Multiscale Modeling of Microstructure and Macrostructure Evolution during Sintering

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Summary

We have developed a model with the unique capability to bridge the gap between the microstructural models and the continuum models to give an integrated approach to understanding sintering on multiple scales. The kinetic, Monte Carlo model for simulation sintering is a rigorous, science-based model with all the necessary materials physics to predict sintering behavior of a porous body. These mesoscale simulations of sintering provide two important results, (1) constitutive equations used in continuum models to predict shrinkage and shape change of a sintering powder compact and (2) microstructures of sintered compacts for engineering properties evaluation. We have also developed finite element capability to incorporate the constitutive equations generated by the mesoscale model. The integrated capability enables us to predict the shrinkage and shape distortions in a sintering component. In this paper, we demonstrate the utility of the model by applying it to study the dimensional changes in a bilayered disk.

Introductions

Sintering is the process by which a compact of individual powder particles weakly held together by inter-atomic forces is fused to form a strong monolithic piece. A powder compact, which typically has 30% to 40% porosity by volume, is sintered by heating it to high temperatures where mass transport between the particles occurs to form a single piece with structural integrity and with other desirable engineering properties. During sintering the porous powder compact will shrink to < 5% porosity and have grains that can be as much as 1 or 2 orders of magnitude larger than the starting particle size. The shrinkage and microstructural changes can lead to significant deformation in the powder compact, often with catastrophic changes that make the component unusable. Thus, it is critical to be able to control and predict the dimensional changes during sintering, particularly for emerging micro- and nano-technologies that require extremely tight dimensional tolerances.

The past and current work in sintering can be divided into two large categories. One set of work treats the microstructural evolution of two or three particles during sintering in great detail[1-6]. This body of work considers driving forces, transport mechanisms, kinetic factors and geometry to give detailed information about the shapes of the particles and sintering rates during various stages of sintering, however it fails to treat a

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macroscopic sintering piece or to answer question such as what is the shape change, density distribution, and stress state in a large body during sintering?

The second set of work treats the evolution of a macroscopic sintering body[7,8]. That work considers the sintering part to be a continuum body and applies continuum deformation mechanics to the sintering body to predict shrinkage and shape change. However, the constitutive laws describing sintering of real crystalline materials systems are unknown. Therefore, application of continuum mechanics to sintering real materials systems has been largely unsuccessful, despite tremendous improvements in continuum simulation numerical capabilities in recent years.

We present a model capable of simulating microstructural evolution during sintering of a geometrically complex powder compact comprising hundreds of arbitrary-shaped particles. The microstructural evolution is simulated at the mesoscale on a sufficiently large scale so that continuum properties can be extracted. These properties are in turn used in a continuum, component scale simulation to describe the overall shrinkage and shape change.

Model

Microstructural Evolution Model The model used to simulate microstructural evolution is a kinetic, Monte Carlo method, which uses a digitized image of the microstructure. The digitization process resolves in a two-phase system of grains and pores with grain boundaries, grain-pore interfaces. The energies of the system are chosen so that grain boundaries and grain-pore interfaces have isotropic interfacial energies. The model simulates the following processes simultaneously

1. Grain growth by short range diffusion of atoms from one side of the grain boundary to the other;
2. Long range diffusion of pores by surface diffusion and of vacancies/material by grain boundary diffusion;
3. Vacancy annihilation at grain boundaries[2].

The complete microstructural evolution during simple, solid-state sintering can be simulated using this model. For a detailed description of this model, please see[9].

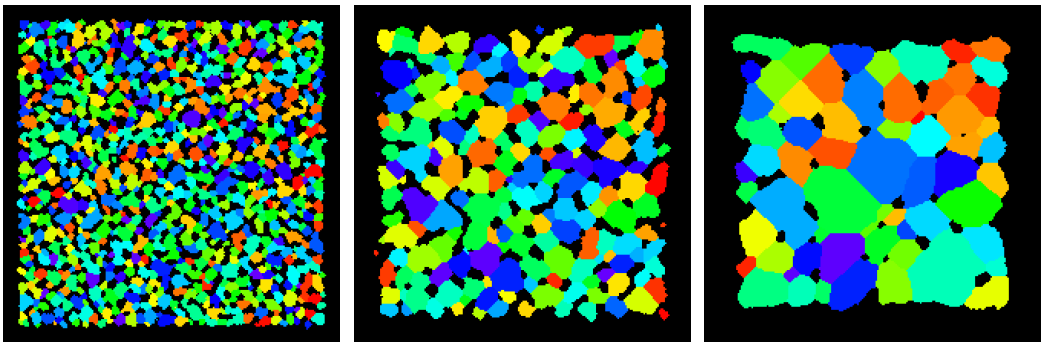
Macro-dimensional Continuum Model The a continuum mechanics model was used to macroscopically simulate the sintering process. It is based on the theories of plastic and nonlinear-viscous deformation of porous bodies. The mathematical constitutive description was developed by V. V. Skorohod[7] and adapted for numerical simulations by E. A. Olevsky[8]. The result is a phenomenological constitutive model whereby a

[2] In this approximation we refer to a single pore site as a vacancy, while denoting more than one contiguous pore sites as a pore

porous medium is considered as a two-phase material that includes a porous body skeleton phase and a void phase. The skeleton is assumed to be made-up of individual particles having a general nonlinear-viscous incompressible isotropic behavior, and the voids are homogeneously distributed. As a consequence, the overall response is isotropic. A linear viscous description of the material deformation was used. For a detailed description of this method, please see[10].

Results

Microstructural Evolution Model The microstructural evolution during sintering of a powder compact is shown in figure 1. The colored features are grains and the black areas are pores. The advantage of this simulation is that images of microstructure are generated as a function of time during sintering. The microstructures show that initially grains are very fine and pores are interconnected, spanning several grains. As the simulation continues, grains grow, the number of pores decreases and they become less tortuous, pores become increasingly isolated and densification occurs as pores shrink and disappear. The final microstructure shows an almost fully dense microstructure with grains that are 2 orders of magnitude larger in area than the starting microstructure. These types of microstructural characteristics as a function of time can be mined from images such as the ones shown in figure 1. We can obtain the shrinkage, density, grain size, the number of neighboring grains that each grain has, the surface area of the pores, the connectivity of the pores, etc from simulations such as the ones shown here. Rapid densification occurs early in the simulation when both grains and pores are small and have highly curved surfaces. Rapid densification at early times is observed in the overwhelming majority of materials. Grains grew during the entire simulation. This was anticipated and is observed in most experimental systems. Pore size remained almost constant as densification progressed suggesting that pore grew by coalescence as overall porosity decreased by annihilation.

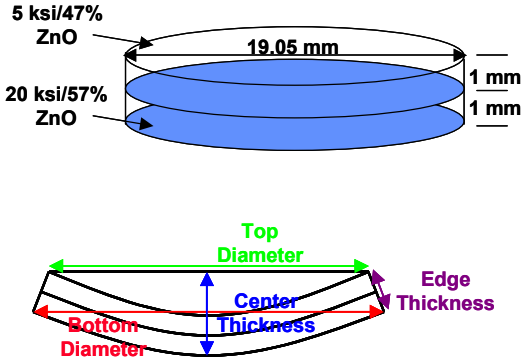


time = 0 MCS **time = 2,000 MCS** **time = 50,000 MCS**

Figure 1. Microstructural evolution during sintering in a powder compact.

As a series of microstructures are generated as a function of time, the interfacial free energy as a function of any time dependent variable can also be determine. This information can be used to calculate the sintering pressure and bulk and shear module for continuum scale sintering models. The sintering stress was calculated as the change in grain-pore interfacial energy as a function of the sintering powder compact volume, a readily calculable quantity. Next the bulk and shear viscous moduli were calculated by dividing the sintering stress by the sintering strain rate (shrinkage rate). Using this information the macroscopic sintering behavior was simulated.

Macro-dimensional Continuum Model The constitutive models generated by the microstructural evolution simulations were incorporated into a continuum model and applied to a case of a bilayered disk of the same material with the same sintering characteristics, but two different initial densities. The initial density of the top layer was 47% and the bottom layer was 57%. As the bilayered disk sintered the top layer shrunk more than the bottom layer as it continued to shrink after the bottom layer had stopped densifying. As a result, the entire disk curled up with the interface between the layers remaining bonded as shown in figure 2. A parallel experiment with ZnO powder formed into bilayer with the same characteristics as the simulation was conducted to validate our model. The results (which are the dimensional changes in the bilayer) of the continuum simulations and the experiments are compared in figure 2. As one can see the two are in very good agreed. The worst agreement is in the center thickness measured from experiment and that obtained from simulations. This is largely due to the difficulty of measuring the center thickness accurately in the ZnO bilayer.



Sintering of ZnO (0.2μm) Bilayer Disk
Garino's Experiment vs. Simulation
(ρ_{0u} = 0.47 & ρ_{0l} = 0.57)

At 925 °C	Experiment	Simulation	Difference
D_T (19.05 mm)	15.24	15.04	1.3%
D_B (19.05 mm)	15.66	15.98	2.0%
T_E (2.00 mm)	1.63	1.61	1.1%
T_C (2.00 mm)	2.72	2.35	13.7%

Figure 2. Comparison of the dimensional changes predicted by continuum simulation of sintering to that observed experimentally in ZnO.

We have presented an example of using two models at different length scales to simulate the microstructural and macro-dimensional evolution in a sintering powder compact. This is a unique and powerful tool for studying sintering behavior as well as for predicting the engineering characteristics of sintering bodies. Other works that

predict macro-dimensional changes, use either analytic constitutive models or have to measure them experimentally for each material that is simulated. This, however, is a tedious process as every small change in the powder characteristic or process results in different constitutive models for sintering.

We have applied the methodology to study other sintering problems. We have considered mechanically constrained systems. The mechanical constraint is introduced by differential shrinkage in the different regions of the system. We observed very unique behavior of higher shrinkage rates due to Gibb-Thomson effect originating from pore size and we found that sintering stress and applied stress are not additive as is assumed in all current continuum models of sintering. We studied systems that shrinkage preferentially in one direction due to alignment of elongated grains. The interesting result of this work was that the higher shrinkage occurred both in the direction parallel and perpendicular to the direction of elongation depending on the details of powder packing. We have also used this model to study sintering of silver nano-particles. These nano-particles were found to experience "de-sintering" for a short duration in their sintering cycle. Using this model we were able to show that the de-sintering phenomena could have been a result of changes in the relative interfacial energies, which made these densification energetically unfavorable.

This model is currently limited by its inability to yield sintering stress and viscous moduli as tensor quantities. Traditionally, these quantities have been treated as isotropic, only because measuring the complete tensor quantity has eluded researchers. We are now in the process of trying to devise techniques that will allow us to obtain these quantities.

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