analysis (DTA, DSC and XRD) of LTCC systems to understand glass characteristics including glass transition and crystallization

The methodology for developing a robust and comprehensive co-sintering model is shown in Fig. 3-1. We would like to note that this methodology is applicable for studying sintering of any co-sintered technology.
Characterize Sintering Behavior for Constituents (Arbitrary Firing Schedule)

Measure Uniaxial Viscosity $f(T, \rho)$ (Isothermal Cyclic Loading Dilatometry). Design Stress Cycles to Minimize Transverse Strain Induced by Cyclic Stress. Check Stress Linearity. Measure Viscous Poisson’s Ratio

Test Models by Comparing Curvature Development in Bi-Layers (Experimental vs. Calculated)

Calculate Constraining Stresses for Material System Under Study

Observe Microstructure and Correlate to Material Behavior.

Develop Design Guidelines Based on Tested Models and Observations

Fig. 3-1. Methodology for Developing Co-sintering Models
Detailed results are presented in the following six chapters. Chs. 4 and 5 describe the techniques for measuring the uniaxial viscosity and viscous Poisson’s ratio of a densifying material. Knowledge of these thermo-mechanical properties is essential to develop sintering models. The uniaxial viscosity depends on both density and temperature. To determine its explicit dependence if viscosity on both temperature and density, isothermal cyclic loading dilatometry is used. In Ch. 4, we demonstrate its merit relative to constant load techniques in minimizing the stress history effects (changes in shrinkage anisotropy and sample microstructure) that arise due to the application of an external load. Optimum conditions for testing the materials are also proposed. Ch. 5 introduces a novel approach based on pressureless constrained sintering for the determination of the viscous Poisson’s ratio of densifying systems. The method involves measuring the sintering rate of a free-sintered specimen, and a specimen constrained by two non-sintering layers. Representative data for a low temperature co-fired ceramic (LTCC) material are reported.

Ch. 6 discusses the measured data on the uniaxial viscosity and master sintering curves of the LTCC materials. Predicting the viscosity accurately is key to developing reliable sintering models. In Ch. 7, we present a theoretical understanding and framework for predicting the complex viscosity of LTCC systems, which is influenced by a host of interdependent factors including temperature, density, contact area, volume fraction of filler particles, percolation, crystallization, phase separation and heating rate.

Ch. 8 discusses the concept of constrained sintering. The microstructural evolution and physical properties of two LTCC materials with different thermo-
mechanical behavior are compared. A detailed stress analysis will be presented and the stresses correlated to the observed microstructures and material properties. In Ch. 9, real-time observations of bilayer curvature and model predictions will be presented. This simple technique will be used to test the sintering compatibility and validate the thermo-mechanical properties of the constituents. And, finally in Ch. 10, some concluding remarks and suggestions for future work are offered.
Chapter 4

MEASUREMENT OF VISCOSITY OF DENSIFYING GLASS-BASED SYSTEMS BY ISOThERMAL CYCLIC LOADING DILATOMETRY

4.1 INTRODUCTION

There is considerable interest in the development of sintering models that can predict shape and dimensional changes during manufacture of multi-layer, multi-component structures such as LTCC (Low temperature co-fired ceramics) packages, solid-oxide fuel cells, multi-layer actuators and other co-sintered systems. In order to achieve reliable predictions, knowledge of thermo-mechanical properties such as viscosity and viscous Poisson’s ratio and how they evolve during sintering is essential. If the sintering materials are considered linearly viscous, simple Newtonian constitutive equations based on the elastic-viscous analogy can be used to evaluate stresses and strains. The sintering of linear viscous systems under stress can be adequately described if the free sintering rates, and either the shear and bulk viscosities, or the uniaxial viscosity and viscous Poisson’s ratio are known. Many theoretical models have been proposed to describe the mechanical behavior of sintering systems\(^1\). However, adequate data are needed to test these models.

Sinter-forging\(^2\text{-}^7\) and bending creep\(^8\) have been proposed to measure the viscosity of glasses, ceramic-filled glasses and polycrystalline ceramics. In sinter-forging, a loading dilatometer\(^9\) was used to study simultaneously the creep and densification of a porous sample and thus calculate the shear and bulk viscosities. For example, Rahaman et al.\(^2\) and Ducamp and Raj\(^5\) reported non-linear variation of viscosity with porosity for soda-lime silica and borosilicate glasses, respectively. In
both studies, empirical functions were used to fit the experimental data. The empirical fit of Rahaman et al.\textsuperscript{2} showed poor agreement with Scherer’s theoretical model\textsuperscript{10} and this discrepancy was attributed to a difference in pore shape. Sura and Panda\textsuperscript{6} performed isothermal constant loading experiments on cordierite-glass powders and showed reasonable agreement between their theory and the experimental data of Rahaman et al.\textsuperscript{2} and Ducamp and Raj\textsuperscript{5}.

Sinter-forging tests are typically done under a constant load. The main weakness of a constant load technique is the irreversible effect of the applied load on the shrinkage anisotropy, density and microstructure. Because the application of an external load enhances densification and thus grain growth, the microstructure of a specimen under load can be very different from that of a pressureless sintered specimen. The effect of load on density can be reduced by using loads that are much lower than the sintering pressure (~1 MPa for ceramic materials). However, for glass-based systems, even low loads can result in significant shear due to low intrinsic shear viscosity of the glass phase. This can result in significant anisotropy and reduced shrinkage in the radial direction\textsuperscript{11}.

A cyclic load with alternating loading and unloading regimes reduces the stress history effects (i.e. changes in anisotropy, density and microstructure) since the specimen is allowed to recover towards a stress-free state after each loading step\textsuperscript{7,12}. These unloading steps serve as stress-free sintering regimes and thus, the strain rate during the unloading period is taken as the free strain rate. Therefore, both the free strain (shrinkage) rate and loaded strain rate can be obtained in a single run. Cai et al. reported the successful use of cyclic loading dilatometry for measuring the uniaxial viscosities of Al\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2}\textsuperscript{12} and their use in predicting camber and stresses in Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} laminates\textsuperscript{13,14}. Likewise, Mohanram et al.\textsuperscript{15} reported use of CLD to
measure viscosity of LTCC and silver systems and their use in predicting camber in silver-LTCC bilayers. Cai et al. used two kinds of cyclic loading tests, 1) a series of isothermal holds with superimposed cyclic loading and 2) constant heating rate with cyclic loading. The first test results in a different thermal history from constant-rate heating and, was shown to be unsuitable for characterizing the mechanical response, as the strain rates were significantly different from that of unloaded specimens at the same temperature. The second test involves continuous variation of both temperature and density and, thus, it is difficult to explicitly determine the dependence of viscosity on either density or temperature. In the current work, we report on the use of isothermal cyclic loading dilatometry (ICLD), to measure the viscosity dependence on both density and temperature. ICLD experiments involve isothermal holds with superimposed cyclic loading to measure the viscosities as the specimen densifies. The tests can be repeated at various temperatures and, thus, the temperature dependence of viscosity can be determined using an activation energy analysis.

Gillia et al. recently reported viscosities of WC-Co compacts and their use in phenomenological modeling. Here, we demonstrate the use of ICLD for measuring the viscosity of glass-based systems, such as low temperature co-fired ceramics (LTCC), that sinter by a viscous flow mechanism. The viscosities of LTCC systems are influenced by a host of complex, interdependent factors such as base glass composition and structure, temperature, density, glass crystallization, volume fraction of ceramic filler particles, percolation phenomena and heating rate. Data on viscosity are essential in understanding the interplay between these factors and for designing materials with tailored properties to achieve optimum sintering behavior. These systems undergo significant deformation under an applied load and, thus are more prone to stress-induced shrinkage anisotropy in comparison to materials that densify
by solid-state sintering mechanisms. The purpose of this paper is to describe the ICLD technique, demonstrate its merit relative to constant load techniques in reducing shrinkage anisotropy, and suggest optimum conditions for measuring the viscosity of glass-based systems.

4.2 THEORETICAL BACKGROUND

A porous material undergoing sintering has been shown to exhibit linear viscous behavior during densification. According to the linear viscous constitutive model for materials that sinter under the influence of an external uniaxial stress, the axial strain rate, stress and the viscosity are related by the following equation,

\[ \varepsilon^{\prime}_z = \varepsilon^{\prime}_{fz} + \frac{\sigma_z}{\eta} \]  

(1)

where, \( \varepsilon^{\prime}_z \) is the true strain rate in the presence of a load, \( \varepsilon^{\prime}_{fz} \) is the free true strain rate in the axial direction, \( \sigma_z \) is the applied uniaxial stress, and \( \eta \), the uniaxial viscosity of the sintering compact. The viscosity is calculated by applying an external load and measuring the stress-induced strain rate. The strain rate of a specimen under load includes the free strain rate, which has to be subtracted before one can extract the viscosity.

For a densifying material, the uniaxial viscosity can be expressed as

\[ \eta = f (\rho, G) \cdot \eta_0 \exp \left( \frac{Q}{RT} \right) \]  

(2)

where, \( \rho \) is the relative density, \( \eta_0 \), a constant, \( T \), the absolute temperature, \( G \), the grain size and \( Q \) is the activation energy. For non-linear materials, the viscosity can
also depend on the applied stress or strain. While the first term of the product on the right-hand side of eqn (2) gives the dependence of viscosity on relative density or conversely, porosity of a sintering compact, and grain size, the second term helps understand the intrinsic viscosity of the glass in the system and its temperature dependence. In systems that sinter by viscous flow such as LTCC systems, the viscosity is only a function of density and temperature unless other microstructural changes, such as crystallization occur. For polycrystalline ceramics, the grain-size dependence of viscosity should be included.

4.3 EXPERIMENTAL PROCEDURE

A commercial low temperature co-fired ceramic (CT2000, Heraeus Inc., PA) material was used for viscosity measurements. Binder was removed from tapes by heating at 2°C/min up to 450°C and holding for 2 h. The powders were uniaxially pressed at ~ 40 MPa into cylindrical pellets of ~ 6.38 mm diameter x 4.4 mm. The compacts were tested in a thermo mechanical analyzer (TMA50, Shimadzu) with a vertical loading rod 3 mm in diameter. A small load of 1 g was applied to ensure contact between the push rod and the sample.

The main concept behind a cyclic load test is to allow the sample to relax to free sintering state after each loading step. The TMA used in this study allows the use of a maximum load of 500 g with a maximum loading rate of 999 g/min, in compression or tension. The maximum initial stress level, however is also limited by the sample diameter. The samples were heated at 5°C/min to the temperature of interest and held for ~ 6.5 h. Such long isothermal holds were used to measure the viscosity over a wide range of densities at a particular temperature. The applied load used in this study was 200 g, which is equivalent to a stress of ~ 60 kPa. The loading
rate was 796 g/min and thus the maximum load was reached in 15 s. The loading rate was maximized to minimize the amount of time the sample was under the influence of applied load. There was not much difference in shrinkage behavior of the LTCC samples when loading rates of 796 g/min and 995 g/min were applied. Based on several test runs, the loading and unloading periods for each step were chosen to be 4 and 14 mins, respectively. This allowed the collection of sufficient data points and at the same time ensured that the specimen was under external load for a minimum period keeping the stress-induced axial deformation to a minimum. Longer unloading periods are possible, but this would lead to a decrease in the number of viscosity measurements, and so a compromise is needed. The mass and dimensions of the powder compacts were measured before and after the test, and the final densities were measured using the Archimedes method. The sample microstructures were examined using SEM (Hitachi SEM model S-3500N).

The true strain (in the axial direction) of a sintering compact of initial length $l_0$ is given by,

$$\varepsilon'_z = \ln(1 + \varepsilon''_z) = \ln(1 + \frac{\Delta l}{l_0}) \quad (3)$$

where, $\Delta l$ is the change in length, and superscripts $e$ and $t$ refer to the engineering and true strains, respectively. The engineering strain at any time can be obtained from the initial length and the specimen length as measured by the TMA in the axial direction. The engineering strain rates, both loaded and free, are obtained by calculating the slope of the strain curve with respect to time during loaded and unloaded conditions (Fig. 1). The true strain and strain rates can then be determined from the above equation.
Figure 4-1. Schematic showing a typical strain curve under a cyclic load and determination of the strain rate from the slope.
The density of a sintering specimen can be calculated for any time as,

$$\rho = \rho_g (1 - \frac{\Delta l}{k l_o})^{-2} (1 - \frac{\Delta l}{l_o})^{-1}$$  \hspace{1cm} (4)

where, $\rho_g$ is the green density, and $k$, the anisotropy factor.

The TMA can measure only axial strains and thus the radial strain is not known. In order to calculate the radial strain, an anisotropy factor is needed for the specimen of interest. To determine the anisotropy constant, first, we measure the fired density using the Archimedes method. Second, based on the linear shrinkage data obtained from TMA tests, we calculate the fired density of the specimen assuming isotropic shrinkage. The densities are compared and matched by choosing a particular value for $k$. Assuming a constant value of $k$ for the whole sintering period, the radial strain (or strain rate) and, thus, the true stress at any time can be calculated using the following equations,

$$\varepsilon_r' = \frac{\varepsilon_z'}{k}$$  \hspace{1cm} (5)

$$\sigma_t = \frac{\sigma_i}{(1 + \varepsilon_r^e)^2} = \sigma_i e^{-2\varepsilon_r^e}$$  \hspace{1cm} (6)

where $\sigma_i$ is the initial stress and $\varepsilon_r^e$ is the engineering radial strain. The true stresses and strains are then used to calculate the viscosity at different temperatures and densities. The relation between axial and radial strains given by equation 5 holds for both free sintered and loaded cases. In the presence of an external compressive load, the additional term that accounts for the reduction in radial shrinkage is included $^1$. An
important feature of the proposed methodology is to keep this reduction as small as possible, such that the stress-induced shrinkage anisotropy is as close as possible to the free shrinkage behavior. For the LTCC, the free sintering behavior is anisotropic. It is however, assumed that the viscous behavior of the sintering body remains isotropic. It is worth noting that sample barreling was insignificant due to the use of low applied loads and viscous nature of the material tested.

4.4 RESULTS AND DISCUSSION

The isothermal strain curves obtained by cyclic loading and constant loading at 765°C are compared with respect to the free strain curve in Fig. 2. As is clearly evident, the application of a constant load significantly enhances the axial deformation of the specimen. In comparison, a cyclic loading test has a relatively smaller effect on the axial shrinkage. Also, a closer look at the loaded strain curves reveals a significant amount of deformation in the initial loading step. This sharp increase in axial strain (or strain rate) is typical of tests done under an external load and is possibly due to the initial rearrangement of the powder. This rapid strain can be decreased by decreasing the load or maximizing the loading rate. The presence of a load, either cyclic or constant can increase the shrinkage anisotropy, density and change the specimen microstructure, which can be different from that of a free-sintered specimen as shown below.

In comparison to a cyclic load test, a constant load method underestimates the loaded strain rate ($\dot{\varepsilon}_z$), because of the gradual decrease in the driving force for sintering in the axial direction $^{12}$. This results in an overestimation of the viscosity, since the viscosity is inversely related to the strain rate. Figure 3 shows the viscosity versus density plots based on the isothermal strain data (Fig. 2). As is evident, the data
Fig. 4-2. Comparison of cyclic and constant loading profiles with the free strain curve (i.e. no load) at 765°C

Fig. 4-3. Viscosity versus density obtained by cyclic loading (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) and constant loading (200 g, 796 g/min) tests at 765°C
obtained by a constant load test are higher by an order of magnitude than for a cyclic load test.

It was found that for low applied loads (< 200 kPa), the densities of specimens heated under load and no load conditions differ by less than 2%. The initial applied load used in this study was 200 g (~ 60 kPa) at a loading rate of 796 g/min. However, for glass-based systems such as LTCC, the viscosities are typically lower than materials that sinter by solid-state sintering\textsuperscript{12}, and so the application of a load can result in significant shear, which in turn can result in greater shrinkage anisotropy and reduced shrinkage in the radial direction. Further, this effect is more pronounced in the viscous regime, where the use of cyclic loading dilatometry instead of a constant load test is even more justified compared to the visco-elastic regime.

The effect of the duration of the unloading period on the axial deformation is shown in Fig. 4. The strain curves were obtained by using two different cyclic load profiles having the same loading period of 4 min, but different unloading periods of 10 and 14 min during isothermal hold at 765°C. The smaller the ratio of loading to unloading period (hereafter called the l-ratio) or, the longer the unloading period, the more closely the loaded curve follows the free strain curve. This is due to the fact that for a given total duration of cyclic loading test at the isothermal hold, a test with a smaller l-ratio has fewer loading regimes and consequently less net axial deformation and therefore, is closer to the free-sintered curve. Conversely, the greater the l-ratio the greater the net axial deformation and, thus, the greater the stress-induced shrinkage anisotropy; the case, where the l-ratio $\rightarrow \infty$, corresponds to a constant loading test. Thus, a cyclic load test with smaller l-ratio gives a more accurate estimation of viscosity, as the stress-induced anisotropy is kept to a minimum.
Fig. 4-4. Strain versus time obtained by ICLD at 765°C for loading period of 4 min and unloading periods of 10 and 14 min. The free strain curve (i.e., no load) is also shown as a reference. (Note: The strain curve for unloading period of 12 min is not shown for clarity)
The measured anisotropy factor \((k)\) is shown as a function of unloading time in Fig. 5. As is evident, the stress-induced anisotropy factor decreases with increase in the unloading time. The value of \(k\) for a free-sintered specimen was \(\sim 1.2\). A linear fit was obtained and the value of the intercept, which corresponds to unloading time of 0 min, was found to be \(\sim 4.1\). The calculated value for a constant load test (when unloading time is zero) was \(\sim 3.8\), which is in good agreement with the extrapolated value. Thus, it is clear that a constant load test results in greater shrinkage anisotropy than a cyclic load test. Also, the linear fit predicts an unloading time of 16.6 min at which time the anisotropy factor reaches 1.2, which is the value for a free-sintered specimen. However, it was found that for a cyclic load test with unloading time of 16.6 min, the value of \(k\) was 1.65. This indicates a slower reduction of \(k\)-value as unloading time is increased, than that predicted by the linear fit.

The SEM micrographs of polished cross-sections of three specimens, free-sintered, and those tested under constant and cyclic loads at 765°C are shown in Fig. 6. The densities for all three specimens were close to 85% of fired density. The microstructures of the free-sintered and cyclic-loaded specimens show similarities, such as the presence of isolated pores, which are not apparent in the constant-loaded specimen. Further, the pore networks or clusters are larger in size, and the presence of low-density regions is more pronounced in the case of the constant-loaded specimen. This can be explained by the fact that an external load reduces radial shrinkage and thus more porosity is observed under the loading surface in the axial direction. From the above observations it is concluded that, a cyclic load test is a better technique for viscosity measurements because it allows for periodic unloading regimes thereby reducing stress-history effects.
Fig. 4-5. Measured anisotropy factor versus unloading time for strain curves shown in fig. 4-4.

Fig. 4-6. SEM micrographs of specimens fired at 765°C with a hold of 6 h 30 min. a) Free-sintered, b) Cyclic load (200g, loading time = 4 min, unloading time = 14 min) after 22 cycles, and c) Constant load (200g).
The viscosities were calculated using equation 1 and the method outlined above. The sintering rate during the unloading period was used as the free sintering rate. At lower temperatures, this results in an underestimation of the viscosity, because the unloaded strain rate is usually less than the free strain rate. This is because a compressive axial load enhances densification and results in reduced driving force for sintering in the axial direction leading to a lower strain rate after the load is removed \(^{19}\). However, the difference between the two strain rates becomes insignificant as sintering proceeds. The viscosity versus density plots for temperatures between 740 and 790°C are shown in Fig. 7 (Note: The system analyzed, a commercial LTCC, is a reactive ceramic-filled glass \(^{20}\). There is a continuous change in chemistry due to filler dissolution in glass and subsequent crystallization. Therefore, defining a single value of theoretical density is not appropriate. However, for the purposes of this study, the fired density (~ 3.1 g/cc) was used to calculate a nominal range of relative densities.) As expected, the viscosity increases with density due to the removal of porosity and decreases with increasing temperature. The viscosity of CT2000 ranges from ~ 1 to 20 GPa.s for relative densities from 70% to 96% between 740°C and 790°C. There are no detailed studies about the viscosity of commercial LTCC systems currently available. However, the results are similar to the viscosity data measured by constant load sinter-forging tests reported by Mikeska et al. \(^{7}\) on a commercial borosilicate glass/ceramic composite that is similar to the material used in this study.

To evaluate the reproducibility of the ICLD technique, the viscosity was measured three times for each temperature as a function of density (Fig. 8). The initial applied load was 200 g with a loading rate of 796 g/min, and the loading and unloading periods were 4 and 14 min, respectively. As is evident, the values obtained
Fig. 4-7. Viscosity versus density plots obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 740°C, 765°C, and 790°C.

Fig. 4-8a. Viscosity versus density obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 740°C, showing reproducibility of technique.
Fig. 4-8b. Viscosity versus density obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 765°C, showing reproducibility of technique.

Fig. 4-8c. Viscosity versus density obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 790°C, showing reproducibility of technique.
from three separate ICLD runs demonstrate good reproducibility of the measurements. This was confirmed with non-parametric Kruskal-Wallis statistical tests. The ‘H’ parameter, which is the Kruskal-Wallis test statistic, was found to be 0.82, 0.09 and 0.11, for viscosity data at 740°C, 765°C, and 790°C, respectively. The ‘H’ value can be considered the same as the chi-squared ($\chi^2$) value, if the number of data points is greater than five. Then, based on the number of sample data sets (in this case, three at each temperature), and the $\chi^2$ (or H) value, one can determine from standard tables on critical $\chi^2$ values, whether the observed $\chi^2$ is above or below a certain significance level (usually 0.05 or 5%). The observed $\chi^2$ values were much less than the critical $\chi^2$ value (= 5.99) at 0.05 significance level, or in statistical terms the difference between the data sets was insignificant for viscosity data at all three temperatures.

Any sample-to-sample variability of the viscosity data can be mainly attributed to the assumption of a constant anisotropy factor and low sensitivity of the dilatometer in measuring very small deformation rates ($\dot{\varepsilon}_z < 10^{-7} /s$). It should further be noted that the viscosity measurements at very high densities (> 92%) or during phenomena such as glass crystallization are subject to greater error, because of the very small deformation rates.

4.5 CONCLUDING REMARKS

A detailed description of the isothermal cyclic loading dilatometry (ICLD) technique to measure the viscosity of a glass-based system was presented. Representative data for a low temperature co-fired ceramic (LTCC) material were reported. In comparison to constant loading sinter-forging experiments, cyclic loading
dilatometry helps minimize the stress history effects that arise due to the application of external load and therefore gives a better estimate of viscosity. The loading rate should be maximized to minimize the effect of external load on sample deformation. The greater the unloading period, the less is the stress-induced shrinkage anisotropy. For the system investigated, loading and unloading periods of 4 and 14 min, respectively were used. However, in the case of polycrystalline materials, which exhibit different shear behavior from glass-based systems, different testing conditions would be required. The viscosity of a sintering compact increases with relative density and decreases with temperature. The viscosity of the LTCC ranges from ~ 1 to 20 GPa.s for relative densities from ~ 70 to 96% between 740°C and 790°C. Statistical analysis revealed insignificant differences between the viscosity data sets at 5% significance level and thus indicates good reproducibility of the testing tool in determining the viscosity of a sintering material. Any variability in the viscosity data would be due to the assumption of a constant anisotropy factor and low sensitivity of the dilatometer tool in measuring very small deformation rates (\( \varepsilon_t' < 10^{-7} /s \)).

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Chapter 5

A NOVEL USE OF CONSTRAINED SINTERING TO DETERMINE THE VISCOUS POISSON’S RATIO OF DENSIFYING MATERIALS

5.1 INTRODUCTION

There is renewed activity in developing characterization and modeling tools for predicting sintering processes based on the viscous analogy \(^1\), and the continuum sintering approach \(^2\). One of the key objectives is to generate experimental constitutive parameters, such as viscosity and viscous Poisson’s ratio (\(\nu\)), to support the development of constitutive models for sintering. The measurements are also valuable for calculating stresses and distortions in co-fired structures \(^3-6\), such as low temperature co-fired ceramic (LTCC) electronic packages, and in developing ways to minimize them. Little is known about how these properties evolve during sintering, and how they change with firing conditions. Different models have been proposed to predict the evolution of these properties with densification, but these disagree in their predictions \(^1\). As repeatedly noted by researchers, there is a clear need to measure the viscous properties, and to understand their relationship with densifying microstructure.

Various techniques including sinter-forging \(^7-10\), and variations of it, such as cyclic loading dilatometry \(^11, 12\), discontinuous sinter forging \(^13\), and bending creep \(^14\), have been used for the measurement of axial viscosity. The viscous Poisson’s ratio is a more challenging parameter to measure as it requires highly accurate measurements of shrinkage rate and density. Recently, simultaneous high resolution measurement of the
shrinkage rate in both the axial and lateral directions has been reported. For example, Zuo et al.\textsuperscript{15} measured the \( \nu \) for alumina during densification by discontinuous hot forging. The \( \nu \) ranged from 0.2 at 65\% of theoretical density to 0.45 at \( \sim \) 96\% and was in good agreement with the model of Venkatachari and Raj\textsuperscript{8}. Similarly, Salamone et al.\textsuperscript{16} measured the \( \nu \) for liquid-phase sintered \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) compacts using sinter-forging under applied stresses of 1 and 2 MPa. The average \( \nu \) ranged between 0.26 to 0.35 from \( \sim \) 70\% to 90\% density, respectively, and the values were in good agreement with Scherer’s model\textsuperscript{17}, which was developed for highly porous glasses such as gels and silica soot pre-forms. Gillia et al.\textsuperscript{18} characterized the \( \nu \) for WC-Co compacts using cyclic loading dilatometry, and a video extensometry apparatus, and found the \( \nu \) to vary between 0.1 at 75\% to 0.5 at full density. It is worth noting that in the theoretical models mentioned above\textsuperscript{1}, the \( \nu \) is assumed to depend only on the density.

In this paper, we propose a novel measurement procedure to determine the \( \nu \). The method utilizes pressureless constrained sintering\textsuperscript{19} and is viewed as a far less complex method than sinter-forging measurements. Constrained sintering is a method that completely inhibits x-y (radial) shrinkage of the sintering material, by sintering the material between two non-sintering layers, thus limiting shrinkage to the z (axial) direction. As a result, there is no need for the application and control of an external load to provide zero in-plane shrinkage. As shown below, for the case of zero external load, the value of the \( \nu \) depends only on the measured shrinkage of the unconstrained and constrained specimens. In this work, we demonstrate the measurement of the \( \nu \) for a commercially available glass-based LTCC system (DuPont 951Tape\textsuperscript{TM}). The data are compared with some theoretical models.
5.2 VISCIOUS POISSON’S RATIO DERIVATION

In this section, we derive an equation for the \( \nu \) of a linear viscous material for the case of constrained sintering. The following derivation is based on the elastic-viscous analogy \(^1\). Consider rigid plates with an intervening linear viscous (isotropic) layer. Applying Newton’s Law for the viscous layer, the strain rates in the presence of stresses are (in Cartesian co-ordinates),

\[
\begin{align*}
\dot{\varepsilon}_x &= \frac{\sigma_x}{\eta} - \frac{\nu \sigma_y}{\eta} - \frac{\nu \sigma_z}{\eta} + \dot{\varepsilon}_{f_x} \\
\dot{\varepsilon}_y &= \frac{\sigma_y}{\eta} - \frac{\nu \sigma_z}{\eta} - \frac{\nu \sigma_x}{\eta} + \dot{\varepsilon}_{f_y} \\
\dot{\varepsilon}_z &= \frac{\sigma_z}{\eta} - \frac{\nu \sigma_x}{\eta} - \frac{\nu \sigma_y}{\eta} + \dot{\varepsilon}_{f_z}
\end{align*}
\]

where \( \dot{\varepsilon} \) is the strain rate, \( \sigma \) is the stress, and \( \eta \) is the uniaxial viscosity. The subscript \( f \) refers to the free sintered case. For layered materials, when the x-y shrinkage is isotropic, but is not equal to the z shrinkage, the free sintered strain rates are related as,

\[
\dot{\varepsilon}_{f_x} = \dot{\varepsilon}_{f_y} = \frac{\dot{\varepsilon}_{f_z}}{k}
\]

where, \( k \) is the anisotropy factor.

Because there is no external uniaxial load,

\[
\sigma_z = 0
\]
For the case of constrained sintering,

$$\varepsilon_x = \varepsilon_y = 0 \quad (6)$$

Substituting equations (5) and (6) into equations (1) and (2) we get,

$$\sigma_x = \sigma_y \quad (7)$$

$$\varepsilon_{fe} = -\frac{\sigma_x}{\eta}(1 - \nu) \quad (8)$$

Substituting equations (4) and (8) into equation (3) we get,

$$\varepsilon_z = \varepsilon_{fe} = \frac{2\nu}{(1 - \nu)k} + 1 \quad (9)$$

Rewriting equation (9), we get,

$$\nu = \frac{k(\varepsilon_z - \varepsilon_{fe})}{k(\varepsilon_z - \varepsilon_{fe}) + 2\varepsilon_{fe}} \quad (10)$$

For the case of isotropic free shrinkage ($k = 1$), equation (10) reduces to,

$$\nu = \frac{\varepsilon_z - \varepsilon_{fe}}{\varepsilon_z + \varepsilon_{fe}} \quad (11)$$

To determine $\nu$ from equation (10), it is important to ensure the assumptions in Table 1 are accurate.
Table 5-1. List of key assumptions in the derivation of $\varphi$

- The sintering material is linear viscous i.e., the strain rate varies linearly with the applied stress
- The constraining stresses are constant through the thickness
- The free sintering rate, $\varepsilon_f$, is not influenced by the constraining stress
- Radial shrinkage of the constrained specimen is zero through the thickness
- $\varphi$ is a function of density only
5.3 EXPERIMENTAL PROCEDURE

A commercially available low temperature co-fired ceramic material, DuPont 951GreenTape™ (DuPont Microcircuit Materials, Research Triangle Park, NC) was used. This is a Pb-borosilicate glass system with alumina filler particles. The material was obtained in tape-cast form. The thickness of the as-received green tape was \( \sim 100 \mu m \). The individual tape-cast layers were isostatically laminated (Model IL-4004, Pacific Trinetics Corporation, San Marcos, CA) with and without symmetric alumina constraining layers. Alternate tapes were rotated by 90° during stacking before lamination to minimize any possible difference between the shrinkage in the x (transverse) and y (casting) directions arising from particle orientation during the tape-casting process. The lamination pressure and temperature were 24 MPa and 80°C, respectively. The density of fully dense tape is 3.12 g/cm³. The alumina constraining layers were prepared by tape-casting nominally 0.5 \( \mu m \) diameter \( Al_2O_3 \) powder (A16SG, Alcoa, Pittsburgh, PA) dispersed in toluene with binder (B77305, Ferro, San Marcos, CA) and modifier (M1111, Ferro, San Marcos, CA) after ball-milling for 72 h. The alumina tape was 100 ± 15 \( \mu m \) thick after drying. The thickness of the LTCC layer in the laminated tapes was \( \sim 1.12 \) mm. The laminates were then blanked to \( \sim 5 \times 5 \) mm sized samples. The shrinkage behavior was measured using a thermo-mechanical analyzer (Shimadzu, TMA-50, Kyoto, Japan) with a vertical loading rod 3 mm in diameter. Binder was removed by heating to 400°C at 2°C/min with a dwell of 1 h. The samples were then fired to a peak temperature of 870°C at 5°C/min. After firing, the \( Al_2O_3 \) constraining layers were removed, and the densities of the constrained and unconstrained LTCC layers were measured by Archimedes’ method. The microstructures were examined using SEM (Hitachi SEM
model S-3500N). Specimens were also sintered in a furnace without contact to any measuring tools for comparison with TMA measurements.

Based on the shrinkage data, the instantaneous density of a sintering specimen can be calculated for any time as,

\[ \rho = \rho_g (1 + \varepsilon_{fx})^{-2}(1 + \varepsilon_{fe})^{-1} \]  \hspace{1cm} (12)

or, expressed in terms of \( k \), using equation (4),

\[ k = \frac{\varepsilon_{fe}}{1 - \sqrt{\frac{\rho_g}{\rho_s (1 + \varepsilon_{fe})}}} \] \hspace{1cm} (13)

where, \( \rho_g \) is the green density, and \( \rho_s \) is the fired density.

For a perfectly constrained specimen,

\[ \rho = \rho_g (1 + \varepsilon_z)^{-1} \] \hspace{1cm} (14)

To obtain reliable data, it is important to get accurate values for the green density and the radial strain of unconstrained specimen. For small specimen dimensions, determination of green density by the dimension method is prone to error. Further, because the TMA only measures the axial strain, the radial strain and thus, the anisotropy factor are not known. We used the following methodology to determine the green density and anisotropy factor. Since the fired density of the constrained specimen and its total axial shrinkage are accurately known, the green density can be calculated using equation (12). Since both the unconstrained and constrained specimens are prepared under the
same experimental conditions, the calculated green density is used for the unconstrained specimen. Based on this information, and data on fired density and free shrinkage, the anisotropy factor of the unconstrained specimen at full density can be determined using equation (13).

In agreement with the literature on glass compacts \(^9,^20\), the anisotropy factor was assumed to stay constant throughout sintering. To verify this assumption for this system, the densities of specimens fired to intermediate sintering temperatures were measured. These intermediate density values were then compared with those calculated based on the final anisotropy factor calculated using the methodology described above. Good matching between the measured and calculated densities would validate the assumption of a constant anisotropy factor. Further, to determine whether the material could be considered viscous during sintering, the compact was tested by cyclic loading dilatometry \(^12\) (initial stress \(~ 60 \text{ kPa}\), loading period of 1 min and unloading period of 3 min and 1 min between 550-740\(^\circ\)C and 740-870\(^\circ\)C, respectively).

5.4 RESULTS AND DISCUSSION

The axial strains of the unconstrained and constrained LTCC samples are plotted as a function of sintering temperature in Fig. 1. The total axial shrinkage at full density was 21.65% and 28.54% for the unconstrained and constrained specimens, respectively. The values were based on at least three separate runs with a variability of \(< 0.5\%\) linear shrinkage indicating good reproducibility. It is worth noting that the free shrinkage, measured using the TMA, is higher than that of a sample fired without contact to any measuring tools in a furnace (~14\%). This difference is due to the application of a small
Fig. 5-1. Z Strain versus sintering temperature of unconstrained and constrained specimens of DuPont 951Tape™
load by the TMA. However, since the same load is applied on both unconstrained and constrained specimens, the derivation of $\nu$ does not change.

Using the methodology mentioned above, the green density of the LTCC layer was determined to be $\sim 69.5\%$. The green density is higher compared to that reported in the literature for this material. This is believed to be due to the higher pressure and temperature, 24 MPa and 80°C, respectively, used for lamination in this work compared to 18 MPa and 65°C reported in the literature. As seen in Fig. 2, there is slight curvature at edge of the LTCC specimen, because of non-uniform shrinkage due to the constraint. The shrinkage is largest at the middle plane and decreases towards the alumina/LTCC interface. Based on shrinkage of $\sim 100$ $\mu$m at the middle plane, measured from the micrograph and initial sample dimension of $\sim 5$ mm, the average radial strain of the constrained specimen was 1%. This nominal shrinkage was taken into account in the calculation of green density. Equation (10) was derived with an assumption of zero-shrinkage in the x-y plane. The shrinkage at the edges is, however, not expected to significantly affect the calculation of $\nu$ as long as the LTCC thickness is small compared to the lateral dimension of the sample. For the current measurements, the aspect ratio was $\sim 5$ to 1. Clearly, we expect that the use of higher aspect-ratio specimens would further reduce the error.

From equation (13), the value of $k$ for the unconstrained sample at full density was 3.95. As noted before, this value was assumed constant throughout sintering. The instantaneous density data for the free-sintered and constrained specimens calculated using equation (12) are plotted in Fig. 3. For most of the sintering cycle, the density of
Fig. 5-2. SEM micrograph showing the curved edge of DuPont 951Tape™ laminate fired to 870°C at 5°C/min; the constraining layers are not shown.

Fig. 5-3. Relative density versus sintering temperature of unconstrained and constrained specimens; the measured densities of specimens from interrupted tests are also shown for comparison.
the constrained material was lower than that of the unconstrained material. The values differ by < 2%. Towards the end of the densification process, the constrained specimen reaches a fired density similar to the unconstrained material. Archimedes’ density data of free-sintered specimens fired to intermediate sintering temperatures are also shown in Fig. 3 for comparison with the calculated data. The margin of error in the measurements was < 2%. The good agreement between the measured and calculated densities validates the assumption of a constant anisotropy factor. The strain rates were obtained by fitting polynomial functions to the strain data and differentiating. The axial strain rates of the two samples at the same density (that of the constrained specimen), shown in Fig. 4, and $k$ were used in equation (10) to determine $\nu$.

It is worth noting that the specimens although at the same density, differ in temperature by 5-10°C, because the constrained specimen lags the unconstrained specimen in densification. We believe this small difference in temperature may not lead to any observable differences in microstructure between the constrained and unconstrained specimens. Also, because the constraint is constant, the technique has the same limitations as constant loading dilatometry experiments with regard to changes in microstructure, density and shrinkage anisotropy $^{11,12}$.

The calculated $\nu$ is plotted as a function of relative density and compared to theoretical models $^{8,17,22}$ in Fig. 5. The Poisson’s ratio varies from 0.25 at ~ 74% density to about 0.45 at ~ 93%. Calculations below 74% density yielded negative values, and those above 93% density gave unrealistic values (> 0.5). The sintering body acts like a predominantly elastic material during the early and final stages of sintering, when the
Fig. 5-4. Z Strain rate versus relative density of unconstrained and constrained specimens

Fig. 5-5. Comparison of calculated viscous Poisson’s ratio as a function of relative density with theoretical predictions
Fig. 5-6 Z strain versus sintering temperature for an unconstrained DuPont 951Tape™ sample under a cyclic load (initial load ~ 60 kPa) showing a viscoelastic behavior. The hatched region indicates a predominantly viscous response.

Fig. 5-7. Relaxation time versus relative density based on the strain response in fig. 6. The hatched region indicates a predominantly viscous response.
strain rates are low (< $10^{-5}$ /s). This behavior is confirmed by Fig. 6, which shows the strain response of an unconstrained sample measured under a cyclic load. The relaxation time for a Maxwell element, which consists of a spring and dashpot in series, defined as the ratio of viscosity to elastic modulus (or strain to strain rate), was calculated based on the strain data in Fig. 6. As shown in Fig. 7, the relaxation time was high compared to the loading period of 60 sec in the early and final stages of sintering, thus indicating the material is predominantly elastic. Thus, the $\nu$ derivation is not applicable in this regime. On the other hand, during the intermediate stage sintering, the elastic strain was negligible, often below the detection limit of the equipment resulting in low relaxation times. At $\sim$ 94% density, the relaxation time was $\sim$ 20 sec. Thus, over the intermediate densification regime, when the strain rates are high, the $\nu$ data are considered quite reliable. As shown in Fig. 5, there is reasonable agreement between experimental $\nu$ data and the models of Venkatachari and Raj $^8$ and Scherer $^{17}$.

5.5 APPLICATION OF THE APPROACH

For convenience, we outline a step-by-step procedure to obtain the best results from the constrained sintering technique,

1) Identify a constraining system for the material to be characterized (hereon called ‘constraining’ and ‘target’ layers, respectively). The constraining layer should be non-sintering, and should adhere to the material. Care should be taken to avoid excessive adhesion, for example, due to chemical interaction, as this will prevent the removal of the constraining material after firing.
2) Prepare flexible tapes of target, and sacrificial systems. Laminate tapes to get specimens of sufficient thickness for shrinkage measurements. For the constrained sample (target + constraining system), place the constraining layers in a symmetric arrangement on either side of the target. To minimize the effect of edge curvature, it is preferable to use an aspect ratio > 10.

3) Measure the shrinkage of target and constrained specimens in a dilatometer. Use base plates to avoid direct contact between the specimens and the dilatometer push rod. The plates should be non-reactive with the push rod and the sample to keep frictional forces to a minimum, and prevent specimen barreling. Remove constraining layers and measure the fired densities, and calculate the shrinkage rates from shrinkage curves.

4) Based on the shrinkage and fired density, calculate the green density using equation (14). Use this information to determine the free shrinkage anisotropy factor \( k \) using equation (13). Then, calculate the densities for the rest of the sintering period. Take into consideration the shrinkage at the free edges.

5) Use shrinkage rates of target and constrained specimens at the density of the latter, along with \( k \) in equation (10) to determine the VPR. If negative or unrealistic values \( (> 0.5) \) are seen, allow for up to \( \pm 2\% \) error in shrinkage and density, and recalculate.

5.6 CONCLUDING REMARKS

A novel method, based on pressureless constrained sintering, was presented for the measurement of viscous Poisson’s ratio. The constrained sintering method is a viable
alternative to more complex techniques, especially for use in an industrial setting. Representative data for a low temperature co-fired ceramic (LTCC) material were reported. The viscous Poisson’s ratio varies from 0.25 at ~ 74% density to about 0.45 at ~ 93%. Unrealistic values are obtained during the early and final stages of sintering, because the sintering material is predominantly elastic at low sintering strain rates (< 10^{-5} /s), which are characteristic of these regimes. The viscous analysis is applicable during the intermediate densification regime, over which the data are in reasonable agreement with the models of Venkatachari and Raj^8 and Scherer^17. To improve the accuracy of the data, simultaneous measurement of the axial and radial strains during free sintering would be useful. We expect the method to work for polycrystalline materials also, if a suitable constraining system is identified. It is also possible to use the technique even if there is a non-zero external load, provided the same load is applied to the two specimens. A possible refinement of the current technique would be to perform these tests on specimens of varying thickness and green density to see their effect on shrinkage, and thus υ.

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Chapter 6

DENSIFICATION AND SINTERING VISCOSITY OF LOW TEMPERATURE CO-FIRED CERAMICS

6.1 INTRODUCTION

Glass-based ceramic materials offer significant advantages, including low sintering temperature, and low dielectric constant, relative to high temperature co-fired ceramics for electronic packaging applications. These materials, known as low temperature co-sintered ceramics (LTCCs), enable the integration of electronic, mechanical, photonic, fluidic, and bio-chemical functions in compact 3-D architectures.

There is considerable interest in the development of a comprehensive modeling tool for prediction of dimensional and shape changes during co-sintering processes. Knowledge of material properties such as uniaxial viscosity and viscous Poisson’s ratio, and how they evolve during the sintering process, is essential for optimal sintering of LTCC devices and for use in continuum sintering models. Viscosities for some glasses and ceramics have been measured by the sinter-forging technique, cyclic loading dilatometry, and bending creep. Earlier works analyzed stress development and distortion during co-firing of LTCC-metal systems, and constrained sintered systems theoretically. We reported measurements of the viscosity of LTCC and silver systems by cyclic loading dilatometry for predicting the warpage of LTCC-silver bilayers. Garino reported the use of measured properties for warpage analysis in LTCC and silver-palladium systems. Recently, Xie et al. reported the viscosity of LTCC systems measured by sinter-forging. They noted the
inadequacy of the currently available models for predicting the viscous behavior during densification. These studies clearly indicate a growing interest in understanding the viscous behavior of sintering materials.

A complementary tool to the aforementioned continuum models is the master sintering curve (MSC) concept\textsuperscript{18}, which is used to predict the density for arbitrary firing profiles. The MSC method assumes that microstructural evolution depends only on density for any given powder type and green body process and that a single mechanism of mass flow dominates during sintering. These assumptions allow the formulation of a single-valued function of density that depends only on the sintering activation energy and the time-temperature profile. Thus, for a given set of sintering data, the method can be used to estimate the sintering activation energy and kinetics under different sintering paths. Further, it allows the detection of any changes in the dominant sintering mechanism such as surface diffusion in crystalline materials, or crystallization in glass systems.

Knowledge of macroscopic thermo-mechanical properties and sintering kinetics would allow prediction of stresses and consequent defects for arbitrary thermal histories. In this paper, we report on the shrinkage behavior and uniaxial viscosities of three commercial LTCC systems (i.e. DuPont 951 Tape\textsuperscript{TM}, Heraeus CT2000\textsuperscript{TM} and Ferro A6M\textsuperscript{TM}). We have chosen these systems since they illustrate the range of characteristics shown by ceramic particle-filled and crystallizable glass systems. Since LTCCs are glass-based, sintering occurs by viscous flow. Ewsuk et al.\textsuperscript{19} proposed a non-reactive liquid phase sintering model for ceramic particle-filled glasses, in which densification occurs via a combination of glass redistribution, grain rearrangement, and viscous flow. The evolution of viscous behavior of these systems can depend on several factors, including the base glass composition, temperature,
porosity, volume fraction and size of ceramic fillers, glass crystallization, and firing rate. Thus, the analysis of the sintering behavior of these systems can be quite complex. The purpose of this study is to present an understanding of the interplay of these diverse factors as interpreted from thermo-mechanical, microstructural, and thermal analysis data.

**6.2 THEORETICAL BACKGROUND**

The viscosity of the glass is intrinsic to the LTCC material and can be expressed as an Arrhenius function of temperature,

\[
\eta = \eta_0 \exp \left(\frac{Q}{RT}\right)
\]

where \( Q \) is the activation energy for viscous flow, and \( \eta_0 \), the pre-exponential constant. Porosity, particle morphology and size, and contact area play an important role in determining the viscosity of sintering glasses. For these systems, the term ‘viscosity’ is defined as the resistance to creep or densification of the material in response to an internal and/or external stress. Depending on the stress state i.e., shear, hydrostatic or uniaxial, the viscosity takes on different meanings. In fact, a sintering material cannot be fully described, unless the shear and hydrostatic (or bulk) viscosities, or the uniaxial viscosity and viscous Poisson’s ratio are known. This description follows the elastic-viscous analogy, and has been found to be quite useful in developing sintering models based on the continuum sintering approach.\(^{7,20}\)

A porous glass undergoing sintering can be treated as a linear viscous material\(^ {21}\). Accordingly, densification of these materials is related to the external uniaxial stress \( (\sigma_z) \), and the viscosity \( (\eta) \) as follows,
\[
\dot{\varepsilon}_z = \dot{\varepsilon}_{f_z} + \frac{\sigma_z}{\eta} \tag{2}
\]

where, \( \dot{\varepsilon}_z \) is the true strain rate in the presence of a load, and \( \dot{\varepsilon}_{f_z} \), the axial strain rate of the free-sintered specimen.

The MSC equation \(^{18}\) is given by,

\[
\Phi(\rho) = \Theta(T,t) \tag{3}
\]

where, \( \Phi(\rho) \), which includes the density \( (\rho) \) dependent microstructural and material properties, is given as,

\[
\Phi(\rho) = \frac{k}{\gamma \Omega D_0} \int_{\rho_0}^{\rho} \frac{G^n}{3\rho^\Gamma} d\rho \tag{4}
\]

where, \( \gamma \) is the surface energy, \( \Omega \) the atomic volume, \( k \) the Boltzmann constant, \( G \) the mean grain diameter, \( \Gamma \) the microstructural scaling parameter, \( n \) is 3 or 4 for volume or grain boundary diffusion, respectively.

The theta parameter, \( \Theta(T,t) \), which includes the time \( (t) \) and temperature \( (T) \) dependent terms, is given as,

\[
\Theta(T,t) = \frac{1}{T} \exp\left(\frac{-Q}{RT}\right) dt \tag{5}
\]

where, \( Q \) is the sintering activation energy, and \( R \) is the gas constant.

It is evident that equation (1) is similar to the MSC equation (3). Both equations assume a single mechanism of diffusion during sintering, which is assumed
to change with temperature in an Arrhenius form. Thus, one would expect the sintering activation energy calculated from equations (1) and (3) to be the same. It is also known that the viscosity of porous materials depends on the density, which is an implicit assumption of the MSC approach. For the case of viscous materials, the grain size term is neglected.

### 6.3 EXPERIMENTAL PROCEDURE

Commercial LTCC tapes such as DuPont 951 Tape™, Heraeus CT2000™ and Ferro A6M™ (henceforth called DU, CT, and FE tapes, respectively) were studied. DU and CT tapes are ceramic particle-filled borosilicate glasses, while FE is a crystallizable Ca-borosilicate glass with no filler particles. DU is a Pb-borosilicate glass with alumina as the ceramic filler particle. To our knowledge, no detailed studies on the glass-filler interaction during heating in this system exist. In case of CT, the alkaline-silicate glass reacts with the alumina and titania filler particles to form high quality factor crystalline phases. The crystalline phases are designed to achieve low dielectric loss and high mechanical strength.

All materials were obtained in the tape-cast form from the manufacturers. Loose powders of the tapes were produced by removing the organic binder by heating the tapes at 2°C/min to 400°C-450°C and holding for 1-2 h. For thermo-mechanical analysis (TMA), the powders were uniaxially pressed at ~ 40 MPa into cylindrical pellets of ~6.38 mm diameter x 4.4-4.5 mm (for CT and DU) and 5.5 mm (for FE). The green densities were ~62 and 65 ± 2% of the bulk fired densities for DU, and CT and FE each, respectively. The compacts were tested in a TMA (TMA50, Shimadzu, MD) with a vertical 3 mm diameter loading rod. For the isothermal tests, the samples were heated at 5°C/min to the temperature of interest and held for ~5-7 h. Such long
holds were used to measure the isothermal viscosity over a wide range of densities. The applied load during testing was 200 g, which is equivalent to a stress of ~ 60 kPa. The loading rate was 398 g/min and thus the maximum load was reached in 30 s. The loading and unloading periods were 4 and 14 min, respectively. A detailed description of the technique and measurement procedures were reported earlier \(^{25}\). 

For non-isothermal tests, the samples were tested under an initial load of 200g at 2ºC/min, 5ºC/min, and 10ºC/min up to a maximum temperature of 890ºC. The loading and unloading periods were 1 and 3 min, respectively for 2ºC/min, and 1 min each for the higher rates. As shown in our earlier work \(^{25}\), greater unloading periods are desirable, because stress history effects during testing are reduced. However, to collect sufficient data, especially at high heating rates, the loading profile was modified. The mass and dimensions of the powder compacts were measured before and after the dilatometry test, and the final densities were measured using the Archimedes method.

The sample microstructures were examined by scanning electron microscopy (SEM) (Hitachi SEM model S-3500N, CA). The compacts from the viscosity measurements were crushed to fine powders using a mortar and pestle for use in x-ray diffraction (XRD) measurements (Cu-K\(\alpha\), Scintag2 PAD V, Scintag Inc., CA). To analyze the glass softening and crystallization behavior, differential thermal analysis (DTA) (SDT 2960, TA Instruments, DE) studies were carried out at 2, 5, 10, 20, 30 and 40ºC/min. The activation energy for crystallization was determined using the Kissinger analysis \(^{26,27}\). The equation is given by,

\[
\ln\left(\frac{\phi}{T_p^2}\right) = -\frac{E_a}{RT_p} + const
\]

(6)
where, $\phi$ is the DTA scan rate (heating rate) in °C/min, $T_p$ is the peak crystallization temperature in °K, $E_o$ is the activation energy in KJ/mol, and $R$ is the gas constant (8.314 J/mol °K). The slope of the ln $\left(\frac{\phi}{T_p^2}\right)$ versus $1000/T_p$ plot gives the activation energy.

6.4 RESULTS AND DISCUSSION

6.4.1 Thermal Analysis, Densification and Microstructural Observations

Glass softening and crystallization have a strong effect on the viscosity of LTCC systems, and thus their sintering behavior. The glass transition temperatures, $T_g$ were ~ 630, 660 and 672 °C for DU, CT and FE, respectively. The onset and peak crystallization temperatures, $T_o$ and $T_p$, respectively, and the activation energy for crystallization calculated from the DTA data measured at 2, 5, 10, 20, 30 and 40 °C/min are summarized for the DU, CT and FE tapes in Table 1. With increase in the heating rate, $T_o$ and $T_p$ move toward higher temperatures.

The activation energies determined by Kissinger analysis for DU, CT and FE were ~ 300, 250 and 350 kJ/mol, respectively. In the case of FE, two crystallization peaks corresponding to wollastonite (CaSiO$_3$) and the calcium borate phases were seen $^{26, 28}$. However, with increase in heating rate, the two peaks merge to form a single peak. The calculated activation energy corresponds to the formation of wollastonite.

The densification of CT, DU and FE pellets heated at 2 °C/min, 5 °C/min and 10 °C/min are shown in Figs. 1 a-c, respectively. The densities were calculated based on the linear shrinkage data from the TMA. Defining a single value of theoretical density is not appropriate, because of filler particle dissolution and crystallization
Table 6-1. Onset and Peak Crystallization Temperatures, and Activation Energies for Three Commercial LTCC Tapes

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>DU Tape</th>
<th>CT Tape</th>
<th>FE Tape</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_o$ (°C)</td>
<td>$T_p$ (°C)</td>
<td>$Q_k$ (kJ/mol)</td>
</tr>
<tr>
<td>2</td>
<td>806</td>
<td>888</td>
<td>835</td>
</tr>
<tr>
<td>5</td>
<td>855</td>
<td>912</td>
<td>858</td>
</tr>
<tr>
<td>10</td>
<td>894</td>
<td>932</td>
<td>885</td>
</tr>
<tr>
<td>20</td>
<td>914</td>
<td>959</td>
<td>907</td>
</tr>
<tr>
<td>30</td>
<td>925</td>
<td>978</td>
<td>927</td>
</tr>
<tr>
<td>40</td>
<td>935</td>
<td>991</td>
<td>938</td>
</tr>
</tbody>
</table>

$T_o$ – Crystallization onset  
$T_p$ – Crystallization Peak  
$Q_k$ – Kissinger Activation Energy

Fig. 6-1a Plot of relative density versus sintering temperature for DU at heating rates of 2°C/min, 5°C/min, and 10°C/min
Fig. 6-1b Plot of relative density versus sintering temperature for CT at heating rates of 2°C/min, 5°C/min, and 10°C/min

Fig. 6-1c Plot of relative density versus sintering temperature for FE at heating rates of 2°C/min, 5°C/min, and 10°C/min
during sintering. However, for the purpose of this study, the fired densities were used to calculate a nominal range of relative densities. In case of DU, the specimens reach similar fired densities (3.14 g/cm$^3$ ± 2%) independent of the heating rate. For CT, the fired density at 2$^\circ$C/min (3.08 g/cm$^3$ ± 2%) was lower than that at heating rates of 5 and 10$^\circ$C/min (∼3.14 g/cm$^3$). The FE specimens fired to a higher density at 2$^\circ$C/min compared to 5 and 10$^\circ$C/min. The fired densities of FE specimens were 2.55, 2.48, 2.48 g/cm$^3$ at 2, 5 and 10$^\circ$C/min, respectively. The higher density at 2$^\circ$C/min is believed to be due to the crystallization of both wollastonite and Ca-borate crystalline phases. Based on the density data and using MSC software $^{29}$, the master sintering curves were determined, and these are shown with the measured data in Figs. 2 a-c. The sintering activation energies (Q) corresponding to the best fit were ∼400 kJ/mol, 530 kJ/mol and 565 kJ/mol, for DU, CT and FE respectively. For the CT and FE tapes, the difference between the data and fit is evident, especially at higher densities, when the data diverge.

One of the known limitations of the MSC approach is its inability to accurately predict the densification behavior, if two or more mechanisms of sintering operate simultaneously. In such cases, more than one activation energy is needed and thus, it is difficult to get an accurate MSC curve. For glass-based systems, the sintering occurs by viscous flow. However, if there is glass crystallization, or a change in the chemical composition of the glass, more than one Q value is needed. It is known that both CT and FE crystallize below peak firing temperature. In the case of CT tape, the alumina fillers react with the borosilicate glass to form anorthite (MA1$_2$Si$_2$O$_8$, M = Ca, Sr or Ba) crystals, while in the FE tape, the Ca-borosilicate
Fig 6-2a Master Sintering Curve of DU based on the data in Fig. 6-1a.

Fig. 6-2b Master Sintering Curve of CT based on the data in Fig. 6-1b
Fig. 6-2c Master Sintering Curve of FE based on the data in Fig. 6-1c
glass crystallizes to form wollastonite (CaSiO$_3$) and Ca-Borate phases. It is also known that slower heating rates promote crystallization. While DTA results predict crystallization for the DU tape below 870°C, no new crystalline phases were detected for the conditions studied here.

The master sintering curves for CT and FE were regenerated using only the densification curves at 5°C/min and 10°C/min. The MSCs are shown in Figs. 3 a-b. A much better fit to the data can be seen. The activation energies were \( \sim 490 \text{ kJ/mol} \) and \( 396 \text{ kJ/mol} \) for FE and CT, respectively. These values are considered to be accurate estimates of the activation energy for glass sintering.

The polished microstructures of all three samples fired at 5°C/min from 740°C to 870°C are shown in Figs. 4-6 a-c. The SEM images are shown in back-scattered mode to distinguish the different phases. The microstructures of DU tape (Fig. 4a-c) reveal the presence of alumina particles (dark) dispersed in the glass matrix as confirmed by energy dispersive spectra (EDS) analysis. No other phases were detected by XRD. The microstructures of CT tape (Fig. 5a-c) are similar to DU microstructures. One notable difference is the formation of anorthite (MAI$_2$Si$_2$O$_8$, M = Ca, Sr or Ba) above 860°C. The contrast between the alumina, anorthite and glass phases is not sharp, but EDS analysis with XRD confirmed the presence of all three phases. The presence of anorthite was also identified by high temperature XRD studies\textsuperscript{26}, which were also in good agreement with DTA results. In contrast to the DU and CT microstructures, the FE tape microstructure (Fig. 6a-c) resembled that of a polycrystalline material with particles of uniform size, and sharp boundaries between them. The FE glass starts crystallizing above \( \sim 97\% \) (\( \sim 790°C \)) density, as indicated by the appearance of small dark-colored phases. The crystalline phase is more clearly
Fig. 6-3a Master Sintering Curve of CT based on the data in Fig. 6-1b for 5 and 10°C/min

Fig. 6-3b Master Sintering Curve of FE based on the data in Fig. 6-1c for 5 and 10°C/min
Fig. 6-4. SEM micrographs of DU specimens heated at 5°C/min to a) 740°C, 74% density, b) 775°C, 92% density and c) 870°C, 20 min, near full density
Fig. 6-5. SEM micrographs of CT specimens heated at 5°C/min to a) 820°C, 73% density, b) 860°C, 97% density and c) 870°C, 20 min, near full density
Fig. 6-6. SEM micrographs of FE specimens heated at 5°C/min to a) 760°C, 83% density, b) 820°C, 100% density and c) 850°C, 20 min, near full density (dark crystalline phase are indicated by the arrow in Fig. 4b)
seen in the specimen fired to 850°C. XRD plus EDS revealed the presence of CaSiO$_3$ (wollastonite) only.

6.4.2 Viscosity Measurement by Cyclic Loading Dilatometry

The axial strain data of CT, DU, and FE pellets were measured at 5°C/min under a cyclic load to determine the uniaxial viscosity $^{13}$. The initial load was $\sim$ 60 kPa with loading and unloading periods of 1 min each, respectively. The anisotropy constant ($k$), the ratio of axial to radial strain, which was determined from fired density and total axial strain $^{25}$ in the presence of a cyclic load, was $\sim$ 2.47, 5.65, 2.25 for CT, DU and FE specimens, respectively. The value of $k$ for the case of free sintering was $\sim$ 1.08, 1.09, 1.09 for CT, DU and FE specimens, respectively. A value of $k$ greater or less than 1 indicates that a material can relax by shear strain or deformation at constant volume $^{30}$. The anisotropy constant is similar to the $\beta$ parameter, the ratio of shear and densification rates, proposed by Raj and Bordia in their study on transient stresses in bimodal powder compacts $^{31}$. The shrinkage anisotropy constant is significantly larger for DU than CT and FE when tested with a uniaxial load. The increase in anisotropy constant is less for a cyclic load than with a constant load, as reported in our earlier work $^{25}$.

During the initial stage of sintering, the strain response is typically elastic or viscoelastic $^{15, 25}$. As the sintering rate continues to increase, the elastic response becomes increasingly negligible relative to the viscous response. As the sample approaches theoretical density, the viscous component decreases. Thus, as noted in our previous works $^{15, 25}$, the linear viscous model is best suited for the intermediate densification regime. Using equation (2) and the methodology described in earlier papers $^{13, 25}$, the viscosity was determined. The data showed good reproducibility
within an error margin of < 5%. The viscosity is plotted as a function of sintering temperature and relative density in Fig. 7 a-b. For all three systems, the viscosity initially decreases with temperature, changes little during the intermediate stage densification, and increases sharply corresponding to the onset of crystallization at 5°C/min (see table 1). The increase in viscosity towards the end of densification occurs between ~ 92-95% relative density for the three materials. The change in viscosity as sintering proceeds is complex due to a host of factors including glass composition, volume fraction of filler particles, contact area and glass crystallization in addition to temperature and density.

The rate of firing can influence the viscosity of a sintering material, because it can affect the density, and glass crystallization. The viscosity changes of CT measured at 2, 5 and 10°C/min are shown in Fig. 8. As is evident, the viscosity of CT is higher at a lower heating rate throughout sintering. This is because, at a particular temperature the density of a sample fired at a slower heating rate is higher than when heated at a faster rate. A sudden increase in the viscosity with a simultaneous retardation in densification can be observed at ~850°C for the sample fired at 2°C/min. The onset of crystallization for 2°C/min is ~840°C for CT. Slower heating rates lead to premature crystallization of the glass, which can increase the viscosity and inhibit sintering. This is why glass crystallization is usually designed to occur at higher temperature. The difference between the glass transition (or softening) temperature and the initial crystallization temperature provides an indication of the sinterability (or ease of viscous flow) of a material. The smaller the temperature difference the lower is the sinterability and vice versa. So, for slower heating rates, the sinterability will be lower for systems that undergo crystallization before the completion of sintering compared to higher heating rates.
Figs. 6-7 Uniaxial viscosity obtained by CLD (200g, 398 g/min, loading time = 1 min, unloading time = 1 min) as a function of a) sintering temperature and b) relative density
It is known that the viscosities of pure glass systems show a significant decrease with temperature, sometimes, greater than four orders of magnitude for a temperature increase of 200 – 300°C. From the constant heating rate viscosity data in Fig. 8, it is obvious that the viscosity does not decrease with temperature as expected from equation (1) for typical activation energies for borosilicate glasses. It is clear that there are other variables, besides temperature, that play a significant role in controlling the viscosity. One important variable, as is obvious from previous studies on viscosity of densifying materials is porosity. The viscosity has been shown to increase with densification, in some cases, by two orders of magnitude.

6.4.3 Isothermal Viscosity

Isothermal tests are useful to determine the explicit dependence of viscosity on density. The viscosity data of CT, DU and FE pellets measured with a cyclic load at three different temperatures (between 700°C and 800°C) are shown in Figs. 9a-c. At any given temperature, the viscosity increases with increase in density. At a constant density, viscosity decreases with increase in temperature. The viscosities range between 0.1 – 100 GPa.s. This is in agreement with other measurements on similar materials. The values are at least an order of magnitude less than those reported for polycrystalline ceramics.

The viscosity curves of DU, CT and FE at different temperatures were reduced to a single master viscosity curve (MVC) at a reference temperature using the principle of superposition with an optimum value for the activation energy, Q in equation (1). The MVCs are shown in Fig. 10. The data are normalized to the viscosity at 73% density. The Q values were ~ 375 ± 30 kJ/mol, 450 ± 10 kJ/mol for
Fig 6-8 Uniaxial viscosity of CT tape at 2°C/min, 5°C/min and 10°C/min

Fig. 6-9a. Viscosity versus density plots for FE tape obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 690°C, 715°C, and 740°C.
Fig. 6-9b. Viscosity versus density plots for DU tape obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 690°C, 715°C, and 765°C.

Fig. 6-9c. Viscosity versus density plots for CT tape obtained by ICLD (200 g, 796 g/min, loading time = 4 min, unloading time = 14 min) at 740°C, 765°C, and 790°C.
Fig. 6-10 Comparison of master viscosity curves of DU, CT and FE tapes (normalized to 73\% density) at reference temperatures of 715, 765 and 715°C, and activation energies of 375 ± 30, 450 ± 10 and 700 ± 20 kJ/mol, respectively to model predictions.
DU, and FE respectively. To our knowledge, data on activation energies of glasses similar in composition to those of materials in this study are not available.

The value for DU tape is comparable to the activation energy (325 kJ/mol) reported by Jean et al.\textsuperscript{6} based on the shrinkage data. For the CT material, the Q value was inaccessible, because of greater non-linearity in viscosity data. However, if only the linear portions of the viscosity curves were used, activation energy of ~700 kJ/mol was obtained. For the CT tape, the increase in viscosity accompanied by retardation in densification is due to anorthite phase formation as confirmed by EDS and XRD studies. Similar observations were also noted for the FE tape.

It should be noted that the activation energies reported here represent average values. Multiple activation energies can exist for systems in which compositional and structural changes occur during the firing process. The activation energy for DU was in good agreement with that determined by the MSC approach. For the FE system, the Q value is in reasonable agreement with that determined by the MSC approach for the higher heating rates. These results show that when a single mechanism is active during sintering, equations (1) and (3) yield similar values for the activation energy.

The viscosity of densifying LTCCs changes little over the intermediate density range (Fig 9 a-c) but rises steeply at densities beyond the closed pore stage (>92%). It is obvious that the density dependence of viscosity is different for the three systems. The greater non-linearity in the data, particularly for the CT system is due to the dissolution of the ceramic filler particles in the glass and subsequent crystallization and retardation in densification, and the fact that the specimens are approaching final density. Premature crystallization caused by filler dissolution and reaction with glass also increases the filler/glass ratio due to glass consumption and formation of a new crystalline phase. On the latter, it has been shown that the intrinsic viscosity (that due

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to base glass composition and structure) of a glassy matrix increases with increase in volume fraction of filler particles and, the rise is significant above the critical percolation threshold $^{34-37}$. The presence of filler particles in DU may explain why this system shows a higher viscosity compared to FE, until crystallization of the latter reduces this difference in viscosity.

Premature crystallization also reduces the densification kinetics. Panda and Raj $^{38}$ reported this trend in their work on cordierite-type glasses. They observed retardation in the shear and densification rates of glass compacts fired at constant heating rates. The shear rate is expected to increase as the temperature increases because the viscosity decreases. However, it was found that the shear rate reached a plateau owing to the onset of crystallization.

In order to examine the effect of crystallization on viscosity, phase formation was followed as a function of temperature by XRD. The XRD patterns of powders made from CT pellets used for ICLD at 765°C and 790°C are shown in Fig. 11. The XRD of the unfired CT shows it contains alumina and titania crystals. The XRD pattern of the sample fired at 790°C indicates the presence of anorthite. This observation is in agreement with the Dai et al. $^{22}$ study on this system. Similarly, XRD analysis on FE samples fired at 740°C revealed the presence of Ca-silicate crystalline phases, whereas the samples fired at 690°C and 715°C showed no sign of crystals. The XRD patterns are shown in Fig. 12. However, unlike CT tape, it appears that the crystallization in FE tape does not inhibit densification. For the DU system, the viscosity was found to be linear at lower densities and slightly non-linear above 95%. The non-linearity in this case is believed to be due to the removal of closed porosity. Although, DTA results reveal the formation of crystals above ~ 860°C, no new phase could be detected by XRD and SEM studies $^{26}$. This is probably due to the slow
Fig. 6-11 XRD patterns of as-received CT2000 and samples used for ICLD tests at 765°C and 790°C (with a dwell of 6 h 30 min). The ICLD sample fired at 790°C shows the presence of anorthite (peak overlap at 2θ = 27.5°).

Fig. 6-12 XRD patterns of as-received A6-M and samples used for ICLD tests at 715°C and 740°C (with a dwell of 5h). The ICLD sample fired at 740°C shows the presence of crystalline Ca- silicate phases.
kinetics of crystallization indicated by the higher Kissinger activation energy (table 1) compared to CT tape. The above observations may help explain the observed difference in Q for the three systems. It is believed that isothermal tests at other temperatures may yield slightly different Q values for the DU system, and more so for the FE and CT systems, because of the chemical interaction between the glass and the filler particles and formation of new crystalline phases.

6.4.4 Comparison with Model Predictions

The normalized uniaxial viscosity, $\eta/\eta^*$ ($\eta^*$, the viscosity at 73% density) is compared with the theoretical predictions of Scherer $^{39}$, Mackenzie and Shuttleworth (M-S) $^{40}$, and empirical models of Rahaman et al., $^8$, and Ducamp and Raj $^{11}$ in Fig. 10. For the models which reported only the expressions for shear and bulk viscosities ($G_p$ and $K_p$), the uniaxial viscosity, was calculated using equation 7,

$$\eta = \frac{9 K_p G_p}{(3 K_p + G_p)}$$  \hspace{1cm} (7)

Rahaman et al. $^8$ and Ducamp and Raj $^{11}$ reported non-linear variation of shear viscosity with porosity for soda-lime silica glass and borosilicate glass, respectively. In both studies, empirical functions were used to fit the experimental data.

As is evident, the observed viscosities for the three materials differ significantly from each other and from the model predictions. The measured data shows a stronger dependence of $\eta$ on density. Similar observations were noted by Xie et al. $^{17}$. The models of Scherer $^{39}$ and Mackenzie and Shuttleworth $^{40}$ were developed based on spherical pore and cylindrical network morphologies. The former model was
used to analyze the shrinkage of a spherical shell, a reasonable representation of the final stage of sintering. Scherer’s 39 model was developed for viscous systems, but for very low-density glasses, such as gels and waveguide performs. As noted by Scherer 39, the cylinder network is not a good representation of powder packed structures. From Fig. 10, it is clearly seen that the model overestimates the viscosities at lower densities (note, the viscosities are normalized to the value at 73% density). This is because a cylinder network has a much larger load-bearing cross-sectional area compared to a powder packed structure at the green density state. For a powder packed structure, at the green density state, the viscosity, which depends on the load-bearing area, is expected to be low for small contact areas. Thus, as noted Jagota et al. 41, density alone, as used in several previous models, is a not a precise indicator of the load-bearing fraction of the cross-sectional area, and thus the constitutive parameters.

Rahaman et al., 8 in their work on soda-lime glass powders showed a strong dependence of creep viscosity on density, and noted that the discrepancy seen between their data and Scherer’s model was probably due to the difference in pore morphology, and particle alignment that caused greater compliance in the axial direction. Jagota et al. 41 showed similar strong dependence of viscosity on density for the same system. Interestingly, in contrast to their earlier work, in their study on borosilicate glass powders, Rahaman et al. 42 showed very good agreement with predictions of Scherer 39. This was attributed to reduced shrinkage anisotropy and use of much broader particle size distribution compared to earlier work. The above discussion leads to the following conclusions, 1) the available viscous models are insufficient, particularly in the low-density regime, and 2) models that can incorporate the effect of contact area, crystallization, and effect of filler particles beyond the percolation threshold are required.
Recently, Xie et al.\textsuperscript{17} reported uniaxial viscosity of two commercial LTCC systems, Ceramtape, a glass-ceramic and Ferro A6M (same as FE used in this study) based on isothermal measurements. The viscosity data are in good agreement with current measurements. The average activation energy (Q) for the Ceramtape was reported to be $668 \pm 76$ kJ/mol, while for FE tape the value was inaccessible. One possible reason for the difference between our data on Q for the FE tape and that of Xie et al. is the different set of the temperatures (720, 740 and 760$^\circ$C in the Xie et al. study) chosen for viscosity measurements. Temperatures that are close to the onset of crystallization may result in glass crystallization leading to multiple mechanisms and activation energies, and increased non-linearity as demonstrated before.

6.5 CONCLUDING REMARKS

The uniaxial viscosity data of three commercial LTCC systems, i.e. DuPont 951Tape, Heraeus CT2000, and Ferro A6, as measured by cyclic loading dilatometry technique were presented. For all three systems, the viscosity initially decreases with temperature, changes little during the intermediate stage and increases towards the end of densification. The viscosity increased sharply by as much as two orders of magnitude beyond the onset of crystallization. At slower heating rates, the increase in viscosity is more pronounced due to glass crystallization.

The shrinkage anisotropy constant was significantly larger for DU than CT and FE when tested with a uniaxial load. The increase in $k$ has significant implications, because a material that can shear more by viscous flow can relax stresses rather than forming defects such as cracks, porosity or warpage. Thus, the anisotropy constant is an important design parameter than can be tailored to achieve optimum sintering behavior. This also opens up possibilities of controlling $k$ through
control of material chemistry, particle morphology, and forming technique. For example, the tapes can be made more anisotropic by adding high aspect ratio nonspherical particles.

The isothermal viscosity of the three materials range from 0.1 to 100 GPa.s between 73% and 95% density. The viscosities of the three materials differ from each other and from the model predictions. It is clear that more robust models, which can incorporate the effect of contact area, crystallization, and effect of filler particles beyond the percolation threshold, are needed to predict the evolution of viscous behavior of densifying materials.

The activation energies for DU and FE determined from isothermal data were in good agreement with those measured by the MSC approach. The MSC analysis is limited to systems that sinter by a single mechanism, without the presence of competing phenomena such as crystallization. However, by using the sintering data at higher heating rates, the phenomenon of glass crystallization can be separated from sintering, thus allowing estimation of the true sintering activation energy.

Acknowledgement

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Chapter 7

TOWARDS PREDICTING THE SINTERING VISCOSITY OF DENSIFYING MATERIALS

7.1 INTRODUCTION

Glass-based ceramics offer significant advantages over conventional ceramic materials, because of their low sintering temperatures \(^1, \, 2\). For example, low temperature co-fired ceramics (LTCC) have increasingly replaced alumina-based substrates in electronic packaging applications. These materials are either ceramic-filled glasses or crystallizable glass systems. As they are composites of glass and ceramic, they can be designed to provide the desired properties of both classes.

There is considerable interest in developing comprehensive models that enable prediction of the shape and dimensional changes that occur during the sintering process \(^3-8\). In order to develop robust models, knowledge of the constitutive behavior i.e. relation between the stress and sintering strains, and thermo-mechanical properties such as the viscosity and viscous Poisson’s ratio are essential \(^9\). Recent studies to characterize the mechanical behavior of sintering materials have focused on glass-based materials such as LTCC, because of their technological importance \(^3-7\). These studies have revealed that the deformation of glass-based materials is controlled by the rheology of the glass controlled by temperature and density, with factors such as filler particle fraction and crystallization playing a crucial role.

Glass and glass-based ceramics sinter by viscous flow. Frenkel \(^10\) was the first to model viscous sintering. He suggested that the energy dissipation due to viscous flow is gained by the reduction in the surface energy of the porous body. For the case
of coalescence of two spheres, the sintering rate was shown to depend on the surface tension, viscosity and particle size, with the temperature dependence of the rate primarily governed by that of the viscosity. Frenkel’s model\textsuperscript{10}, though verified by experimental studies, has been limited in its applicability to the initial stage of sintering, because of its simplifying assumptions that neglect particle rearrangement. Jagota and Dawson\textsuperscript{11} analyzed the same problem using finite element analysis, and found that Frenkel’s model overestimated the viscosity.

Mackenzie and Shuttleworth\textsuperscript{12} used Frenkel’s\textsuperscript{10} methods to analyze the shrinkage of a spherical shell. This geometry is a good representation of the final stage of sintering, which is characterized by the presence of isolated pores, typically beyond 92% relative density. Later, the analysis was extended to include the effect of applied pressure or gas entrapment. Scherer\textsuperscript{13} proposed the cylinder model as a representation of intermediate stage of sintering, which is characterized by interconnected pores. The model was intended to represent highly porous structures such as gels and soot performs. Interestingly, it was found that the predicted sintering rates of all the models were similar. An important conclusion of the analyses is that the sintering rate does not strongly depend on the geometry of the microstructure. Later, Jagota et al.\textsuperscript{14} noted that density alone is not a sufficient parameter to describe the evolution of a sintering body. They suggested that the effect of contact area between sintering particles on viscosity must be taken into consideration.

For the case of ceramic particle-filled glasses, Ewuk\textsuperscript{15} proposed a non-reaction liquid phase sintering model, in which densification occurs by a combination of glass redistribution, grain rearrangement and viscous flow. In their work on particle-filled glass systems, they found that the composite densification improved with decreasing filler content and increasing filler particle size. While decreasing the
filler content reduces the viscosity of the composite and thus aids in densification, increasing the particle size improves the glass redistribution kinetics, because larger particles tend to have larger pores, through which the glass can penetrate. Ewsuk et al. 15 also observed that good wetting between the glass and ceramic, and a moderately high viscosity resulted in improved densification behavior. Although low viscosity increases the densification rate, a more viscous mass provides greater time for grain rearrangement leading to better intermediate stage sintering.

These studies have identified viscosity as a key design variable for sintering glass-based materials. Several studies, both theoretical and experimental have been developed for polycrystalline materials and glasses that describe viscosity as a function of densification 16-32. In contrast to its temperature dependence, the viscosity of a porous material increases with densification. However, the various models differ in their predictions. For details about the models, the reader is referred to excellent reviews by Bordia and Scherer 16, Olevsky 9 and Gillia 17. Thus, a major challenge is to develop accurate models that take into account the evolution of many variables including porosity, contact area, crystallization, and percolation of fillers and their combined effect of the effective viscosity of a densifying material. In this paper, we present a theoretical understanding for the observed viscosity of LTCC materials, and a framework for predicting the evolution of their viscous behavior during sintering. A model based on the simplifying assumption that these variables are mutually exclusive is presented.
7.2 VISCOS BEHAVIOR OF POROUS GLASSES

Porous materials sinter by mass flow due to capillary forces, but the kinetics are almost always influenced by external forces such as applied stresses as in the case of hot pressing, friction due to contact with external surfaces, and internal constraints due to microstructural inhomogenieties and inclusions. The ‘viscosity’ of sintering bodies is defined as the resistance to creep or densification of the material in the presence of an internal and/or external stress. Depending on the stress state i.e., shear, hydrostatic or uniaxial, the viscosity takes on different meanings. In fact, a sintering material cannot be fully described, unless the shear and hydrostatic (or bulk) viscosities, or the uniaxial viscosity and viscous Poisson’s ratio are known. This kind of description follows the elastic-viscous analogy, and has been found to be quite useful in developing sintering models based on the continuum sintering approach 9,16.

A few studies have examined the evolution of viscosity of porous glasses 25-29. Recently, we reported the viscosity of three commercial LTCC materials i.e. DuPont 951Tape™, Ferro A6-M™, and Heraeus CT2000™ (hereon called DU, FE, and CT, respectively) 33. The isothermal viscosity, which ranged between 0.1-100 GPa.s showed an increase with density and the increase was more pronounced for ceramic particle-filled and crystallizing glasses. A key finding of the study 33 was that some of the theoretical and empirical models developed for viscous systems fail to explain observed behavior. The non-isothermal viscosity showed a complex pattern indicating an influence of many sintering variables. As we noted, the viscosity of a sintering glass depends on a host of factors including the temperature, porosity, and particle morphology, size and contact area, volume fraction of filler particles, heating rate, and crystallization. In the following section, we examine in detail the explicit
influence of these variables on the viscosity. This provides a basis for predicting and controlling the viscosity of sintering systems. It is noted that a similar approach should work for polycrystalline materials, although for these systems grain size also plays an important role.

7.2.1 Effect of temperature

The viscosity of a glass depends strongly on the temperature.\(^{35}\)

\[ \eta = f(T) \quad (7.1) \]

where, \(f(T)\) is typically either an Arrhenius or Vogel-Fulcher-Tammann (VFT) equation.\(^{35}\) The viscosity, which depends on the glass composition, can vary significantly with change in temperature. The viscosity can vary by even 3-4 orders of magnitude over a temperature span of 200-300°C, which is typically the range of sintering. The viscosities of some commercial glasses are shown as an example in Fig. 7.1. It is worth noting that there is limited data on the viscosity of LTCC materials and systems of similar compositions as a function of temperature. The viscosity of glass systems strongly depends on their chemical composition and thus, by controlling the glass chemistry, the viscosity of sintering glasses can be controlled.

7.2.2 Effect of density and contact area

The viscosity of a densifying material increases with decrease in porosity.\(^{34}\) A schematic of the evolution of microstructure of a ceramic particle-filled glass is shown in Fig. 7.2. In the green state (a), there is limited contacts between the particles.
Fig. 7-1 Viscosity versus temperature curves for commercial borosilicate systems (source: Ref [35]); the shaded region corresponds to LTCC sintering regime

(a)  
(b)  
(c)

Fig. 7-2 Schematic diagram showing the evolution of microstructure for a ceramic particle-filled glass a) green state b) glass softening and redistribution and particle rearrangement c) reaction between glass and ceramic and percolation
As the glass softens and sintering begins (b), the contacts between the glass particles increase. The glass also penetrates the region between the ceramic particles. This is accompanied by grain rearrangement. The final stage (c) involves the removal of closed porosity and percolation of the filler particles. In case of reactive systems, there is reaction and dissolution of the ceramic in the glass resulting in new crystalline and glass phases and increase in the amount of crystals.

As noted earlier, numerous models, experimental and theoretical have been proposed to describe the evolution of viscous behavior as function of density. These are shown in Fig. 7.3. Experimental studies on glass-based materials reveal a stronger dependence on density than theoretical models. This, as noted by Jagota et al.\textsuperscript{14}, is due to ignoring the effect of contact area on the viscosity at the green state. At the green state, when the contacts between the particles are very little, the viscosity is expected to be quite low. In fact, one would expect the viscosity to approach zero, when there are no contacts. The models predictions which consider only density predict a much larger viscosity. Thus, as noted by Jagota et al.\textsuperscript{14}, density alone is an insufficient parameter to describe the viscosity. The effect of contact area must be included.

Experimental and theoretical predictions for viscous materials reveal that the viscosity increases almost linearly with density until the onset of closed pore stage or glass crystallization. The increase in viscosity with densification partly compensates for the decrease due to the temperature effect, but the effect of the former is less pronounced compared to the latter. For most part of the sintering, the viscosity changes by 1-2 orders of magnitude with densification, although there is a sharp increase towards the end of densification, beyond the closed porosity stage.
Fig. 7-3 Empirical and theoretical models for viscosity as a function of density (source: Ref [17]); note, the viscosity is normalized to the value at 75% density
To account for the effect of density (and contact area), equation 1 can be modified as

\[ \eta = f(T) \cdot g(\rho, c) \]  

(7.2)

where \( g(\rho, c) \) takes into account the effect of both relative density and contact area, respectively. According to Jagota and co-workers\textsuperscript{14,36}, the uniaxial viscosity of a line of spheres is proportional square root of the contact area. Based on numerical simulations, they found that the viscosity varied more sharply, especially at the green state, than the models of Scherer and Mackenzie and Shuttleworth, and more closely matched with experiment. In Fig. 7-4, we compare the measured data of LTCC materials\textsuperscript{33} with the results of Jagota et al.\textsuperscript{14}, which were fit using a power law equation, given by,

\[ \eta (\rho^\prime) = m \cdot (\rho^\prime)^a \]  

(7.3)

where, \( m = 0.696 \) and \( a = 3.2343 \). The symbol \( \rho^\prime \) is used to highlight its difference from \( \rho \), as \( \rho^\prime \) includes the effect of contact area. It is noted by Jagota et al.\textsuperscript{14} that their model fails to predict viscosity in the limiting case of full density. There is good agreement between the measured data of FE material and numerical results. This is expected as the FE tape is a pure glass system, which does not crystallize until beyond \(-95\%\) density shown by the sudden increase in viscosity. The DU and CT systems, unlike FE contain filler particles. The CT undergoes crystallization before complete sintering.
Fig. 7-4 Comparison of measured isothermal viscosity of CT, DU and FE with Jagota’s model
7.2.3 Effect of volume fraction of filler particles

The presence of filler particles has a significant influence on the viscosity of a glass\textsuperscript{37-45}. LTCC materials typically have filler particles such as alumina to prevent the formation of cristobalite phase\textsuperscript{46, 47}. The fillers also provide mechanical strength and improve electrical performance. During sintering, the filler particles act as rigid inclusions, and retard the densification of the glass matrix\textsuperscript{43, 48}. The particles can also chemically react with the glass to change the glass composition and form new crystalline phases.

We studied the effect of filler (alumina) content on glass viscosity for filler fraction up to 30 vol\% using loading dilatometry\textsuperscript{37}. The measured data\textsuperscript{37}, shown in Fig. 7-5 were in good agreement with the experimental data of Demana and Drummond\textsuperscript{39}. The following equation fits the experimental data,

\[
\ln(\eta_c/\eta_o) = n \cdot (V) \cdot b
\]

where \(\eta_c\) and \(\eta_o\) are the viscosities of the composite and glass, respectively, and \(n = 10.663\) and \(b = 1.5\). Demana and Drummond’s work, one of the few experimental studies, reported viscosity of a borosilicate glass containing up to 50 vol\% alumina using beam-bending viscometry. The viscosity was found to increase by over 8000 times at 50 vol\%. Similar observations were made by Tewari et al.\textsuperscript{40} and Banuprakash et al.\textsuperscript{41} on borosilicate glass composites containing different metallic and non-metallic inclusions. Non-Newtonian flow behavior was observed at high volume fraction and aspect ratio of inclusion particles. Dutton and Rahaman\textsuperscript{42} investigated creep behavior of soda-lime silica glass with Ni spherical inclusions as a
function of inclusion content and size. A loading dilatometer was used to measure the creep rates and, thus, the creep viscosity. It was found that above ~ 10-15 vol % inclusions, the viscosity increased significantly in case of smaller inclusion size and the increase was attributed to formation of a percolating network. In addition to the above studies on the viscosity of glass composites, many modeling and theoretical studies \(^{43-45}\) have been devoted to understanding the effect of inclusions on the densification and microstructure of composites.

The analysis of particle-filled composites is difficult, because the viscous behavior is strongly influenced by the phenomenon of percolation for highly concentrated dispersions. The schematic diagram in Fig. 7.6 is a representation of dilute \((\nu_f < 0.1)\), intermediate \((0.1 > \nu_f > 0.3)\) and high concentration \((\nu_f > 0.3)\) of filler particles in a matrix. As the filler fraction increases, the particles begin to form clusters and when the fraction is beyond the threshold, a continuous network is formed. As noted by Scherer \(^{45}\), for the case of bonded inclusions (that sinter together, or mechanically interlock due to surface roughness) the rigidity of the composite increases considerably at the percolation threshold (which occurs at \(\nu_f \sim 0.16\) for randomly arranged particles). Thus, the percolation threshold is said to coincide with the so-called rigidity threshold. However, when there is wetting of the inclusions by the matrix, which results in lubrication of the contacts between the inclusions, the rigidity threshold can occur at a much higher volume fraction of inclusions compared to the percolation threshold. Thus, the composition of the matrix and its physical and chemical compatibility with the filler particles play a very important role in determining the rheology of particle-filled glass systems. This may explain the difference between the various experimental and theoretical values for the threshold value at which the viscosity shows a sharp increase \(^{38,45}\).
Fig. 7-5 Effect of filler particles on glass viscosity: comparison of measured viscosities and theoretical predictions

Fig. 7-6 Schematic diagram showing the presence of filler particles in a glass matrix for a) low (< 0.1) b) intermediate (0.1 to 0.3) and c) high filler fraction (> 0.3)
As observed by Ewuk et al.\textsuperscript{15} the size and size distribution of the filler particles also influence the viscous behavior. Equation 7.2 can be rewritten for the composite as,

\[ \eta_e = f(T) \cdot g(\rho^*) \cdot h(v_f) \]  

(7.5)

where \( h(v_f) \) is a function of the filler volume fraction. As seen from Fig. 7-5, models used to describe the rheological behavior of liquid-solid suspensions do not work well for solid-solid systems\textsuperscript{37, 39}. As noted by Scherer\textsuperscript{45}, self-consistent and Hashin-Shtrikman models also fail to predict percolation or the viscosity beyond the percolation threshold. Thus, there is a clear need for more detailed experimental studies and reliable models to describe the effect of fillers on viscosity.

### 7.2.4 Effect of crystallization

The prediction of viscosity is more challenging for glass systems that undergo crystallization during sintering\textsuperscript{44}. Crystallization can result in a considerable change in the composition of the glass, and increase the volume fraction of filler particles, grain boundary area and grain growth and retard the densification process\textsuperscript{43, 48}, all of which can greatly influence the viscosity. Crystallization can initiate either in bulk or the surface of a glass. Surface crystallization can increase the viscosity of a system drastically, even if the bulk of the glass shows little crystallization. Detailed studies that extend on the works of Chang and Jean’s and Jean et al.\textsuperscript{46, 47} are required to understand the effect of crystallization on sintering and viscosity.

While it is difficult to accommodate glass crystallization in a sintering model, if we simply treat the crystals as non-reactive rigid inclusions, the effect of crystallization on viscosity can be factored into equation 7.5 as follows,
\[ \eta = f(T) \cdot g(\rho) \cdot h(\nu_T + \nu_c). \]

(7.6)

where, \( \nu_c \) is the volume fraction of the new crystalline phase and \( \nu_T \) is the volume fraction of original fillers after crystallization. It is also important to note that the activation energy is now represented by \( Q' \), the activation energy for viscous flow of glass in the presence of crystals. While equation 7.6 is rather simplistic, it can serve as a starting point for the development of a more complicated sintering model. We demonstrate below the use of the equation for a model LTCC system.

### 7.2.5 Effect of heating rate

In addition to the variable discussed above, the viscosity is also influenced by firing conditions. The viscosity typically increases with decrease in the heating rate \(^{33}\). The heating rate however is a secondary parameter in that its influence on viscosity is through the change in density and/or the glass crystallization. At slower heating rates, the density of a sintering material is higher compared to that at faster rates, which results in an increase in the viscosity of the system. Similarly, at slower rates, there is a greater chance for glass crystallization, because of the increased time for nucleation and growth. However, a substantial increase in viscosity due to slower rates can result in slower crystallization kinetics, because of greater resistance to atomic movement.
7.3 APPLICATION OF MODEL: PREDICTION OF LTCC VISCOSITY

In this section, we present an example of predictions for the viscosity of a densifying LTCC material. The predictions are provided for a commercial LTCC system, Heraeus CT2000™. As noted before, we reported the viscosity of three commercial LTCC materials i.e. DuPont 951Tape™, Ferro A6-M™, and Heraeus CT2000™ (hereon called DU, FE, and CT, respectively) 33. DU and CT tapes are ceramic particle-filled borosilicate glasses, while FE is a crystallizable Ca-borosilicate glass with no filler particles 49-51. DU is a Pb-borosilicate glass with alumina as the ceramic filler particle. To our knowledge, no detailed studies on the glass-filler interaction during heating in this system exist. In case of CT, the alkaline-silicate glass reacts with the alumina and titania filler particles to form high quality factor crystalline phases 49. The crystalline phases are designed to achieve low dielectric loss and high mechanical strength.

For the purposes of this analysis, we chose the CT system, as it is representative of both the DU and the FE tape. CT tape is a ceramic particle-filled system like DU, but also undergoes crystallization before complete sintering like the FE system. The chemical composition data of all the three systems determined by DC spectrochemical analysis are summarized in table 1. The compositional data was used in the SciGlass™ software, an extensive database of experimentally measured glass properties and theoretical models, to predict viscosity as a function of temperature.
<table>
<thead>
<tr>
<th>Component</th>
<th>CT</th>
<th>FE</th>
<th>DU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>45</td>
<td>-</td>
<td>51</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22.4</td>
<td>46</td>
<td>30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>8.76</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>5.34</td>
<td>10.1</td>
<td>2.37</td>
</tr>
<tr>
<td>BaO</td>
<td>2.98</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>7.67</td>
<td>42</td>
<td>5.19</td>
</tr>
<tr>
<td>SrO</td>
<td>4.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.95</td>
<td>-</td>
<td>1.04</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>-</td>
<td>8.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>-</td>
<td>1.57</td>
</tr>
<tr>
<td>CoO</td>
<td>-</td>
<td>-</td>
<td>0.24</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>-</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 7-1 Composition of LTCC tapes based on DC Spectrochemical analysis
There are more than a dozen models in SciGlass™ based on combined mathematical and chemical approaches, but almost all except the model by Priven do not provide predictions for glasses containing boron oxide. This is a limitation, as all of the LTCC compositions contain a significant amount of boron oxide. And, even this model has restrictions on the maximum amount of a component oxide that can be present in the glass. Thus, caution should be exercised in using the predicted values. Based on the chemical composition data, Priven’s model was used to predict the viscosity as a function of temperature. The predicted viscosity is shown for all three LTCC materials in Fig. 7.7. It is interesting to note that the complete viscosity data are not available for the DU and FE tape in the sintering regime of interest.

The SciGlass predictions (for $f(T)$) were used in conjunction with Jagota’s model (for $f(\rho)$), the experimental data of ours and Demana and Drummond (for $h(v_i)$) in equation 7.6. In order to do the analysis, the temperature regime was divided into pre and post-crystallization periods. Based on the compositional and density data, the volume fraction of alumina filler particles in the CT glass was ~40%. This value was used for temperatures below the onset of crystallization (~850°C). Beyond the onset, the precise amount of anorthite crystalline phases was not known. It has been reported that at least 9 wt% of alumina fillers dissolves in the glass. As the exact amount of crystals is not known, we performed the calculations assuming a net increase in volume fraction filler particles of 10, 15 and 20 vol%. The effect of titania on glass viscosity was not taken into consideration, as their amount and particle size (< 300 nm) were negligible compared to the alumina phases. It is also important to note that as the filler fraction increases, there is a simultaneous change in glass
Fig. 7-7 SciGlass™ Predictions of the viscosity for DU, CT, and FE tapes as a function of temperature
composition, which will affect the viscosity. This change in glass composition is not considered in the model calculations.

The agreement between the measured and predicted viscosity data shown in Fig. 7.8 as a function of relative density is reasonably good. In pre-crystallization regime, different variables including temperature, density, contact area, changes in glass chemistry and filler fraction influence the viscosity. In the post-crystallization period, glass crystallization plays a major role. Both the measured and predicted data show an increase in viscosity beyond the onset of crystallization. As noted in our earlier works 32, 33, the measured data in the post-crystallization regime are more prone to error because of the very small deformation rates (< 10^{-7}/s). The difference in the data is also expected, as the precise composition, amount of filler particles and amount of crystals are not known. Also, errors due to SciGlass™ may influence the accuracy of the predictions.

It is interesting to note that the FE system, which does not have ceramic filler particles, shows viscosities similar to that of DU and CT 33. This, we believe is due to the effect of surface crystallization, the mechanism proposed by Jean et al. 46 for the same system based on thermal analysis and SEM observations. Another factor that can significantly affect the viscosity is phase separation, as noted earlier. However, based on the compositional data and phase diagrams for the Ca-borosilicate system 53, we don’t expect any significant phase separation to occur. It is clear from this analysis that detailed studies on the crystallization and phase separation behavior and the dynamic change in glass chemistry of these systems are warranted to gain a better understanding and control of the sintering behavior of these systems.
Fig. 7-8 Comparison of measured and predicted constant heating viscosity at 5°C/min as a function of relative density for CT tape; The dotted line indicates the onset of crystallization
7.4 CONCLUDING REMARKS

The complex evolution of viscosity during sintering of particle-filled and crystallizable glasses was discussed in light of new experimental data on commercial LTCC systems. The currently available models fail to capture the viscous behavior over the whole density range. A simple model that considers the effect of important variable including temperature, porosity, filler fraction, and crystallization has been proposed. The model assumes that the effects of these variables are mutually exclusive. It does not take into consideration the effect of contact area and any compositional changes, which can be important in these reactive systems.

It appears that temperature, filler particles and crystallization have the most significant effect on viscosity. However, phenomena such as percolation and phase separation can also be important. The effect of density is significant beyond the closed pore stage. Regarding filler particles, more experimental data, particularly at high volume fraction of filler particles are needed. Further, detailed studies on the crystallization behavior of LTCC systems are also required. We note that tools such as SciGlass™ can be useful for predicting viscous behavior of sintering systems, particularly for materials for which experimental data are not available.

Acknowledgement

The authors wish to express their thanks to Prof. George Scherer for useful discussions.
Chapter 8

CONSTRAINED SINTERING OF
LOW TEMPERATURE CO-FIRED CERAMICS

8.1 INTRODUCTION

The concept of constrained sintering (also called “zero shrinkage” technology) has gained increasing attention, particularly in the low temperature co-fired ceramic (LTCC) industry, for the precise control and maintenance of sintering shrinkage and tight dimensional tolerances \(^1\). During co-firing, stresses develop, because of mismatch in sintering behavior of different components \(^7\)-\(^10\). These co-firing stresses can lead to warpage, and non-uniform shrinkage resulting in poor dimensional tolerances. Zero shrinkage technology is thus an attractive option as it completely inhibits the in-plane (transverse) shrinkage, and allows only out-of-plane (longitudinal) shrinkage, resulting in extremely small dimensional changes in the plane of the structure, thus maintaining tight tolerances. The technique involves the use of non-sintering layers, either porous or fully dense, to constrain the densifying material. Variants of this technique used in the LTCC industry include pressure-assisted sintering (PAS), pressure-less assisted sintering (PLAS), self-constrained sintering, and the LTCC-M approach \(^1\)-\(^6\). Except for the PAS technique, all use either an internal or external non-sintering material to constrain in-plane shrinkage of the LTCC.

Although, the technique of constrained sintering has been widely adopted, fundamental understanding of how the constraint works, and the nature of material
response to the constraint is still lacking. Guidelines for designing constraining systems based on the material properties and shrinkage behavior are also currently unavailable. To develop a better understanding, two issues demand more attention including 1) constraining stresses and its effects, and 2) physical and chemical interaction between the LTCC and constraining layers. These can result in lower fired densities, non-uniform porosity, interfacial porosity, waisting at the edges, and distortion of features. Tzeng and Jean studied stress development in a Ca-borosilicate glass constrained by alumina layers. They adopted the viscoelastic theory to map the stress distribution using finite element analysis, and correlated it to the porosity distribution in the LTCC layer. The residual porosity was found to increase from the free edge towards the middle in the x-y (in-plane) direction and decrease from the interface to the middle in the z (thickness) direction.

Our earlier work studied the effect of constraint on two commercial LTCC systems DuPont 951Tape (DU) and Heraeus CT2000 (CT) with different viscous behavior. The observed difference in the shrinkage, microstructure and fired densities were correlated to the viscous behavior of the systems. The DU showed significant deformation under an external load compared to CT. Based on the viscous model, a higher value of the viscous Poisson’s ratio was speculated to be the cause for higher z-shrinkage. For CT, the fired densities were found to be lower for constrained specimens compared to free-sintered specimens.

This study is an extension of our earlier work. We investigate in detail some key issues including, 1) the effect of external load on LTCC deformation and shrinkage
anisotropy 2) the evolution and distribution of porosity in the LTCC layer, and 3) the influence of firing conditions on the effect of constraint. Detailed stress calculations based on the viscous model are presented. The materials used in this study are the same as those used in the earlier work. The DU tape is a Pb-borosilicate glass filled with alumina particles. The CT tape is an alkaline borosilicate glass with alumina and titania as filler particles. While both are ceramic-filled glass systems, the CT crystallizes to form anorthite phases before complete densification.

The experimental methodology used in this work is based on a phenomenological approach. The material properties such as viscosity and viscous Poisson’s ratio are measured using loading dilatometry and pressure-less constrained sintering, respectively. The microstructural evolution of constrained LTCC systems is examined. The measured properties are used to calculate stresses and strains, which are then correlated to the microstructural observations, and physical properties.

8.2 STRESS-STRAIN RELATIONS FOR CONSTRAINED SINTERING

We derive below the relations between stress and strain for the case of zero radial (in-plane) shrinkage under a) Uniaxial compression and b) Pressure-less constrained sintering

a. Uniaxial compression

According to Newton’s law, the constitutive equations for the strain response of a porous sintering body that is linear and isotropic under an external constraint, and assuming the stresses are constant throughout the thickness, and the free sintering rate, $\dot{\varepsilon}_f$, is not influenced by the stress, are given as (in Cartesian co-ordinates),
\[ \dot{\varepsilon}_x = \frac{\sigma_x}{\eta} - \frac{\nu \sigma_y}{\eta} + \frac{\nu \sigma_z}{\eta} + \dot{\varepsilon}_{f_x} \]  
\[ \dot{\varepsilon}_y = \frac{\sigma_y}{\eta} - \frac{\nu \sigma_z}{\eta} - \frac{\nu \sigma_x}{\eta} + \dot{\varepsilon}_{f_y} \]  
\[ \dot{\varepsilon}_z = \frac{\sigma_z}{\eta} - \frac{\nu \sigma_x}{\eta} - \frac{\nu \sigma_y}{\eta} + \dot{\varepsilon}_{f_z} \]  

where \( \dot{\varepsilon} \) is the strain rate, \( \sigma \) is the stress, \( \nu \) is the viscous Poisson’s ratio, and \( \eta \) is the uniaxial viscosity. For the case of a cylindrical sample under uniaxial compression \( (\sigma_z \neq \sigma_x = \sigma_y = 0) \), equations 1-3 reduce to,

\[ \dot{\varepsilon}_z = \dot{\varepsilon}_{f_z} + \frac{\sigma_z}{\eta} \]  
\[ \dot{\varepsilon}_r = \dot{\varepsilon}_{f_r} - \frac{\nu \sigma_z}{\eta} \]  

where \( \dot{\varepsilon}_r \) is the radial strain rate. The free shrinkage and stress-induced anisotropy constants are defined as,

\[ k = \frac{\dot{\varepsilon}_{f_z}}{\dot{\varepsilon}_{f_x}} \]  
\[ k' = \frac{\dot{\varepsilon}_r}{\dot{\varepsilon}_r} \]
The compressive stress required for zero radial shrinkage rate is then given by,

\[ \sigma_z = \frac{\eta}{\nu} \varepsilon_{fr} \]  

(8)

b. Pressure-less constrained sintering

Consider rigid plates with an intervening linear viscous (isotropic) layer. As there is no external uniaxial pressure,

\[ \sigma_z = 0 \]  

(9)

For the case of zero x-y shrinkage,

\[ \varepsilon_x = \varepsilon_y = 0 \]  

(10)

Substituting equations (8) and (9) into equations (1), (2) and (3) we get,

\[ \sigma_x = \sigma_y \]  

(11)

\[ \varepsilon_{fx}^* = -\frac{\sigma_x}{\eta} (1 - \nu) \]  

(12)

Or, the stress in the x-y plane is given as,

\[ \sigma_x = -\frac{\eta}{1 - \nu} \varepsilon_{fx}^* \]  

(13)
For the case of isotropic free shrinkage \((\varepsilon_{fx} = \varepsilon_{fy} = \varepsilon_{fz} = \varepsilon_f)\), using equations (11) and (12), the \(z\)-shrinkage from equation (3) can be written as,

\[
\dot{\varepsilon}_z = \dot{\varepsilon}_f \left( \frac{1 + \nu}{1 - \nu} \right)
\]  

(14)

For the case of anisotropic free shrinkage \((\varepsilon_{fx} = \varepsilon_{fy} \neq \varepsilon_{fz})\), equation (14) is modified as,

\[
\frac{\dot{\varepsilon}_z}{\dot{\varepsilon}_{fz}} = \left[ \frac{2\nu}{(1 - \nu)k} + 1 \right]
\]

(15)

The hydrostatic sintering stress for isotropic free shrinkage is given as,

\[
\Sigma = 3K_p \dot{\varepsilon}_f
\]

(16)

where \(K_p\) is the bulk viscosity given by,

\[
K_p = \frac{\eta}{3(1 - 2\nu)}
\]

(17)
8.3 EXPERIMENTAL PROCEDURE

8.3.1 Thermo-mechanical Analysis

Commercial LTCC tapes i.e. DuPont 951Tape (“DU”, DuPont Microcircuit Materials, Research Triangle Park, NC) and Heraeus CT2000 (“CT”, Heraeus Circuit Material Division, Conshohocken, PA) were selected for this study. Binder was removed from tapes by heating at 2°C/min up to 400-425°C and holding for 1-2 h. The powders were uniaxially pressed at ~ 40 MPa into cylindrical pellets of ~ 6.38 mm diameter x 4.4-4.5 mm. The green densities were ~62 and 65 ± 2% of the bulk fired densities for DU and CT, respectively. The compacts were tested in a thermo mechanical analyzer (TMA50, Shimadzu) with a vertical loading rod 3 mm in diameter. A small load of 1 g was applied to ensure contact between the push rod and the sample. The linear shrinkage of the pellets was measured by heating at 2°C/min to 870°C. From the shrinkage data, sintering strain and strain rate were calculated.

In order to study the effect of uniaxial load on LTCC deformation, the materials, in the form of cylindrical pellets were subjected to different uniaxial loads, and their deformation response measured (see schematic in Fig. 1). The initial stresses (based on the cross-sectional area before sintering) were between ~15 and 150 kPa. The samples were heated to a maximum temperature of 870 °C at 2°C/min. The load was applied throughout sintering. Platinum base plates were used to prevent contact between the loading rod (of the TMA) and the specimen.
To measure the viscosity, we used cyclic loading dilatometry. The technique involves applying intermittent loads, and measuring the viscosity from the difference in loaded and unloaded strain rates. The pellets were tested under a cyclic load of 200g (~60 kPa) with loading and unloading period of 1 min each. The viscosity was measured at 2°C/min. To calculate the viscous Poisson’s ratio, the concept of pressureless constrained sintering was used. This method involves measuring the shrinkage of a constrained specimen (a sandwich structure with sacrificial, non-sintering layers), and a free-sintered specimen. The specimens were made by laminating tape-cast Al$_2$O$_3$ and LTCC layers, as described below. Detailed descriptions of these techniques can be found in the literature 17-19.

### 8.3.2 Tape-casting and Lamination

The LTCC tapes were used as-received. The thickness of the DU and CT tapes were 90 μm and 120 μm, respectively. The Al$_2$O$_3$ constraining layers were prepared by tape casting a dispersion of 42 wt% of Al$_2$O$_3$ powder (A16, Alcoa, Pittsburgh, PA) in 25 wt% of toluene, 33 wt% of binder (B77305, Ferro, San Marcos, CA) and 0.6 wt% of modifier (M1111, Ferro, San Marcos, CA). This mixture was ball-milled in a polyethylene bottle with a 5 mm diameter ZrO$_2$ ball milling media for 72 h. The slurry was de-aired in a vacuum chamber (~100 mm Hg). After aging for 2 h, the slurry was cast onto a silicone coated polyester film, (Mylar type C, Teijin Film, DuPont Wilmington, DE) at 20 mm/sec. The alumina tape was ~ 90 μm thick after drying.
Fig. 8-1 Configuration of specimens under uniaxial compression and pressure-less constraint
Symmetric layers were prepared by placing Al$_2$O$_3$ tapes on the top and bottom layer of the LTCC layer (see schematic in Fig. 1). The LTCC layer was ~700 μm and consisted of 6 or 8 individual tapes of CT or DU, respectively. To obtain the required thickness of LTCC layer, the appropriate number of tapes were stacked and laminated. These stacks were laminated by isostatic lamination system (Model IL-4004, Pacific Trinetics Corporation, San Marcos, CA) at 80°C under 24 (for DU) or 30 (for CT) MPa for 10 min. To study the microstructural evolution, the laminates were fired to 775°C, 800°C, 820°C, and 870°C for DU and 830°C, 850°C, and 870°C for CT at 2°C/min. The sample microstructures were examined using SEM (Hitachi SEM model S-3500N). The bulk densities of tapes and pellets were measured using the Archimedes method.

8.4 RESULTS AND DISCUSSION

8.4.1. Thermo-mechanical analysis

The linear (axial) shrinkage of DU and CT pellets measured at 2°C/min are shown in Fig. 2. The deformation is complete between 850 to 900°C. The total shrinkage was ~16% and 13.5% for DU and CT, respectively. The free shrinkage anisotropy constant was ~ 1.1 for both materials. The shrinkage anisotropy constant was measured based on the total axial shrinkage and fired density $^{17}$. Thus, this is the value at full density and is assumed to be constant throughout sintering.
Fig. 8-2 Linear shrinkage of DU and CT pellets fired to 870°C at 2°C/min

Fig. 8-3a Linear shrinkage rate of DU pellets fired to 870°C at 2°C/min under different uniaxial loads; the free-sintered specimen is shown as a reference
Fig. 8-3b Linear shrinkage rate of CT pellets fired to 870°C at 2°C/min under different uniaxial loads; the freesintered specimen is shown as a reference.
Table 8-1. Shrinkage Data of DU and CT fired to 870°C at 2°C/min

<table>
<thead>
<tr>
<th>Uniaxial Load (kPa)</th>
<th>DU Tape</th>
<th></th>
<th></th>
<th>CT Tape</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon$ (%)</td>
<td>$k / k'$</td>
<td></td>
<td>$\varepsilon$ (%)</td>
<td>$k / k'$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>15.98</td>
<td>1.1</td>
<td></td>
<td>13.5</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>26.89</td>
<td>3.4</td>
<td></td>
<td>16.40</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>29.26</td>
<td>4.75</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>33.22</td>
<td>8.6</td>
<td></td>
<td>19.65</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>39.41</td>
<td>38.5</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>42.84</td>
<td>-11.2</td>
<td></td>
<td>23.29</td>
<td>3.64</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-</td>
<td>-</td>
<td></td>
<td>27.82</td>
<td>6.7</td>
<td></td>
</tr>
</tbody>
</table>

$\varepsilon$ – Linear shrinkage  
$k / k'$ – Shrinkage Anisotropy Constant
The strain rates of DU and CT, tested under different uniaxial loads, are shown as a function of sintering temperature and stress in Fig. 3 a-b. Different loads were used for the DU and CT specimens to determine conditions that inhibited radial shrinkage. The strain rate of the free sintered sample is shown as a reference. The shrinkage data are summarized in Table 1. Three key observations are noted, 1) the loaded strain rates show two clear maxima compared to one for the free strain rate, especially for the DU tape 2) the strain rate increases as the applied load increases, and 3) the maximum strain rates occur at lower temperatures as the applied load increases. The significant increase in the rate of sintering (note: second maxima) for the DU specimen under compression indicates the ease of deformation of this system compared to CT as also indicated by Fig. 4.

All DU specimens reached the same fired density of ~3.15 g/cc, irrespective of the initial load. This shows that although the deformation increases in the axial direction with increase in the load, it is, however, compensated by the reduction of shrinkage in the radial direction. This is also indicated by the loaded shrinkage anisotropy constant discussed below. In contrast to the DU specimens, all CT specimens, except the specimen under initial stress of ~150 kPa, reached a density of 3.08 g/cc. The specimen under ~150 kPa reached ~3.15 g/cc. The CT system is known to crystallize before complete sintering, and the crystallization is more pronounced at low heating rates. Crystallization leads to retardation in densification. The presence of load aids densification and this may explain why the specimen under initial stress of ~150 kPa reached a greater density.
Fig. 8-4 DU (left) and CT (right) specimens a) before and b) after sintering to 870°C at 2°C/min under uniaxial load of 60 kPa

Fig. 8-5 Shrinkage anisotropy constant of DU and CT pellets fired to 870°C at 2°C/min under different uniaxial loads; the free-sintered specimen (zero load) is shown as a reference
The shrinkage anisotropy constant is shown as a function of the applied load in Fig. 5 for both materials. Both the axial strain and $k$ increase with increase in the applied load. For DU, the change in $k$ is increasingly non-linear as the applied initial stress increases. At low stresses, the shrinkage in the radial direction is inhibited, but the specimens still shrink considerably. However, beyond ~50 kPa, the radial shrinkage of DU specimen is prevented and the sample expands radially, resulting in a diameter greater than the initial diameter of the sample as is evident from Fig. 4. This is also indicated by the negative value of $k$. For CT, the increase in $k$ with applied stress is more or less linear. In contrast to DU specimens, CT specimens shrank considerably in the radial direction even at an initial stress of > 60 kPa. It is worth noting that the instantaneous stress can be lower or higher than the initial stress depending on whether the specimen’s radial area increases or decreases as sintering proceeds.

For the purposes of stress calculations, in addition to the free-sintering kinetics, data on viscosity ($\eta$) and viscous Poisson’s ratio ($\upsilon$) are required. The viscosity data of the DU and CT materials measured using cyclic loading dilatometry with an initial load of ~60 kPa (200 g), and loading and unloading periods of 1 and 3 min each, are shown in Fig. 6. The viscosity ranges from 0.1-100 GPa.s. A detailed discussion on the measurement and interpretation of viscosity data can be found in our earlier works. The viscosity decreases rapidly during the initial stage of sintering, shows little change during the intermediate stage, and increases towards the end of densification. The values are similar for the DU and CT systems before the onset of crystallization in the latter.
Fig. 8-6 Uniaxial viscosities of DU and CT pellets measured using cyclic loading dilatometry at 2°C/min

Fig. 8-7 Viscous Poisson’s ratio of DU measured by pressureless constrained sintering along with the predictions of Venkatachari and Raj’s model for DU and CT
increase in viscosity of the CT is due to glass crystallization as confirmed by XRD and
differential thermal analysis (DTA) studies. The onset temperature of crystallization at
2°C/min was ~835°C. The CT material contains Al₂O₃ filler particles in a glassy matrix.
During sintering, the Al₂O₃ dissolves and reacts with the glass to form anorthite phases. This results in a simultaneous increase in the viscosity, and consequent retardation of
densification.

The viscous Poisson’s ratio was measured using the concept of pressure-less
constrained sintering. The technique involves the measurement of the shrinkage rates
of constrained and free-sintered specimens, and calculating using equation (14). We
demonstrated the applicability of the technique for the DU system. The measured data are
shown in Fig. 7 as a function of relative density. The viscous Poisson’s ratio varied from
0.25 at ~ 75% density to about 0.45 at ~ 93%, which showed good agreement with model
predictions. The measured data was found to fall between the predictions of Scherer and
Venkatachari and Raj’s models. Scherer’s model was developed for low-density glasses
such as silica soot preforms, while Venkatachari and Raj’s was based on sinter-forging of
MgO-doped Al₂O₃.

As noted in our earlier work, it is difficult to obtain accurate data on the viscous
Poisson’s ratio, if the difference in density between the constrained and free-sintered
specimens is significant. For accurate measurements, the strain rates of the constrained
and free-sintered specimens should be at the same density and temperature. However, this
is difficult, because the constrained specimen lags the free-sintered specimen in
densification. The greater the lag, the greater is the difference in temperature, and thus
greater is the possibility of differences in microstructure. As will be shown later, this is indeed found to be the case for the CT.

The shrinkage data under uniaxial compression (Table 1) were used to estimate the integrated viscous Poisson’s ratio (ratio of the net radial to axial strain for whole sintering) for both materials. The integrated $\nu$ was obtained by calculating the stress-induced strains in the axial and radial directions. The integrated $\nu$ of CT was found to be similar for DU. This simple analysis tells us that the $\nu$ of these two ceramic particle-filled glasses are similar. However, for CT, beyond of onset of crystallization, which happens at $\sim 93\%$ density, we expect the $\nu$ of CT to saturate. The model of Venkatachari and Raj was modified to fit the measured data of DU and calculate the $\nu$ of CT. This is shown in Fig. 7.

8.4.2 Microstructural observations during pressure-less constraint

As noted earlier, the concept of pressure-less constraint is of great interest to LTCC manufacturers and other co-fired technologies, and thus it is quite useful to understand the microstructures and their dependence on material properties to help design constrained-sintered systems with tailored properties. The microstructure of a polished DU specimen (parallel to z plane) fired to $870^\circ$C at $2^\circ$C/min is shown in Fig. 8. As is evident, the density of residual pores increases from the edge towards the center in the tranverse direction. Image analysis (using CLEMEX™ software) also showed increase in pore size from the edge towards the center (see Fig. 9). Interfacial porosity can arise either due to the tensile stress or physical diffusion of the glass from the LTCC into the alumina layer. Compositional analysis using EDS and XRD showed no sign of glass
(from the LTCC) in the alumina layer leading us to believe that the observed porosity is
due to the tensile stress.

In the thickness (z) direction, the pore density was found to be higher away from
the interface. The pore density is expected to decrease away from the interface towards
the middle of the sample, because the tensile stress due to the constraint is greatest at the
alumina/LTCC interface. However, the region near the interface is denser compared to
the bulk. These observations are in good agreement with those of Tzeng and Jean11.

The polished microstructures of DU specimens fired to 775°C, 800°C, 820°C, and
870°C at 2°C/min are shown in Fig. 10a-d. At lower temperatures, the pore structure (size
and shape) near the alumina/DU interface (this region extends to around 50-100 μm) is
different from the region away from the interface. As the temperature increases, the width
of this region decreases, resulting in a relatively dense interface region compared to the
bulk. It is important to remember that while the transverse shrinkage is inhibited by the
tensile stress due to the constraint, the specimen is free to shrink in the z direction. The
amount of z-shrinkage depends on the value of υ as shown in equation 14 (15). The
higher the value of viscous Poisson’s ratio, higher is the z-shrinkage of a constrained
specimen. As discussed earlier, the DU exhibits significant creep under load and thus,
high stress-induced shrinkage anisotropy.
Fig. 8-8 Polished microstructure of a constrained DU (6 layers) fired to 870°C at 2°C/min

Fig. 8-9 Map of the porosity and pore size distribution in a constrained CFG (6 layers) fired to 870°C at 2°C/min
Fig. 8-10 a-b Micrographs of constrained DU specimens fired to 775°C and 820°C at 2°C/min (Bottom of the picture shows the alumina/DU interface)
Fig. 8-10 c-d Micrographs of constrained DU specimens fired to 820°C and 870°C at 2°C/min
In contrast to the DU specimens, the CT specimens fired to 870°C, showed more interfacial and bulk porosity (Fig. 11), and the amount of porosity was higher at the interface than the bulk. Examination of CT microstructural evolution revealed trends similar to DU specimens with the bulk pore morphology different from the region close the interface. However, unlike DU, the densification near the interface was not complete leading to a porous region extending to ~25 μm. This, we believe is due to a combination of higher viscosity, lower shrinkage anisotropy and lower viscous Poisson’s ratio constant of the CT material, leading to lower z-shrinkage.

It is essential to know the influence of firing conditions on the microstructure and properties of materials. The fired densities of free sintered DU and CT are shown along with their constrained counterparts in Fig. 12. For the DU specimen, the influence of firing rate is negligible, both for free-sintered and constrained specimens. But, for the CT system, the fired density decreases as lower firing rates are used. And, the effect is more pronounced for constrained specimens. The decrease in density is partly due to premature glass crystallization that inhibits the sintering kinetics. Crystallization is known to be kinetically favored at lower firing rates. The observation of lower densities for constrained specimens has been reported for both polycrystalline films and glasses. The reason for the lower fired densities in constrained CT specimens compared to free-sintered specimens is due to the additional effect of in-plane tensile constraining stresses that counteract the hydrostatic sintering stresses. The magnitude of these stresses is mainly dependent on the thermo-mechanical properties of the materials, η and v, as
Fig. 8-12 Bulk densities of free-sintered and constrained DU and CT specimens fired to 870°C at heating rates of 1, 2, 5, and 10°C/min.

Fig. 8-11 Polished microstructures of DU and CT specimens fired to 870°C at 2°C/min (Top of the picture corresponds to the region close to the alumina/LTCC interface)
shown below. In fact, the ratio of these stresses is dependent only on the viscous Poisson’s ratio. This indicates the importance of $\nu$ as a design parameter. The design of materials having the desired $\nu$ is challenging. However, studies on auxetic materials $^{27}$, for example, have revealed that the Poisson’s ratio depends on the architecture of sintering microstructures, in addition to the relative density.

### 8.4.3 Stress calculations

#### 8.4.3.1 Uniaxial compression

The uniaxial compressive stress required to prevent radial shrinkage throughout sintering, calculated based on the thermo-mechanical data using equation 8 is plotted as a function of sintering density for both CT and DU tapes in Fig. 13. The calculated stress is in the range of $\sim$10 – 180 kPa, and follows the sintering rate curve i.e. it increases initially, reaches a maximum at $\sim$760°C for DU and $\sim$820°C for CT, and then decreases with increasing temperature. The data are in good agreement with those reported by Huang and Jean $^{28}$ for a borosilicate glass. The calculated non-isothermal stress values are lower than the measured isothermal stress data reported by Zuo et al. $^{29}$. The reported isothermal values at 800°C ranged between 0.3 and 2 MPa. The viscosity decreases with temperature and this may explain the lower stress values during non-isothermal tests.
Fig. 8-13 Uniaxial compressive stress for DU and CT as a function of sintering density

Fig. 8-14 Constraining tensile stress for DU and CT as a function of sintering density
It is interesting to note that the actual uniaxial compressive stress required to prevent radial shrinkage of the DU tape as discussed in section 8.4.1 is much less than the calculated maximum stress shown in Fig. 13. As noted earlier, the radial shrinkage of DU specimens is completely inhibited for stresses as low as \(~50 \text{ kPa}\). The reason for this difference is due to the significant creep (as indicated by the second strain rate maxima in Fig. 3a) because of low viscosity of DU. For the DU tape, the relation between \(k'\) and stress is highly non-linear beyond 50 kPa. Thus, in real experiments, as we increase the stress, DU shrinks more in the axial direction. For CT, unlike DU, there is reasonable agreement between the calculated maximum stress and the actual stress required for zero radial shrinkage. The relation between the stress and anisotropy constant is more or less linear for this system and there is no abnormal creep behavior as seen for DU. The CT specimen shrinks radially even at an initial compressive stress of 150 kPa. Thus, one would expect the stress required for zero radial shrinkage to be close to the calculated value. It is also noted that gravitational forces may play an important role in increasing the axial shrinkage. The current analysis does not take this into account.

8.4.3.2 Pressure-less constrained sintering

The constraining stress (CS) calculated with equation 13 is plotted as a function of relative density for DU and CT in Fig. 14. The stress curve, as expected from the equation, follows the sintering rate curve. The maximum values are not very different for the two systems. However, for the CT system, beyond the onset crystallization, the stress is higher than that for DU. This may help explain the greater porosity in CT microstructures compared to DU. The calculated stresses are significantly higher than
that reported by Tzeng and Jean based on finite element analysis. An important difference between the two studies is the use of measured thermo-mechanical data in this work.

The magnitude of the constraining stress is significantly less compared to the uniaxial stress for zero shrinkage. It is important to note that in the case of the pressure-less constrained specimen, the LTCC layer is completely interlocked with the alumina layers, unlike the uniaxially compressed specimen, which has minimal contact with the platinum base plates. In fact, it is this mechanical interlocking which helps in maintaining the zero in-plane shrinkage of the LTCC layer throughout sintering in the former case. Thus, frictional forces, which are not part of the analysis, may play an important role in constraining the LTCC layer. It is also important to note that the actual stress in the radial plane for the uniaxially compressed specimen is a product of the compressive stress and \( \nu \), and this is in the same range as the constraining stress.

The ratio of constraining stress to hydrostatic sintering stress (CS/SS) is plotted in Fig. 15. This ratio, which depends on \( \nu \) alone, provides more insights than the data on constraining stress alone. The hydrostatic sintering stress represents the compressive stress required to densify a sample. In contrast, the constraining stress represents the tensile stress needed to prevent densification. Thus, a higher CS/SS ratio is more effective in the retardation of densification and vice versa. Based on the measured viscosity values, shrinkage and viscous Poisson’s ratio data, the CS/SS ratio is similar for the two systems compared to DU.
Fig. 8-15 Ratio of constraining stress to hydrostatic sintering stress for DU and CT as a function of sintering density
However, beyond onset of crystallization, the ratio for CT saturates at around 20%, while that of DU reduces to a low value. This may explain the greater amount of porosity in CT microstructures. The effect of viscous Poisson’s ratio is amplified because of the factor ‘2’ in the denominator of equation 17. Thus, even a small difference in viscous Poisson’s ratio between any two materials can lead to sizeable differences in the bulk viscosity and the hydrostatic sintering stress.

8.5 CONCLUDING REMARKS

The effect of an external constraint (uniaxial compression and pressure-less constraint) on the microstructure, density and shrinkage anisotropy during the sintering of two commercial LTCC systems, i.e. Heraeus CT2000™ and DuPont 951Tape™ was studied. The difference in the thermo-mechanical behavior of the two materials leads to significantly different microstructures, density and shrinkage anisotropy.

The shrinkage anisotropy constant of DU was significantly higher than that of CT and non-linear under uniaxial compression. In contrast to CT, DU exhibits an ‘abnormal’ creep behavior that results in greater z-shrinkage. A combination of higher viscosity, lower viscous Poisson’s ratio, and higher constraining stresses, beyond the onset of crystallization lead to lower densities for CT compared to DU. The maximum tensile stress due to a pressure-less sacrificial constraint, assuming the viscous model, is in the range of ~10-100 kPa. The calculated uniaxial compressive stress required for zero radial shrinkage in the perpendicular plane is in the range of ~10 – 180 kPa. For more accurate
calculations the non-linear behavior of the shrinkage anisotropy constant and the effect of frictional and gravitational forces must be incorporated in the analysis.

The ratio of the constraining to hydrostatic sintering stress was found to be almost twice for CT relative to DU. This results in greater porosity in CT microstructures. A key finding of this study is that the stress and deformation of sintering materials can be controlled by controlling the viscosity, viscous Poisson’s ratio and shrinkage anisotropy constant. This maybe possible by optimum control of material chemistry, glass crystallization, powder characteristics and network architecture of the microstructure.

Acknowledgement

The authors wish to express their thanks to Thomas Hochheimer of Heraeus Circuit Materials Division, John Pepin of DuPont Electronic Materials or supplying the LTCC tapes used in this study.
Chapter 9

IN-SITU OBSERVATION OF BILAYER CURVATURE: A TOOL TO UNDERSTAND THERMO-MECHANICS OF CO-SINTERING

9.1 INTRODUCTION

Differential sintering between two or more materials that share an interface during co-firing leads to stress development that causes undesirable shape and dimensional changes. Control of these stresses is key to producing flat products with minimum shrinkage variation. This is especially important to manufacturers of co-fired multilayer devices including low temperature co-fired ceramic packages, solid-oxide fuel cells, functionally graded materials, and multilayer ceramic capacitors. One of the best examples of deleterious effects of sintering mismatch is curvature development, particularly in asymmetric structures. Earlier works by Lu et al. and Jean et al. analyzed stress development and distortion during co-firing of LTCC-metal systems based on theoretical models for describing the viscous behavior of the materials. However, as noted by the authors, knowledge of measured thermo-mechanical properties is essential for reliable predictions for stresses and distortion. We reported observations and model predictions of curvature in LTCC-silver bilayers based on measured viscosities using cyclic loading dilatometry. Similarly, Garino reported curvature analysis in LTCC and silver-palladium systems.

Different techniques are used to minimize or eliminate curvature such as applying an external load, designing symmetric structures, and using sacrificial or self-constraining techniques. These methods often involve additional costs and
materials and add further steps to the manufacturing process. Thus, it is essential to understand the factors that control curvature and stresses for optimal sintering of cofired systems. Curvature during co-sintering depends mainly on the mismatch in sintering kinetics between two materials \(^{12}\). The larger the mismatch, the greater is the curvature. However, it also depends on the relative thickness and thermo-mechanical properties such as viscosity and Poisson’s ratio of the individual materials. Thus, if data on thermo-mechanical behavior are available, the curvature can be predicted. Examples of such predictions can be found in earlier works \(^{9-12}\).

Alternatively, in-situ observation of curvature development during co-firing can be used to understand the sintering incompatibility between dissimilar materials and to validate measured thermo-mechanical properties. There is a growing literature on the measurements of the thermo-mechanical properties of densifying materials, but the measured data have not been validated. Real-time curvature observations provide a wealth of information that can be used to modify material properties and/or processing conditions. In this paper, using the bilayer strip model, we demonstrate the use of such observations for testing sintering compatibility between dissimilar materials including silver, LTCC and alumina, and validating their viscosities measured by cyclic loading dilatometry. The validated properties are then used in model calculations for predicting the stress state in bilayers.
9.2 VISCOUS MODEL FOR DISTORTION AND STRESSES

The equation for the rate of distortion of an asymmetric bilayer (see Fig. 9-1) is given as,\textsuperscript{12,18}

\[
k = \frac{6(m+1)^2 mn}{m^2 + 2mn(2m^2 + 3m + 2) + 1} (\Delta \varepsilon_{2-1})
\]

(9.1)

\[
n = \left( \frac{\eta_1}{1 - \nu_1} \right) \left( \frac{1 - \nu_2}{\eta_2} \right) \quad m = \left( \frac{h_1}{h_2} \right)
\]

where \( k \) is the normalized curvature rate, \( n \), the biaxial viscosity ratio (\( \eta \) is the viscosity and \( \nu \) is the viscous Poisson’s ratio), \( \Delta \varepsilon_{2-1} \), the differential strain rate, and \( m \), the bilayer thickness ratio. According to equation 9.1, the magnitude of distortion depends mainly on the differential sintering rate, the relative thickness and viscosity of the constituent materials, with the differential rate being the dominant variable. The sign of distortion (upward or downward curvature) depends on the sign of the differential sintering rate. The method used to calculate the curvature in a bilayer strip is shown in Fig. 9-1. Note, that equation 1 was derived from the elastic problem\textsuperscript{18} using the elastic-viscous analogy\textsuperscript{10}.

In practice, it is difficult to match the sintering rate of two different materials without degrading other crucial functions, such as the electrical performance of the device. In such cases, the viscous model suggests control of the secondary parameters \( m \) and \( n \). It should be noted that the thickness and viscosity terms change during the co-firing process and so does the distortion rate.

In addition to identifying conditions for minimum distortion, it is important to understand the evolution of stress state in the system. The following equations based
on simple beam theory, and plane stress models provide estimation of the surface and interface stresses in asymmetric laminates\textsuperscript{12,19},

\[
\sigma_1(z = h_1) = -\left[\frac{m^2n(2m + 3) - 1}{m^4n^2 + 2mn(2m^2 + 3m + 2) + 1}\right]^{\Lambda}\sigma
\]

\[
\sigma_1(z = 0 / L1) = \left[\frac{m^2n(4m + 3) + 1}{m^4n^2 + 2mn(2m^2 + 3m + 2) + 1}\right]^{\Lambda}\sigma
\]

\[
\sigma_1(z = -h_2) = -\left[\frac{m^4n - m(3m + 2)}{m^4n^2 + 2mn(2m^2 + 3m + 2) + 1}\right]^{\Lambda}\sigma
\]

\[
\sigma_1(z = 0 / L2) = -\left[\frac{m^4n + m(3m + 4)}{m^4n^2 + 2mn(2m^2 + 3m + 2) + 1}\right]^{\Lambda}\sigma
\]

where,

\[
\frac{\Lambda}{\sigma} = \eta_1 \Delta \varepsilon_{2-1}
\]

The most important factors in controlling the stresses are the viscosity and the mismatch in strain rate. Low viscosity values and minimum mismatch will lower the magnitude of the tensile stresses. However, the stresses are also dependent on \( m \) and \( n \).

A schematic of the viscous stresses in asymmetric laminates is shown in Fig. 9-2. The stress varies linearly with thickness. Depending on the degree of warpage, the slopes of the stress lines change influenced by the additional bending stresses due to warpage. The largest tensile stress in layer 1(L1) is at the interface. At any given instant in time, when the rate of sintering of L1 is higher than that of layer 2 (L2), L2
Fig. 9-1 Method used for curvature measurement

\[ k = \left( \frac{1}{R_{\text{curvature}}} \right) \]

Fig. 9-2 Schematic showing the stress state in a bilayer as a function of layer thickness for the cases of no, small and large curvature

- L1
  - \( z = h_1 \)
  - \( z = 0 \)
  - \( z = -h_2 \)

- L2
  - Compressive
  - Tensile
  - No warpage
  - Small warpage
  - Large warpage
is put under uniform compression (CD) and the L1 under uniform tension (AB), if there is no curvature. As the amount of curvature increases, points A and D move toward tension (path A-A’-A’”) and compression (D-D’-D’”), respectively. Similarly, points B and C trace the paths B-B’-B’” and C-C’-C’”, respectively, depending on the amount of curvature controlled by the variables in equation 9.1. For the case when L2 sinters at a faster rate, the same equations 9.1-5 apply, but now with the layers interchanged. Ceramic materials, in general are prone to failure under tension. Thus, for the case when L1 sinters faster than L2, the outer surface of L2 and interface at L1 are the surfaces that are prone to failure.

9.3 EXPERIMENTAL PROCEDURE

The curvature evolution during co-sintering of a bilayer strip was observed in-situ using a tube furnace open at one end and a digital video camcorder (Sony, DCR-TVR320). Bilayer strips were used instead of plates, as the viscous Poisson’s ratio terms in equation (1) can be neglected for strips provided the width of strip is sufficiently less than its length. Four kinds of bilayers, silver-LTCC, silver-Al₂O₃, LTCC-LTCC, LTCC-Al₂O₃ were prepared. Commercial LTCC tapes such as DuPont 951 Tape™ and Heraeus CT2000™ (henceforth called DU and CT, respectively) were studied. DU is a Pb-borosilicate glass with alumina as the ceramic filler particle 

To our knowledge, no detailed studies on the glass-filler interaction during heating in this system exist. In case of CT, the alkaline-silicate glass reacts with the alumina and titania filler particles to form high quality factor crystalline phases. The silver (Ag, TC2303, Heraeus Circuit Materials Division Inc., PA) was obtained in both paste and powder forms, for screen-printing and shrinkage measurements, respectively.
The silver-LTCC bilayers were made by screen-printing Ag inks on CT tapes of size 1 x 1” and drying at 80°C for 5-10 min. The typical dried thickness of the silver layer was 15-25 µm. The required number of LTCC layers were isostatically laminated (Model IL-4004, Pacific Trinetics Corporation, San Marcos, CA) at 70-75°C under 30 MPa for 10 min. After lamination, the samples were cut into beams of size ~25 mm x 3 mm. Binder was removed by heating to 425°C at 2°C/min and holding for 1.5h. Samples were co-sintered in a tube furnace using the recommended heating profile of 5°C/min up to 870-875°C. To study the effect of heating rate different ramp rates, 2°C/min, 5°C/min and 10°C/min were used to heat the samples after binder burnout to the final peak temperature. We would like to note that the CT tapes used for studying the effect of heating rate was from a different batch than the above. Henceforth, it is denoted as CT⁰ to avoid confusion.

The CT-DU bilayers were made by isostatically laminating 3 and 4 layers of CT and DU, with a layer thickness of ~ 120 and 90 µm, respectively at a pressure of 28 MPa and temperature of 75°C so that the thickness ratio, m was close to one. Thin beams of size ~ 25 x 0.3 mm were then cut and co-fired at 5°C/min up to a peak temperature of 870°C. Prior to co-firing, binder burn-out was done at 450°C with a dwell period of 90 min.

In order to study the effect of a non-sintering layer on LTCC warpage, bilayers of Al₂O₃-LTCC were examined. Unlike viscous-viscous composites discussed above, this is a case of an elastic-viscous composite. A non-sintering material is essentially elastic in nature and thus, studies on Al₂O₃-LTCC bilayers provide insights into understanding mechanical behavior of elastic-viscous composites. The concept of constrained sintering is a great example, which takes advantage of such composites. Bilayers specimens of Al₂O₃-DU of different thickness were made by stacking 4, 8 or
12 layers of DU (each layer of DU ~90 μm thickness) on 3 layers of Al₂O₃ ~100 μm thickness, and laminating by warm isostatic pressing at 70-75°C under 24 MPa for 10 min. After lamination, the samples were cut into rectangular beams of size ~ 25 mm x 3 mm.

The axial shrinkage and the uniaxial viscosity of Ag, CT and DU were measured using a thermo-mechanical analyzer (TMA, TMA50, Shimadzu, MD) with a vertical 3 mm diameter loading rod. Loose powders of the LTCC tapes were produced by removing the organic binder by heating the tapes at 2°C/min to 400°C-450°C and holding for 1-2 h. (TMA), the powders were uniaxially pressed at ~ 40 MPa into cylindrical pellets of ~6.38 mm diameter x 4.4-4.5 mm (for CT and DU). The green densities were ~62, 65 and 69 ± 2% of the bulk fired densities for DU, CT, and Ag, respectively. The thermo-mechanical data were used in equations 1-5 to calculate the rate of distortion and mismatch stresses.

9.4 RESULTS AND DISCUSSION

9.4.1 Thermo-mechanical analysis

The linear shrinkage and shrinkage rate of CT, DU and Ag pellets measured at 5°C/min are shown in Figs. 9-3 and 9-4. The total axial shrinkage was ~13.4%, 15.9%, and 13% for the three materials, respectively. From density measurements, the anisotropy constant, k, the ratio of axial to radial strain, was found to be ~1.08, 1.09, 1.65 for CT, DU and Ag specimens, respectively. The Ag specimen expands considerably between ~220-350°C and shrinks thereafter at a uniform rate.

The viscosity data of CT, DU and Ag measured by cyclic loading dilatometry are shown in Fig. 9-5. The values range from 0.1 to 100 GPa.s. For the glass-based LTCC material, the viscosity initially decreases with temperature, and changes little
Fig. 9-3 Linear shrinkage versus sintering temperature for Ag, CT and DU pellets

Fig. 9-4 Linear shrinkage rate versus sintering temperature for Ag, CT and DU pellets
during the intermediate stage densification. For CT, there is a sharp increase during the final stage of densification corresponding to the onset of crystallization at 5°C/min. A detailed discussion on LTCC viscosity and measurement procedure can be found in our earlier works \(^\text{22, 23}\). For Ag, the viscosity is more or less constant throughout sintering reflecting the uniform strain rate behavior.

### 9.4.2. In-situ Curvature Observations

**9.4.2.1. Ag-CT and CT-DU bilayers**

Curvature evolution in Ag-CT bilayers was reported in our earlier work \(^\text{10}\). The normalized curvature rate based on *in-situ* observations and model predictions are plotted as a function of sintering temperature in Fig. 9-6. The Ag layer begins to sinter first leading to an upward curvature (indicated by the positive curvature rate). When the CT layer starts densifying, the upward curvature is compensated, and a significant downward curvature develops (indicated by the negative curvature rate). We found that the initial expansion of Ag seen in the shrinkage data does not lead to any appreciable curvature. We believe, this is because the screen-printed Ag does not exactly follow the same kinetics as the uniaxially pressed Ag pellet.

The predicted data were obtained by using the viscosity and shrinkage data in equation 9.1. While there is good agreement between the two on the temperature at which the rate of curvature is maximum, the theoretical prediction underestimates the actual observed value. The discrepancy, we believe, is due to non-representative shrinkage data, and its use in calculating the thickness of the silver film. The shrinkage data was collected using cylindrical pellets of Ag and CT in a TMA, which measures the axial shrinkage. This data was used to calculate the differential sintering

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Fig. 9-5 Uniaxial viscosity measured by cyclic loading dilatometry (initial load = 200g, loading time = 1min , unloading time = 1 min) versus sintering temperature for Ag, CT and DU pellets

Fig. 9-6 Comparison of predicted and observed normalized curvature rate versus sintering temperature for 1:2 (m ~ 0.0833 ) Ag-CT bilayer
rate, and also the change in the thickness of silver and CT in the bilayer. However, warpage experiments were done by screen-printing silver on tape-cast (and subsequently laminated) layers of CT. It is possible that shrinkage behavior of silver and CT pellets do not completely represent the sintering behavior of layered materials.

Laser-based scanning techniques have been used to measure the in-plane shrinkage of screen-printed silver layers in other works \(^8,^9\). It is important to have data on the in-plane shrinkage of silver paste rather than axial shrinkage of silver powder compacts, before one can make reasonable comparisons between theory and experiment. Garino \(^1^1\) recently reported reasonable agreement between observed and predicted curvature in Ag/Pd alloy-LTCC bilayers. The theoretical predictions underestimated the observed curvature, and this was attributed to inaccurate predictions of the change in the thickness of the bilayer. Cai et al. \(^1^2\) and Ravi et al. \(^2^4\) report good agreement between observed and predicted curvature for alumina/zirconia bilayers and alumina/alumina bilayers (with differential densities). We found good agreement between theory and experiment for CT-DU bilayers. The measured and predicted curvature rates for a CT-DU bilayer specimen are plotted as a function of firing temperature in Fig. 9-7. The agreement between the two datasets is good indicating that the measured properties are in the right range. It is worth noting that the bilayer strip model allows validation of only the relative viscosity and not the absolute values of the viscosity. From these studies, it is clear that obtaining accurate data on the sintering kinetics of the materials, especially the metallization layers is key to providing reliable predictions.

Thin films of metallization and dielectric materials on substrates can come under considerable stresses than can lead to catastrophic failure. Thus, it is important
to know the stress state of the individual layers to determine criteria for damage and to prevent failure of the films. The stress analysis is complicated in that the parameters, m, n, and $\Delta \varepsilon_{z,z}$, change in a complex fashion during sintering and thus the stress state in the layers can vary in a continuous manner, both in magnitude and sign. For the case of a bilayer, the net stress in a layer (shown in equations 9.2-5) is determined by the combination of the mismatch and bending stresses.

The validated viscosity and shrinkage data were used to calculate the stresses in the Ag-CT bilayer. Fig. 9-8 shows the stress evolution in Ag-CT bilayer during co-sintering. These are viscous stresses at the interface and convex surfaces in Ag and LTCC layers (at points A, B, C and D in the schematic figure). By convention, compressive stress is taken to be negative and tensile stress is taken to be positive in sign. It can be observed that the stresses in the silver layer are tensile until around 800°C. Beyond that, the densification of CT results in tension in the CT surface and compression in Ag.

As noted in our earlier work 23, densifying materials are predominantly viscous in the intermediate stage of sintering, and viscoelastic in the initial and final stages. The stresses are expected to be high in the viscoelastic regime compared to viscous regime, because the viscosities are relatively high in former. Thus, while the maximum stress in the bilayer during early stages of CT sintering is ~ 150 kPa, in the viscous regime it is less than ~50 kPa. Thus, it is better to have low-viscosity materials than rigid, elastic or viscoelastic layers. It is also worth noting that both the magnitude and sign of the stresses will be different if the relative thickness and viscosity are modified.
Fig. 9-8 Comparison of predicted and observed normalized curvature rate versus sintering temperature for 3:4 (m ~ 1) CT-DU bilayer

Fig. 9-7 Viscous stresses at the interface and convex surfaces in Ag and CT layers (points A, B, C, D) for 1:2 Ag-CT Bilayer (m ~ 0.0833)
9.4.2.2 Distortion and constrained sintering

Equation 9.1 anticipates constrained sintering, wherein the in-plane shrinkage of one layer is completely constrained by the other. According to equation 9.1, this occurs when either the difference in viscosity or thickness between the two materials is significantly different. Two bilayer specimens, one, Ag on a fully dense Al₂O₃ substrate and another on a porous CT co-fired to 900°C are shown in Fig. 9-9. The bilayers were of similar thickness ratio (m = ~0.1). As is evident, the Ag-Al₂O₃ bilayer specimen is flat, while the Ag-CT specimen has a finite warpage.

Equation 9.1 predicts a finite warpage for a finite value of the differential strain rate. Although, the differential rate is finite for the Ag-Al₂O₃ bilayer, and even higher than that for Ag-CT bilayer, there is no distortion in the former. This is because of the significant difference in viscosity between Ag and Al₂O₃. The viscosity of a fully dense specimen is extremely high compared to a porous material. On the other hand, similar viscosities of Ag and CT lead to a finite curvature in Ag-CT bilayers.

9.4.2.3 Curvature in elastic-viscous composites

The evolution of curvature in Al₂O₃-DU bilayers of different thickness is shown in Fig. 9-10. In this case, both the alumina and DU are porous. The curvature increases with increase in the thickness of the DU layer. There is little or no curvature in the bilayer with the thinnest DU layer. This is because the thickness of the non-sintering Al₂O₃ is sufficient to constrain the in-plane shrinkage of the DU layer without any warpage. An interesting finding is the development of periodic cracks in the Al₂O₃ layer, especially in the highly curved specimen. The significant bending
Fig. 9-9 Ag-Al$_2$O$_3$ and Ag-CT bilayers fired to 900°C @ 5°C/min

Fig. 9-10 Curvature evolution in DU-Al$_2$O$_3$ bilayer for 4, 8, and 12 layers of DU on 3 layers of Al$_2$O$_3$ (layer thickness of DU and Al$_2$O$_3$ ~ 90 and 300 μm) [Note: The white Al$_2$O$_3$ layer shows cracking as indicated by the rough curling]
results in cracking of the weak and elastic Al₂O₃ layer. This weakening of the Al₂O₃ layer is useful in that it is easy to remove the material after sintering of the LTCC material. In fact, this is taken advantage of in the concept of sacrificial constrained sintering. It is worth noting that equation 1 is applicable only for the case when layers 1 and 2 materials both show viscous behavior. Any densifying material can be treated as viscous and before the onset of sintering, the mechanical response is predominantly elastic. The alumina layer, as it does not begin sintering within the temperature range of testing, is thus best treated as an elastic material.

### 9.4.3 Effect of heating rate on distortion

The curvature evolution in Ag-CT * bi-layers at 2°C/min, 5°C/min and 10°C/min is shown in Fig. 9-11. As noted earlier, the rate of curvature depends directly on the differential sintering rate, relative viscosity and thickness of the bilayer components as shown in equation 1. A change in the heating rate can influence all these three variables. Glass softening and crystallization are also known to depend strongly on the heating rate. As shown in our earlier work 23, glass crystallization has a strong effect on its viscosity.

The bi-layer samples heated at 2°C/min has some residual curvature after sintering compared to those heated at higher rates. Possible reasons proposed for the observed difference in warpage for different heating rates, are 1) a change in the viscosity of the system (owing to glass crystallization) or 2) a change in differential sintering rates due to a change in the heating rate. Differential sintering rates (based on TMA shrinkage data) for Ag and CT * at 2°C/min, 5°C/min and 10°C/min are shown in Fig. 9-12. As is evident, the differential strain rate increases with increasing
Fig. 9-11 Curvature evolution in 1:2 Ag-CT* bilayer for 2°C/min, 5°C/min, and 10°C/min
heating rate. Because the rate of curvature is directly proportional to the differential sintering rate, one would expect it to increase with increase in heating rate. But, this is not so as shown in Fig. 9-11. This leads us to believe that the residual curvature in the specimen fired at 2°C/min is due to the increase in viscosity because of the formation of crystalline anorthite phases on the CT* system. The increase in viscosity leads to greater resistance to viscous flow, which in turn reduces the rate of curvature. Or in other words, the bilayer specimen begins to “freeze” in its curved state, when the rate of glass crystallization increases. This also suggests that glass crystallization can be used for constrained sintering. A fully crystallized layer can be used to constrain the in-plane shrinkage of a sintering layer.

9.4.4 Design Guidelines

The bilayer strip model has been successfully tested in earlier studies and can be used to derive useful guidelines for designing materials to achieve minimum stress and distortion during co-firing. For a given differential sintering rate, the theory predicts a maximum distortion when \( m^2n = 1 \) (see Fig. 9-13). The normalized stress, \( (\sigma_{\text{max}} / \eta_1 \Delta \varepsilon) \) is plotted as a function of \( m \) and \( n \) in Figs. 9-14 and 9-15 for \( m = 0.1 \) and 10. The value of \( m = 0.1 \) (i.e. when layer 1 is one-tenth the thickness of layer 2) is representative of screen-printed thick film metallization, or passive component (capacitor, resistor etc.) in a typical LTCC device. For both values of \( m \), as \( n \) increases, the maximum stress in layer 1 decreases. However, the stress in layer 2, while compressive for the range of \( n \) values shown for \( m = 0.1 \), becomes tensile and passes through a maximum for \( m = 10 \). As a general rule, the stress in layer 2 changes to tension when \( n > (3m + 2)/m^3 \).
Fig. 9-12 Differential sintering rate for Ag and CT* at heating rates of 2°C/min, 5°C/min, and 10°C/min

Fig. 9-13 Normalized distortion rate versus viscosity ratio for different relative thickness according to equation (1)
Fig. 9-14 Normalized maximum stress versus viscosity ratio for $m = 0.1$ at the interface of L1 and convex surface of L2 for the case of upward curvature.

Fig. 9-15 Normalized maximum stress versus viscosity ratio for $m = 10$ at the interface of L1 and convex surface of L2 for the case of upward curvature.
Fig. 9-16 Normalized distortion rate and maximum stress in layer 1 versus viscosity ratio for $m = 0.1$

Fig. 9-17 Normalized distortion and maximum stress in layer 1 versus viscosity ratio for $m = 10$
It is also possible that conditions that reduce stress may result in increase in the distortion rate. The effect of viscosity ratio on the maximum stress in layer 1 and the distortion rate for \(m = 0.1\) and \(10\) is shown in Figs. 9-16 and 9-17. For example, when \(m = 0.1\), it is found that the situations that decrease stress tend to increase distortion rate, whereas for \(m = 10\), both stress and distortion can be decreased at viscosity ratios \(> 0.01\). Thus, optimum values of \(m\) and \(n\) can be chosen to minimize both stress and distortion. Similar guidelines can be obtained from the viscous model for other specific cases.

9.5 CONCLUDING REMARKS

We demonstrated the use of in-situ observations of curvature in bilayers and the bilayer strip model for testing sintering compatibility and validating the viscosities measured by cyclic loading dilatometry. There was good agreement between the observed data and model predictions for CT-DU bilayers. The theoretical model underestimates the curvature for CT-Ag bilayers. This, we believe is due to non-representative shrinkage data for the silver metallization. For more reliable predictions, accurate data on the shrinkage is essential. The good agreement between theory and experiment indicates that the thermo-mechanical data are reliable.

The bilayer strip model predicts maximum warpage for \(m^2n=1\) for a given differential rate. It is important to determine optimum conditions that lead to both minimum distortion and stress, as conditions that guarantee minimum warpage may not necessarily yield low stresses. The model also anticipates constrained sintering. For a given thickness, the difference in viscosity should be at least three orders of magnitude for one layer to completely constrain another.
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Chapter 10

SUMMARY AND FUTURE WORK

10.1 SUMMARY

10.1.1 Measurement of Thermo-mechanical Properties

Isothermal cyclic loading dilatometry was proposed for measuring the uniaxial viscosity of densifying materials as a function of both density and temperature. In comparison to constant loading sinter-forging experiments, cyclic loading dilatometry helps minimize the stress history effects that arise due to the application of external load and therefore gives a better estimate of viscosity. The loading rate was maximized to minimize the effect of external load on sample deformation. The greater the unloading period, the less is the stress-induced shrinkage anisotropy. In the case of polycrystalline materials, which exhibit different shear behavior from glass-based systems, different testing conditions would be required. The viscosity of a sintering compact increases with relative density and decreases with temperature. The viscosity of the LTCC ranges from \( \sim 1 \) to \( 20 \) GPa.s for relative densities from \( \sim 70 \) to \( 96\% \) between \( 740^\circ C \) and \( 790^\circ C \). Statistical analysis revealed insignificant differences between the viscosity data sets at 5% significance level and thus indicates good reproducibility of the testing tool in determining the viscosity of a sintering material. Any variability in the viscosity data would be due to the assumption of a constant anisotropy factor and low sensitivity of the dilatometer tool in measuring very small deformation rates \( (\varepsilon'_s < 10^{-7} /s) \).

A novel method, based on pressureless constrained sintering, was proposed for the measurement of viscous Poisson’s ratio. The constrained sintering method is a viable
alternative to more complex techniques, especially for use in an industrial setting. Representative data for a low temperature co-fired ceramic (LTCC) material were reported. The viscous Poisson’s ratio varies from 0.25 at ~74% density to about 0.45 at ~93%. Unrealistic values are obtained during the early and final stages of sintering, because the sintering material is predominantly elastic at low sintering strain rates (<$10^{-5}$/s), which are characteristic of these regimes. The viscous analysis is applicable during the intermediate densification regime, over which the data are in reasonable agreement with the models of Venkatachari and Raj$^8$ and Scherer$^{17}$. To improve the accuracy of the data, simultaneous measurement of the axial and radial strains during free sintering would be useful. We expect the method to work for polycrystalline materials also, if a suitable constraining system is identified. It is also possible to use the technique even if there is a non-zero external load, provided the same load is applied to the two specimens. A possible refinement of the current technique would be to perform these tests on specimens of varying thickness and green density to see their effect on shrinkage, and thus $\nu$.

10.1.2 Densification and Sintering Viscosity of LTCC materials

The uniaxial viscosity data of three commercial LTCC systems, i.e. DuPont 951Tape, Heraeus CT2000, and Ferro A6, as measured by cyclic loading dilatometry technique were presented. For all three systems, the viscosity initially decreases with temperature, changes little during the intermediate stage and increases towards the end of densification. The viscosity increased sharply by as much as two orders of magnitude
beyond the onset of crystallization. At slower heating rates, the increase in viscosity is more pronounced due to glass crystallization.

The shrinkage anisotropy constant was significantly larger for DU than CT and FE when tested with a uniaxial load. The increase in $k$ has significant implications, because a material that can shear more by viscous flow can relax stresses rather than forming defects such as cracks, porosity or warpage. Thus, the anisotropy constant is an important design parameter than can be tailored to achieve optimum sintering behavior. This also opens up possibilities of controlling $k$ through control of material chemistry, particle morphology, and forming technique. For example, the tapes can be made more anisotropic by adding high aspect ratio non-spherical particles.

The isothermal viscosity of the three materials range from 0.1 to 100 GPa.s between 73% and 95% density. The viscosities of the three materials differ from each other and from the model predictions. It is clear that more robust models, which can incorporate the effect of contact area, crystallization, and effect of filler particles beyond the percolation threshold, are needed to predict the evolution of viscous behavior of densifying materials.

The activation energies for DU and FE determined from isothermal data were in good agreement with those measured by the MSC approach. The MSC analysis is limited to systems that sinter by a single mechanism, without the presence of competing phenomena such as crystallization. However, by using the sintering data at higher heating rates, the phenomenon of glass crystallization can be separated from sintering, thus allowing estimation of the true sintering activation energy.
The complex evolution of viscosity during sintering of particle-filled and crystallizable glasses was discussed in light of new experimental data on commercial LTCC systems. The currently available models fail to capture the viscous behavior over the whole density range. A simple model that considers the effect of important variable including temperature, porosity, filler fraction, and crystallization has been proposed. The model assumes that the effects of these variables are mutually exclusive. It does not take into consideration the effect of contact area and any compositional changes, which can be important in these reactive systems.

It appears that temperature, filler particles and crystallization have the most significant effect on viscosity. However, phenomena such as percolation and phase separation can also be important. The effect of density is significant beyond the closed pore stage. Regarding filler particles, more experimental data, particularly at high volume fraction of filler particles are needed. Further, detailed studies on the crystallization behavior of LTCC systems are also required. We note that tools such as SciGlass™ can be useful for predicting viscous behavior of sintering systems, particularly for materials for which experimental data are not available.

10.1.3 Constrained Sintering and In-situ Bilayer Curvature

The effect of an external constraint (uniaxial compression and pressure-less constraint) on the microstructure, density and shrinkage anisotropy during the sintering of two commercial LTCC systems, i.e. Heraeus CT2000 and DuPont 951Tape was studied. The difference in the viscous behavior of the two materials leads to significantly different microstructures, density and shrinkage anisotropy.
The shrinkage anisotropy constant of DU was significantly higher than that of CT and non-linear under uniaxial compression. The higher viscous Poisson’s ratio for the DU system compared to CT leads to greater z-shrinkage. Higher viscosity, lower viscous Poisson’s ratio, and higher constraining stresses lead to lower densities for CT compared to DU. The maximum tensile stress due to a pressure-less sacrificial constraint, assuming the viscous model, is in the range of ~10-100 kPa. The calculated uniaxial compressive stress required for zero radial shrinkage in the perpendicular plane is in the range of ~10 – 180 kPa. For more accurate calculations the non-linear behavior of the shrinkage anisotropy constant and the effect of frictional and gravitational forces must be incorporated in the analysis.

The ratio of the constraining to hydrostatic sintering stress was found to be almost twice for CT relative to DU. This results in greater porosity in CT microstructures. A key finding of this study is that the stress and deformation of sintering materials can be controlled by controlling the viscosity, viscous Poisson’s ratio and shrinkage anisotropy constant. This is possible by optimum control of material chemistry, glass crystallization, powder characteristics and network architecture of the microstructure.

We demonstrated the use of in-situ observations of curvature in bilayers and the bilayer strip model for testing sintering compatibility and validating the viscosities measured by cyclic loading dilatometry. There was good agreement between the observed data and model predictions for CT-DU bilayers. The theoretical model underestimates the curvature for CT-Ag bilayers. This, we believe is due to non-representative shrinkage data for the silver metallization. For more reliable predictions,
accurate data on the shrinkage is essential. The good agreement between theory and experiment indicates that the thermo-mechanical data are reliable.

The bilayer strip model predicts maximum warpage for $m^2n=1$ for a given differential rate. It is important to determine optimum conditions that lead to both minimum distortion and stress, as conditions that guarantee minimum warpage may not necessarily yield low stresses. The model also anticipates constrained sintering. For a given thickness, the difference in viscosity should be at least three orders of magnitude for one layer to completely constrain another.
10.2 FUTURE WORK

In this work, we made significant strides towards developing a comprehensive model for the sintering process. But, there is more to be done. We offer here some suggestions for future work:

1) There is a need to standardize the tools currently available for measuring the thermo-mechanical properties. Cyclic loading dilatometry (CLD) technique is now an established method for measuring uniaxial viscosity. Discontinuous sinter-forging, although more cumbersome than CLD, offers an alternative. More materials should be characterized using these techniques. The approach of constrained sintering for measuring the viscous Poisson’s ratio must be explored further as it is a convenient technique. New tools must also be explored.

2) Equipments with higher sensitivity are needed for greater accuracy in the measurements. This will be useful to characterize materials that have very high viscosity and thus undergo very low deformation under load.

3) The effect of green density on the thermo-mechanical behavior must be investigated. In this work, the green densities were not varied. Past studies have shown that the sintering rate changes with change in the green density. Thus, the viscosity, which is inversely proportional to the strain rate, maybe different for samples with different starting densities.

4) The viscosity of pure glass systems must be explored in greater detail. In this work, we concentrated on commercial LTCC systems which were either crystallizable or ceramic particle-filled glasses. Studies on pure glass systems will
provide further insights in understanding the evolution of viscosity as a function of density. Viscosity data on densifying pure glass systems will also be useful for validating models that do not take into account the effect of fillers.

5) The effect of filler particles on glass viscosity must be studied in greater detail. It is clear that the composite viscosity increases significantly with increase in filler fraction, but it is not obvious when the percolation threshold would occur for a given system. Detailed studies on the chemical and physical interaction between the fillers and the glass including investigations on the wetting characteristics would be useful.

6) There is need to study the crystallization and phase separation behavior of glass compositions used in LTCC. Crystallization and phase separation can have a significant effect on the viscosity. Further studies on the effect of crystallization on viscosity would be quite useful to develop guidelines for design and control of LTCC systems. The use of phase equilibria diagrams to determine optimum glass compositions for LTCC applications with tailored viscosities should be explored.

7) Our study has revealed that the shrinkage anisotropy constant can be a useful design parameter than can be tailored to achieve optimum sintering behavior. Possibilities of controlling $k$ through control of material chemistry, particle morphology, and forming technique are fascinating. For example, it would be interesting to study the viscous behavior for particles with different aspect ratios.

8) The effect of constraint on the microstructure, shrinkage and density of LTCC systems must be studied further. A better understanding how the thermo-mechanical properties of the material influence the evolution of the microstructure
is required. The stress analysis must also be extended to enable prediction of the stress profile as a function of position and thickness, especially in regions close to the free edges of the sample.

9) There is a need to develop theoretical and numerical models to predict the complex viscosity of LTCC systems. These models should take into account the effect of contact area, crystallization, filler percolation, contact area, changes in glass composition and phase separation.

10) Numerical models can now take advantage of the database of thermo-mechanical properties developed in this work and similar studies, for developing 2-D and 3-D simulations of co-sintering of integrated ceramics.

11) The drive towards miniaturization has resulted in the fabrication of sub-micron features in integrated packages. Mechanical tools such as a micro or nano-indenter can be used to determine the thermo-mechanical response of sub-micron or nano-sintering materials.
APPENDIX A

SPECTROCHEMICAL ANALYSIS

The chemical composition data of all three LTCC materials, DU, CT, and FE determined by DC spectrochemical analysis are summarized in table A-1. DU and CT tapes are ceramic particle-filled borosilicate glasses, while FE is a crystallizable Ca-borosilicate glass with no filler particles. DU is a Pb-borosilicate glass with alumina as the ceramic filler particle. The CT system is an alkaline-silicate glass with alumina and titania filler particles.

<table>
<thead>
<tr>
<th>Component</th>
<th>CT</th>
<th>FE</th>
<th>DU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>45</td>
<td>-</td>
<td>51</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22.4</td>
<td>46</td>
<td>30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>8.76</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>5.34</td>
<td>10.1</td>
<td>2.37</td>
</tr>
<tr>
<td>BaO</td>
<td>2.98</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>7.67</td>
<td>42</td>
<td>5.19</td>
</tr>
<tr>
<td>SrO</td>
<td>4.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.95</td>
<td>-</td>
<td>1.04</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>-</td>
<td>8.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>-</td>
<td>1.57</td>
</tr>
<tr>
<td>CoO</td>
<td>-</td>
<td>-</td>
<td>0.24</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>-</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table A-1 Composition of LTCC tapes based on DC Spectrochemical analysis
APPENDIX B
DIFFERENTIAL THERMAL ANALYSIS

The LTCC materials i.e. DU, CT and FE tapes were characterized by DTA to understand their glass transition and crystallization characteristics during firing. Glass softening and crystallization have a strong effect on the viscosity of these systems and understanding them is key to the design of LTCC systems. The DTA tests were done at heating rates of 2, 5, 10, 20, 30 and 40°C/min. The DTA curves are shown in Figs. B-1a-c (the curve at 2°C/min is not shown for clarity). The glass transition temperature, T_g and the onset and peak crystallization temperatures, T_o and T_p, respectively are summarized for the LTCC tapes in Table B-1. As expected, with increase in heating rate, T_o and T_p move toward higher temperatures and vice versa. As discussed in previous reports, premature crystallization of the glass can inhibit sintering of these systems. This is why glass crystallization is usually delayed so that sintering can reach completion. The sinterability (or viscous flow) of these systems can be evaluated by determining the difference between the glass transition (or softening) temperature and onset of crystallization. The smaller the difference, the lower is the sinterability and vice versa. So, for low heating rates, the sinterability is expected to be lower for systems, which undergo crystallization before the completion of sintering compared to higher heating rates.
The activation energy for crystallization can be determined using the Kissinger analysis. The Kissinger equation is given by,

$$\ln\left(\frac{\phi}{T_p^2}\right) = - \frac{E_a}{RT_p} + \text{const}$$

where, $\phi$ is the DTA scan rate (heating rate) in $^\circ$C/min, $E_a$ is the activation energy, and $R$ is the gas constant (8.314 J/mol $^\circ$K). By plotting $\ln\left(\phi/T_p^2\right)$ versus 1000/$T_p$, the activation energies can be obtained by calculating the slopes. The plots for DU, CT and FE tapes are shown in Figs. B-3a-c, respectively. The activation energies for crystallization in DU, CT and FE tapes were found to be $\sim$ 300 kJ/mol, 250 kJ/mol and 345 kJ/mol, respectively. In case of FE, two crystallization peaks can be seen from the DTA curves. The first peak corresponds to the crystallization of the wollastonite (CaSiO$_3$) phase and the second peak corresponds to the calcium borate phase. With increase in heating rate, the amount of wollastonite phase increases until the two peaks merge in to a single peak at $40^\circ$C/min. The calculated activation energy corresponds to the formation of wollastonite phase.
Table B-1. Onset and Peak Crystallization Temperatures, and Activation Energies for Three Commercial LTCC Tapes

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>DU Tape</th>
<th>CT Tape</th>
<th>FE Tape</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_o$ (°C)</td>
<td>$T_p$ (°C)</td>
<td>$Q_k$ (kJ/mol)</td>
</tr>
<tr>
<td>2</td>
<td>806</td>
<td>888</td>
<td>835</td>
</tr>
<tr>
<td>5</td>
<td>855</td>
<td>912</td>
<td>858</td>
</tr>
<tr>
<td>10</td>
<td>894</td>
<td>932</td>
<td>885</td>
</tr>
<tr>
<td>20</td>
<td>914</td>
<td>959</td>
<td>907</td>
</tr>
<tr>
<td>30</td>
<td>925</td>
<td>978</td>
<td>927</td>
</tr>
<tr>
<td>40</td>
<td>935</td>
<td>991</td>
<td>938</td>
</tr>
</tbody>
</table>

$T_o$ – Crystallization onset  $T_p$ – Crystallization Peak  $Q_k$ – Kissinger Activation Energy

Fig. B-1a. Differential Thermal Analysis (DTA) scan curves of DuPont 951Tape at various heating rates.
Fig. B-1b. Differential Thermal Analysis (DTA) scan curves of CT tape at various heating rates.

Fig. B-1c. Differential Thermal Analysis (DTA) scan curves of FE tape at various heating rates.
Fig. B-2a. The Kissinger Plot of DU tape

Fig. B-2b. The Kissinger Plot of CT tape
Fig. B-2c. The Kissinger Plot of FE tape
APPENDIX C

X-RAY DIFFRACTION ANALYSIS

The LTCC materials i.e. DU, CT, and FE were characterized by hot stage XRD (Cu-Kα, Scintag2 PAD V, Scintag Inc., CA) to under glass crystallization. The X-ray diffraction patterns are shown in Figs. C-1a-c. The DU tape contains only alumina fillers as the crystalline phase. The CT tape contains both alumina and titania, and also anorthite phases (MAi₂Si₂O₈, M= Ca, Sr, Ba) indicated by the overlap at 2theta ~ 27.5 (shown by the arrows) at 855 and 900°C. The FE tape is non-crystalline at room temperature, but crystallizes beyond ~ 790°C to form CaSiO₃. The XRD results are in good agreement with the DTA results shown in appendix B.
Fig. C-1a XRD Patterns of DU, as-received and specimens heated to 825°C, 865°C, 875°C, and 900°C showing presence of Al₂O₃
Fig. C-1b XRD Patterns of CT, as-received and specimens heated to 7355°C, 835°C, 855°C, and 900°C showing the presence of Al₂O₃ and TiO₂; The arrows indicate the formation of anorthite phases
Fig. C-1b XRD Patterns of FE, as-received and specimens heated to 785°C, 810°C, 830°C, 830°C, and 885°C; All specimens except as-received tape show crystallization of CaSiO$_3$ phase; There is no indication of CaB$_2$O$_4$ phase in the temperature range investigated.
APPENDIX D

VISCOSITY OF CERAMIC-Glass COMPOSITES

In the case of ceramic particle-filled LTCC systems such as DU and CT, the ceramic filler particles act as rigid inclusions that result in viscosities higher than those of unfilled glasses. The inclusions also provide mechanical strength and moderate the electrical and thermal properties of the LTCCs. The intrinsic viscosity of an LTCC is controlled by the base glass composition. The composite viscosity increases with increase in volume fraction of filler particles and, the increase is particularly significant above a critical volume fraction, called the percolation threshold \(^1\text{-}^4\). Above the percolation threshold, the filler particles form continuous networks resulting in a drastic increase in composite viscosity. The filler particles can either be inert inclusions or may react with the base glass components to form secondary phases, which may in turn result in an additional change in the viscosity.

In this work, we investigated the effect of filler content on the viscosity of glass. Alkaline silicate glass powders were used to study the effect of alumina content on the glass viscosity using constant loading dilatometry \(^6\). The glass system (composition is proprietary) obtained from Heraeus Inc. is representative of dielectric glasses used in LTCC materials. Cylindrical pellets of glass and glass + alumina composite powders with alumina volume fraction of 0.1, 0.2, 0.3, 0.4 and 0.5 and 2 wt % binder (PVA) were pressed using uniaxial pressing. The pellets were sintered to full density by firing between 700°C and 750°C with a dwell of 10 h. The choice of temperature and dwell
time is important, because of the viscous nature of the glass, and also depends on the amount of alumina present. There is significant deformation as the viscosity decreases with rise in temperature. For example, Fig. D-1 shows pellets of glass and glass + alumina after firing to a peak temperature of 870°C. The difference in shape of the glass and composite pellets is obvious. There is significant creep (viscous flow) of the glass compared to the composites and densification.

In order to prevent excessive deformation, the samples were allowed to densify at a temperature when the viscosity was not low enough to cause significant creep, and not too high to inhibit densification. The time-temperature profiles were selected by trial and error. The glass was presintered at 700°C with a dwell of 10 h, while the composite (with \( v = 0.3 \)) was presintered at 750°C with a dwell of 10 h. The fired bulk densities of the glass and composite specimens ranged from 2.6 to 2.9 g/cc. After pre-sintering to full density, the specimens were tested in a thermo-mechanical analyzer (TMA) using a constant load. The technique involves application of a constant uniaxial load for a given time, and the measurement of the deformation response of the specimen. All fully dense specimens, glass and composites were heated to 700°C at 5°C/min and held for 3 h. An initial load of 200 g was applied. The initial diameter of the specimens was \( \approx 5.50 \) mm.

The limitation of the TMA is that the radial strain cannot be measured, and thus accurate measurements of instantaneous stress, and thus viscosity are not possible. Also, as there is no change in density, it is impossible to calculate the anisotropy factor, which can be calculated for porous samples as previously demonstrated in this study (see Ch. 4).
But, we know that the viscosity is inversely proportional to the creep rate \(^5\). So, by measuring the relative change in the strain (or strain rate), the relative change in viscosity (\(\eta_{\text{composite}}/\eta_{\text{glass}}\)) can be calculated. The deformation of glass and composite specimens (with \(\nu = 0.1, 0.2, \text{ and } 0.3\)) is shown as a function of loading period in Fig. D-2. Composites with higher filler content (\(\nu = 0.4 \text{ and } 0.5\)) showed little deformation under load, and therefore are not shown. As expected, the amount of deformation is less for the composite specimens than the glass, and decreases more with increase in volume fraction of alumina. The relative change in strain is plotted as a function of volume fraction and the loading period in Fig. D-3. The behavior at longer loading time is a bit different from shorter periods, but follows the general pattern of increase with volume fraction. The difference is possibly due to the build-up of stress history effects such as changes in microstructure and shrinkage anisotropy with time.

The observed effect of filler content on glass viscosity was compared with available theoretical and experimental studies. Experimental studies dealing with the effect of rigid inclusions on the viscosity of a glass system are limited. Demana and Drummond \(^1\) measured the viscosity of a borosilicate glass containing up to 50 vol\% alumina using beam-bending viscometry. They found that the viscosity increased by over 8000 times at 50 vol\%. Similar observations were made by Tewari et al. \(^2\) and Banuprakash et al \(^3\) on borosilicate glass composites containing different metallic and non-metallic inclusions. Non-Newtonian flow behavior was observed at high volume fraction and aspect ratio of inclusion particles. Dutton and Rahaman \(^4\) investigated creep behavior of soda-lime silica glass with Ni spherical inclusions as a function of inclusion content and size. A loading dilatometer was used to measure the creep rates and, thus, the
creep viscosity. It was found that above ~ 10-15 vol % inclusions, the viscosity increased significantly in case of smaller inclusion size and the increase was attributed to formation of a percolating network. In addition to the above studies on the viscosity of glass composites, numerous modeling and theoretical studies have been devoted to understanding the effect of inclusions on the densification and microstructure of composites.

The observed relative viscosity ($\eta_{\text{composite}}/\eta_{\text{glass}}$) is plotted along with the data of Demana and Drummond, and some theoretical expressions, as a function of volume fraction filler content in Fig. D-4. The theoretical expressions $^8,^9$ are those used to describe the viscosity of liquid suspensions. Boccaccini’s model $^9$ was derived to describe the viscosity of glass composites, is based on the analogy between field properties of two-phase materials and the viscous flow of suspensions. According to this model, the viscosity of a composite is given by,

$$
\eta = \eta_0 (1 - f)^m \\
m = (3F-2)/3F(1-2F)
$$

where, F is a shape factor, which depends on the axial ratio of the inclusions. For example, for spherical particles, F is 0.333, while for fibers, it is 0.5. A value of F = 0.483 is shown to result in a good fit for the data of Demana and Drummond and a value of F = 0.333 fits the data of Dutton and Rahaman below the percolation threshold. A reasonable match is also found between the data obtained in the current work, and that of Demana and Drummond. The materials used in these studies are similar, although the testing methodology is different. Other expressions used to describe rheology of
suspending are summarized in table D-1 and these underestimate the viscosity of glass composites.
<table>
<thead>
<tr>
<th>Author</th>
<th>Expression for Relative viscosity ($\eta_{composite}/\eta_{glass}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Einstein</td>
<td>$1 + 2.5 \nu$</td>
</tr>
<tr>
<td>Mooney</td>
<td>$\exp (2.5 \nu/1 - k \nu)$, $k$ is the crowding factor</td>
</tr>
<tr>
<td>Krieger-Dougherty</td>
<td>$(1 - \nu/\nu_{max})^{2.5 \nu_{max}}$, where $\nu_{max}$ is maximum packing fraction, usually between $0.6 - 0.7$</td>
</tr>
<tr>
<td>Thomas (empirical)</td>
<td>$1 + 2.5 \nu + 10.05 \nu^2 + 0.0027 \exp (16.6 \nu)$</td>
</tr>
</tbody>
</table>

Table D-1: Theoretical expressions for viscosity of suspensions
Fig. D-1 Creep deformation in glass and composites (from left to right: \( \nu = 0.2, 0.3, 0.4 \) and 0.5) after firing to 870°C at 5°C/min.

Fig. D-2 Axial shrinkage versus hold time for glass and composites (\( \nu = 0.1, 0.2 \) and 0.3)
Fig. D-3 Relative viscosity versus volume fraction fillers at loading periods of 1, 2 and 3 h.

Fig. D-4 Comparison of measured viscosities and theoretical predictions
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Aravind Mohanram was born June 22, 1979 in Chennai, India. He obtained his B. Engg. with Honors Distinction in Ceramic Engineering at Regional Engineering College, Rourkela, India in 2000. After graduation, he joined the graduate program in Materials Science and Engineering at the Pennsylvania State University in August 2000. He has since been working towards his Ph.D under the guidance of Prof. Gary L. Messing and Prof. David J. Green. At Penn State, he worked on the problem of co-sintering low temperature co-fired ceramics funded by the Center for Dielectric Studies at the Materials Research Institute. His research has been presented in numerous conferences including the Annual Meetings of the American Ceramic Society, the Materials Research Society, the International Microelectronics and Packaging Society, the Gordon Research Conferences, Sintering Conference, and the meetings of the Center for Dielectric Studies. He is a member of the American Ceramic Society and the Materials Research Society. He will be employed as a senior research engineer at Saint-Gobain corporation in their High Performance Materials center at Northboro, MA.