ABSTRACT

High-performance powder materials frequently use liquid phase sintering to reach the full, or near-full density required to obtain the superior material and mechanical properties desired. As the high performance materials are often expensive, it is advantageous to have computer models that can be used to design and develop materials, processes and parts without wasting time and energy on trial-and-error evaluation. Models focused on predicting the densification and distortion experienced during liquid phase sintering are presented here, along with the experimental procedures needed to characterize these models accurately. The sinter models are based on the creep flow law constitutive equations developed for continuum modeling of sintering. Methods used for obtaining critical insight into microstructural evolution and influence of parameters such as liquid capillary force, pore collapse, solid-liquid morphology, solid phase connectivity, grain growth, and system rheology are described. These parameters are used to characterize the models for these semisolid powder-liquid mixtures.

INTRODUCTION

Liquid phase sintering (LPS) is used to sinter near full or full density materials from porous bodies that become high-performance materials once densified [1]. The liquid phase provides a high diffusivity pathway, resulting in densification is that enhanced beyond simple solid state sintering. However, due to the semisolid nature of the body during sintering, the influence of external factors, such as gravity and substrate friction, can significantly affect the distortion of the body during sintering, even after full density has been reached. Sinter models for the densification during solid-state sintering are based on diffusional sintering theory and take the form of creep flow laws [2,3]. These models must be further developed for LPS by linking the models to the evolution of influential microstructural parameters such as the capillary stresses in the liquid filled pores, solid-liquid morphology, the solid skeleton and grain growth. For example, in the first few minutes of liquid phase sintering most of the pores are annihilated, some solid dissolves in the liquid so the solid-liquid ratio is not constant, also the newly formed liquid significantly weakens the microstructure, meanwhile the grain size enlarges and the number of solid grains decreases, and eventually solid-solid bonds form to create a rigid structure. To create
a link that incorporates the delicate interaction of all these concomitant events, tools for determining the influence of such factors are used.

Green body characterization has been used to develop models that predict the green body shape and density, including green density gradients. Sintering monitors such as shrinkage, density, and grain size are used to characterize and train the models. Dilatometers measure sintering shrinkage that can be used to determine the apparent viscosity of the porous body during sintering. The results from the dilatometer runs can also be used to verify the density and shrinkage predicted by the sinter models continuously over the time-temperature profile. Quenching experiments are used to determine final density, but more importantly to capture the microstructure at specific points in the sinter cycle. Quantitative microscopy of these quenched microstructures allows for the influences of grain and pore size, distribution and growth to be determined, as well as the influence of evolving phases during sintering. In situ videoimaging captures the distortion of the porous body under the influence of all external forces, gravity and substrate friction included, and can be used to verify three-dimensional simulations of shape change during sintering. Thermal analysis of the materials identifies important phase changes, interactions and reactions that take place during sintering of specific materials. The evaluation of in situ strength is important in determining the rheological response of the porous body during sintering, especially the resistance the body has to material flow that results in densification and in particular the Bingham threshold stress [2].

In this paper, the models used to simulate sintering are presented, along with the experimental methods used to characterize them and evaluate their performance. It is shown that using the widely accepted continuum model of sintering and the associated constitutive equations, and coupling the most significant microstructural influences to these equations allows accurate simulation of densification and distortion during liquid phase sintering to full density.

**MODEL**

**Governing Equations**

Sintering occurs due to diffusional mass transport, and is described by the constitutive equation for sintering that assumes the form of a creep flow law [3]. The porous body is considered to be a homogeneous, porous continuum with the constitutive equation for sintering relating the 3D stress state, \( \sigma_{ij} \), to the 3D strain rate within the continuum, \( \varepsilon_{ij} \) as follows:

\[
\dot{\varepsilon}_{ij} = \frac{1}{2\mu} \sigma'_{ij} + \frac{1}{3K} (\sigma_m - \sigma_s) \delta_{ij}
\]  

(1)

In Equation (1), the infinitesimal strain rate is defined as \( \dot{\varepsilon}_{ij} = (\dot{u}_{i,j} + \dot{u}_{j,i})/2 \) where \( u_i \) is the displacement component. The first term describes the distortional behavior of the continuum by relating the deviatoric stress \( \sigma'_{ij} \) to the deviatoric strain rate \( \dot{\varepsilon}'_{ij} \) through the apparent shear viscosity \( \mu \). The second term describes the shrinkage behavior of the continuum by relating the hydrostatic stress \( \sigma_m \), and the sintering potential \( \sigma_s \), to the volumetric strain rate \( \dot{\varepsilon}_{kk} \) through the apparent bulk viscosity \( K \). In this equation \( \delta_{ij} \) is the Kronecker delta, and \( i \) and \( j \) are dummy indices indicating coordinate system.

The shear and bulk viscosity describe the rheological response of the sintering body and its resistance against deformation. These temperature dependent parameters are influenced by the evolving density and grain size during solid state sintering, and additionally by the liquid content, wetting, and contiguity during liquid phase sintering. In situ videoimaging of bending beam experiments [4], dilatometry [5], and quantitative microscopy of quenched microstructures provide the means to characterize the viscosities during sintering.

The sintering potential can be described in mechanical terms as a surface tension induced stress [1]. It depends on the grain size, liquid wetting conditions, and pore saturation with liquid. These details are captured by quenching experiments. The capillary stress causes densification.
The link between the volumetric strain rate \( \dot{e}_{kk} \) and the densification rate \( \dot{\rho} \) is provided by the conservation of mass:

\[
\dot{\rho}/\rho = -\dot{e}_{kk} \tag{2}
\]

While the influence of gravity is included through the conservation of momentum:

\[
\sigma_{g,j} - \rho g d \dot{g}_j = 0 \tag{3}
\]

The stress due to the weight (\( \rho d g \) per unit area) of each element increases as the porous continuum densifies and shrinks. The relative density \( \rho \) is the ratio of the instantaneous density to the theoretical density of the material \( d \).

These equations provide a mathematical description of the sintering behavior and are used to implement the model in finite element analysis. There are key parameters in the constitutive equations that characterize the sintering response for specific materials. These parameters of sintering potential, shear and bulk viscosity are given in two different models in the appendix. The 2-parameter model is based on the suggestion by Olevsky [2], while the 5-parameter model was developed by Kwon [6,7]. Microstructure parameters are embedded throughout the model in terms of evolving relative density and grain size \( G \). Additional influences based on the diffusional properties of the material are activation energy for densification flow \( Q^F \), grain boundary diffusion \( Q^b \) and grain growth \( Q_G \). These parameters are usually determined via quantitative microscopy and related test techniques.

**Implementation of model**

The constitutive and governing equations given above are programmed for finite element analysis, using a software package specifically developed for sintering, PIMSolver. Finite element software packages like ABAQUS can also be used for simulations through programming their creep subroutines. Three dimensional finite element analysis is more computationally intensive than two dimensional axisymmetric simulations. Therefore choosing a cylindrical, or axisymmetric geometry for developing a sinter model is helpful [8].

**EXPERIMENTAL TECHNIQUES**

A number of experimental techniques that are used to gather the data necessary for characterization of the constitutive equation of sintering have been mentioned. A brief description of how these techniques are used follows.

**Dilatometry**

Dilatometry provides a means of tracking the dimensional change of a porous body continuously during sintering by using a probe or pushrod to measure the shrinkage or expansion of the sample in situ. Through this experimental technique, the sintering response of a particular material can be determined [5]. Changes in the rate of shrinkage are linked to microstructural evolution and thermophysical events or chemical reactions. Additionally, the shrinkage output from the dilatometer can be used to evaluate the accuracy of sinter models.

**In situ videoimaging**

While dilatometry gives a precise measurement of the linear shrinkage, distortion in three dimensions is evaluated through in situ videoimaging. A video camera is set up to record the image of the sample during sintering. The camera receives the image through a quartz window into the furnace, focused through a Frensel lens and reflected off a mirror. A strobe light is used to illuminate the sample. This experimental technique can be used to track the distortion of a sample, as well as to measure the midpoint deflection of a simply supported beam during sintering. The midpoint deflection measurement can be used to
characterize the apparent viscosity of the porous body [4]. The recorded image is evaluated using image analysis software.

**Quenching experiments**  
The microstructure of the porous body can be captured as it evolves during sintering through quenching experiments [9]. At key points during the sintering cycle, a trapdoor in the furnace is opened and the hot sample is dropped into an oil or water bath for quenching. In this way, the effects of slow cooling that can influence the phases in the material or allow for further densification are removed. This method can also be used to evaluate the density of the sample at specific points in the sintering cycle. Samples from quenching experiments are frequently mounted and polished for further analysis using quantitative microscopy.

**Quantitative microscopy**  
The micrographs or SEM images of polished samples, collected from quenched or sintered samples, can be analyzed through quantitative microscopy. A variety of microstructural parameters, such as grain size, shape and distribution, contiguity, connectivity, relative amounts of phases including porosity and liquid-solid ratios, and neck size between grains can be determined this way. Image analysis software is often used to automate the measurements, allowing microstructural evaluation to be more accurate and efficient. The interplay between grain size, viscosity, density, and strength requires quantification of the microstructure and is important in developing accurate models for sintering.

**Thermal analysis**  
Thermophysical events such as phase changes, reduction of oxides, and melting can be characterized through thermal analysis, using tests like thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Thermal conductivity can be evaluated using laser flash measurement. This thermal information can help in identifying influences on sintering so that they can be incorporated into the sinter models.

**Strength testing**  
The strength of a porous body during sintering influences the sintering response of the compact [9]. *In situ* three point bending tests can be used to evaluate the strength during sintering and then link this information back to the sinter model. From strength testing during sintering, Bingham response instead of Newtonian response creep flow laws have been developed that more accurately describe the rheological response of a porous body during sintering [10].

**SIMULATION RESULTS**

Two sample structures are simulated in this study: a right cylinder of about 12.5cm or ½” diameter, and a T-shaped EPMA test geometry compact. The material system chosen is a tungsten heavy alloy with 80wt.% tungsten. This material shows extensive distortion during sintering and was chosen so as to evaluate the predictive capabilities of the sinter models.

For initial characterization of the sinter model, analytical models that link sintering parameters like time, temperature and ramp rate to the grain growth and densification are needed. Figure 1 shows the results of sinter models that have been characterized for tungsten heavy alloys through quenching experiments and quantitative microscopy.
Figure 1. Analytical models of grain growth and densification characterized for use in finite element analysis.

Figure 2 shows the *in situ* videoimages of the right cylinder during sintering and how it distorts as the liquid forms, dissolves solid-solid bonds and causes the rigidity of the cylinder to collapse. By adding the influences into the sinter model, step-by-step the final distortion can be simulated. This is shown in Figure 3 where the influences of surface tension, friction and gravity are shown. Surface tension and friction are added as boundary conditions. Once the sinter model has been trained to accurately simulate the final distortion, the model can be used to evaluate the distortion with time, as shown in Figure 4.
When describing the distortion, dimensionless parameters are used to describe the height and radius of the cylinder: H/L is the dimensionless height and R/L is the dimensionless radius, both reported relative to some arbitrary length L. Figure 5 shows the three dimensional rendering of the simulated shape.

Using the characterized model, the three dimensional simulation of the EPMA T-shape is calculated. As shown in Figure 6, the predicted distorted shape is similar to the actual sample.
Figure 3. Sinter model simulation of LPS cylinder, showing influences of gravity, surface tension and friction.

Figure 4. Axisymmetric simulation of LPS cylinder, showing the distortion profile with time.
CONCLUSIONS

This study gives an overview of the varying capabilities of finite element computer simulations of sintering, based on the constitutive equations of sintering, as related to the microstructure of the solid-liquid-pore structure. Factors such as distortion due to gravity, prediction of final sintered size, substrate friction, and the influence of surface tension during liquid phase sintering can be addressed through these models. Guidelines for setting up such simulations are given, as well as two examples of models for the constitutive equations for sintering.

The ability to predict such size and shape changes during sintering provides a useful tool for the powder metal industry for tool and sinter cycle design.

REFERENCES


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