A Combined Statistical-Microstructural Model for Simulation of Sintering

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Abstract

Sintering theory has been developed either as the application of complex diffusion mechanisms to a simple geometry or as the deformation and shrinkage of a continuum body. We present a model that can treat in detail both the evolution of microstructure and the sintering mechanisms, on the mesoscale, so that constitutive equations with detail microstructural information can be generated. The model is capable of simulating vacancy diffusion by grain boundary diffusion, annihilation of vacancies at grain boundaries resulting in densification, and coarsening of the microstructural features. In this paper, we review the stereological theory of sintering and its application to microstructural evolution and the diffusion mechanism, which lead to sintering. We then demonstrate how these stereological concepts and diffusion mechanisms were incorporated into a kinetic Monte Carlo model to simulate sintering. Finally, we discuss the limitations of this model.

Introduction

The theory of sintering has been developed primarily by considering sintering of simple geometry with varied and complex transport mechanisms. Most of the work treats the microstructural evolution of two or three particles during sintering in great detail. Some of the earliest and most rigorous analytical models of sintering were proposed in the 1950's of two particles with different diffusion mechanisms[1]. 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. Almost 50 years later, current microstructural models of sintering[2] still consider a limited number of particles. While today's models give more accurate results, they fail, like their predecessors, to treat a macroscopic sintering piece – what is the shape change of, density distribution in, and stress state in a large body?

We propose a model that can simulate the microstructural evolution during sintering of a powder compact comprised of hundreds of particles. Such a model can be used to bridge the gap between mesoscale and continuum models by generating constitutive equations describing the deformation and shrinkage of a sintering compact as a function of its microstructure, i.e. grain size distribution, pore size distribution, etc.

DISCLAIMER

We have incorporated the concepts from the stereological model of sintering[3] into the kinetic, Monte Carlo model to simulate microstructural evolution on sintering. The kinetic Monte Carlo model has been demonstrated to simulate a variety of microstructure evolution phenomena. The stereological model of sintering treats the evolution of a sintering compact of large number of particles as the evolution of stereological constructs (such as grains, pores, grain boundaries, pore-grain surface, etc) during sintering. This model relies on the mechanism of vacancy migration from the pores to grain boundaries and once a layer of vacancies is 'painted' on a grain boundary, the entire layer is annihilated yielding densification with the center of mass of the adjacent grain moving towards the grain boundary. Analytic modeling of this process requires several simplifications that severely limited its application to realistic powder compacts. By incorporating these concepts into the kinetic Monte Carlo model, we are able to extend its application to complex and realistic power compact geometries.

Model

A kinetic Monte Carlo model[4] was used to simulate microstructural evolution during sintering. The model presented here is limited to the considering the following processes: (1) grain growth by short range diffusion of atoms from one side of the grain boundary to the other, (2) long range diffusion of material to pores by grain boundary diffusion and surface diffusion, (3) vacancy annihilation at grain boundaries. In the model, an ensemble of grain sites and pore sites is allowed to populate a square lattice. The grain sites can assume one of Q distinct, degenerate states, where the individual state is designated by the symbol q and the total number of states in the system is Q, $q_{grain} = [1, 2, \ldots Q]$. The pore sites can assume only one state, $q_{pore} = -1$. Contiguous grain sites of the same state q form a grain and contiguous pore sites form a pore. Grain boundaries exist between neighboring grain sites of different states, q, and pore-grain interfaces exist between neighboring pore and grain sites. The equation of state for these simulations is the sum of all the neighbor interaction energies in the system given by

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{8}\left(1-\delta\left(q_i, q_j\right)\right) \qquad \text{eq. 1}$$

where N is the total number of sites, δ is the Kronecker delta with $\delta(qi = qj) = 1$ and $\delta(qi \neq qj) = 0$, q_i is the state of the grain or pore at site i and q_j is the state of the nearest neighbor at site j. Thus, the only energy considered in the simulation is the interfacial energy and all unlike neighbors contribute one arbitrary unit of energy to the system. As pore sites can assume only one state, $q_{pore} = -1$, there are no pore boundaries and all pores sites coalesce. In contrast, grain sites can assume many different states making grain boundaries possible. This yields a two-component, two-phase system with uniform, isotropic interfacial energies between grains and between grains and pores.

Grain growth is simulated using the method developed in previous works[5]. First a grain site is chosen at random from the simulation space. Then a new state q is chosen at random from the Q possible states in the system. The grain site is temporarily assigned the new state and the change in energy is evaluated using eq. 1. Next the standard Metropolis algorithm is used to perform the grain growth step based on Boltzmann statistics. A random number, R, between 0 and 1 is generated. The transition probability, P, is calculated using

$$P = \begin{cases} \exp\left(\dfrac{-\Delta E}{k_B T}\right) & for \quad \Delta E > 0 \\ 1 & for \quad \Delta E \leq 0 \end{cases} \qquad \text{eq. 2}$$

where k_B is the Boltzmann constant and T is temperature. If the $R \leq P$, then the grain growth step is accepted, if not, the original state is restored. The simulation temperature used for grain growth was $k_B T = 0$, which has been shown to simulate grain growth well[5].

Pore migration is simulated using conserved dynamics[6], so that the total number of pore sites and grain sites remains constant throughout the simulation. A pore site is chosen and next a neighboring grain site is chosen. The two sites are temporarily exchanged with the grain site assuming a new state q where q results in the minimum energy. This minimum-energy, pore-grain exchange simulates pore migration by surface diffusion[7]. The change in energy for this exchange is calculated using eq. 1 and again the standard Metropolis algorithm is used to perform the pore migration step using eq. 2 to determine the transition probability. The simulation temperature used for the pore migration step was $k_B T = 0.7$. This higher temperature was necessary to simulate pore migration and is discussed in another work[8]. Time in the Potts model is measured in units of Monte Carlo step; 1MCS corresponds to N attempted changes where N is the total number of sites in the system.

The stereological concept of densification[3], which is vacancy annihilation at the grain boundaries with the center of mass of the adjacent grain moves toward the annihilation site, is simulated by pore annihilation in our mesoscopic model. In this algorithm a pore site is chosen and, if it happens to be an isolated pore site in contact with a grain boundary, it is annihilated. Annihilation is simulated by first, drawing a line from the isolated pore site through the center of mass of the adjacent grain to the outside boundary of the sintering compact; and second exchanging the isolated pore site and the outside grain site with the grain site assuming the q state of the adjacent grain. This algorithm conserves mass globally, moves the center of mass of the adjacent grain towards the annihilation site and annihilates a vacancy.

Results and Discussion

Microstructures at different stages during simulation of a sintering compact are shown in figure 1. Simulations were performed starting with a random distribution of grain and pore sites with 30% porosity. The ratio of grain growth to pore migration to pore annihilation attempts is 10:10:1. Thus, curvature driven grain growth, mass transport by grain boundary diffusion, and pore annihilation at the grain boundaries is simulated simultaneously. The simulation is performed with periodic boundary conditions, but layers of pore sites placed along the unit cell boundaries effectively block interaction between adjacent unit cells. This is essential in the proposed algorithm to define the area where annihilated pore sites can be moved.

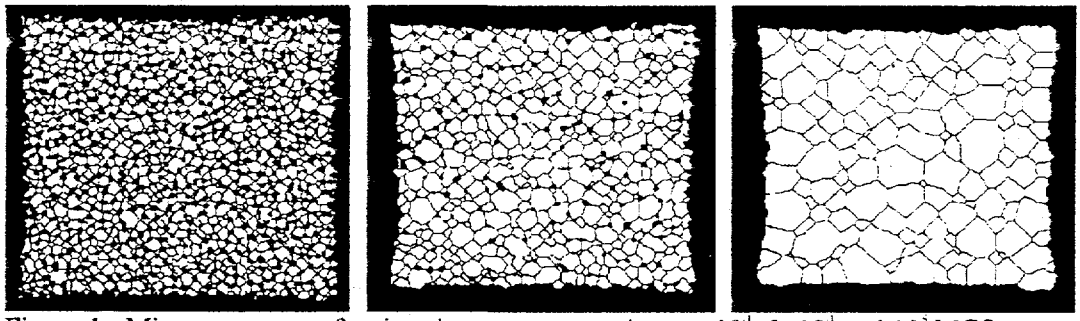

Figure 1. Microstructures of a sintering compact at times = 10^4, $3x10^4$ and 10^5 MCS. Grains are the white features separated by black grain boundaries. Pores are drawn in black.

The densification curve, figure 2, shows that densification occurred rapidly at the early stages of sintering where grains are smaller and pores have high curvatures. The corresponding grain and pore growth curves are shown in figure 3.

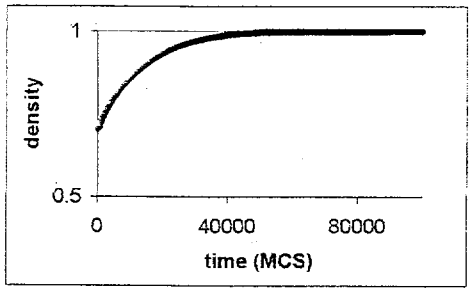

Figure 2. Densification curve

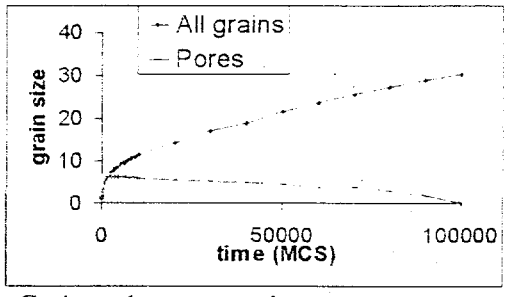

Figure 3. Grain and pore growth curves

Although the pore size decreases slightly from the start to the time = 2,000 MCS where the most rapid densification occurs, the curvature of the pore actually decreases as pore snake around small grains at early times.

Examination of the microstructures has shown that the algorithm used in this study simulates grain boundary diffusion of pore sites. Previous work[3] has shown that the number of isolated pore sites (analogous to vacancy formation) generated by a pore is given by the Gibbs-Thomson effect, thus, number of isolated pore sites (analogous to vacancy concentration) is inversely proportional to the pore size. Furthermore, isolated pore sites occur with higher probability at grain boundaries of higher curvature simulating vacancy concentration at grain boundaries that is inversely proportional to the grain boundary curvature.

The advantage of such a simulation that generates a picture of microstructure as a function of time during sintering is that the simulated microstructures can be used to calculate the driving force for sintering as a function of the compact density. This information can be used to calculate the constitutive deformation and shrinkage laws used by continuum models for predicting macroscopic shrinkage and shape change of a sintering component. This is a unique ability of this model and has not been done before.

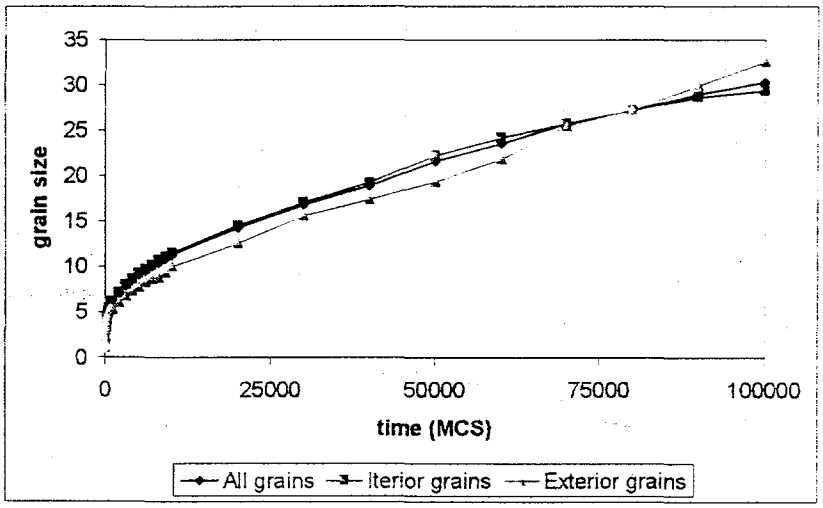

Figure 4. Grain growth curves for interior and exterior grains.

The major artifact of this model is that simulation of the annihilation mechanism removes mass from an exterior grain and deposits it in an interior grain. A plot of the grain growth curves of exterior grains and of interior grains, figure 4, shows that exterior grains are slightly smaller than the interior grains until time t = 70,000 MCS. Figure 2 reveals

that at t = 70,000 densification is almost complete, thus, exterior grains are no longer being depleted of mass.

Another problem is the overall shape of the sintering compact changes during sintering, with the boundary becoming artificially curved as seen in figure 1. This is due to the fact that the middle points of the simulation boundary are more likely to be depleted of grain sites in the proposed algorithm than the points closer to the corners.

Conclusion

We have demonstrated a model that is capable of simulating microstructural evolution during sintering in a powder compact on the mesoscale. The algorithm shown here simulates curvature driven grain growth in the presence of pores, mass diffusion along grain boundaries and by pore-grain surface diffusion and vacancy annihilation. The algorithm used to simulate annihilation of vacancies does introduce some artifacts. New algorithm will be developed and tested in future work to remove these artifacts.

Acknowledgement

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