A kinetic, Monte Carlo model, capable of simulating microstructural evolution sintering in a two-dimensional system of three structural particles, has been presented. The model can simulate several mechanisms simultaneously. It can simulate curvature-driven grain growth, pore migration and coarsening by surface diffusion, and densification by diffusion of vacancies to grain boundaries and annihilation of these vacancies. Morphologic changes and densification kinetics are used to verify the model.

I. Introduction

Prediction of microstructural evolution during solid-state sintering of crystalline materials is difficult. In the simplest case of isotropic energies, single-component, single-phase systems it is still very complex because the details of local geometry are critical in the way that they influence thermodynamics and kinetics. Many predictions of microstructural evolution were first attempted starting in the 1940s. Frenkel treated sintering as a viscous flow phenomenon. Kuczynski treated it as a diffusive process. This diffusive approach was adopted by many to refine solid-state sintering theories. In general, these theories assumed highly idealized geometries of two or three spherical particles or spherical particles on a plate with a number of diffusion paths to analytically predict shrinkage rates. A couple of other simple geometries were also treated. While microstructural evolution and shrinkage rates were predicted by these models, the biggest accomplishment of these models is that they provided insight into the thermodynamics that drive sintering and the influence of the transport mechanism that control sintering kinetics. The other big accomplishment of these investigators was the understanding of the role of grain boundaries as the sink for vacancies by annihilation due to stresses on grain boundaries exerted by the pores at the grain junctions.

The prediction of microstructural evolution during sintering continues to be of great interest. Many numerical simulation techniques have been developed in recent years to study sintering. These include finite element methods, a micromechanical approach, molecular dynamics simulations, continuum thermodynamics solutions, and unit cell solutions. These models continue to provide insights and more accurate solutions to this problem. However, they are still simulations of small, highly simplified systems with a limited number of particles. Furthermore, they are not readily extendable to larger, more complex systems consisting of hundreds of particles, and therefore they are limited in their applicability for the study of real systems.

In this paper, we present a kinetic, Monte Carlo model that can simulate sintering in a three-particle system. We make no a priori assumptions about the geometry of the system such as the curvature of the neck or the curvature of the particles; rather the three-particle system is allowed to evolve under conditions similar to that during sintering. The model is very similar to ones used in the past to simulate many microstructural evolution processes including normal grain growth in single-phase materials, abnormal grain growth, recrystallization, phase separation, Ostwald ripening, pore migration, and final-stage sintering. It has been adapted here to simulate all stages of sintering by adding an algorithm that simulates the formation, diffusion, and annihilation of vacancies, which distinguishes it from the previous work of Hassold et al. They modeled final-stage sintering by determining the mean distance between pores and eliminating pore sites with a frequency that was in proportion to the mean distance between pores. In this work, vacancy formation, diffusion, and annihilation are simulated. We demonstrate the model and its utility by applying it to simulate sintering in a simple geometry. Future work will extend the simulation capability to much larger systems with hundreds of particles.

II. Model Description

Consider the classical three-particle sintering problem modeled by many previous researchers. In this system, all three particles are circular and of the same size. Sintering in such a system occurs by diffusion of material into the pore, diffusion of vacancies from the pore to the grain boundary, and annihilation of the vacancies at the grain boundary. Murch has shown that diffusion can be simulated by a random walk in kinetic Monte Carlo models. Furthermore, simulation of long-range diffusion in microstructural models similar to the one used here has been shown previously in other works. We introduce a new algorithm for vacancy annihilation in this work. This vacancy annihilation is applied to the three-circular-particle sintering geometry to demonstrate that the kinetic Monte Carlo model can simulate sintering.

The model presented here is limited to consideration of the following geometry and processes: three circular particles of equal size sintering as shown in Fig. 1: grain growth by short-range diffusion of atoms from one side of the grain boundary to the other; long-range diffusion of material to pores by grain boundary diffusion and along pore surfaces by surface diffusion; vacancy annihilation at grain boundaries.

In the model, an ensemble of grain sites and pore sites is allowed to populate a square lattice. We consider three-grain sintering; therefore, grain sites can assume one of three distinct, degenerate states, \( q_{\text{grain}} = \{1,2,3\} \). The pore sites can assume only
one state, \( q_{\text{pore}} = -1 \). 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 of the neighbor interaction energies in the system given by

\[
E = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{8} (1 - \delta(q_i, q_j))
\]

(1)

where \( N \) is the total number of sites, \( \delta \) is the Kronecker delta with \( \delta(q_i = q_j) = 1 \) and \( \delta(q_i \neq q_j) = 0 \), \( q_i \) 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, \( q_{\text{pore}} = -1 \), there are no pore boundaries and all pore sites coalesce. In contrast, grain sites can assume many 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.\(^{19, 21}\) First a grain site is chosen at random from the simulation space. Then a new state \( q \) is chosen at random from the three 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\(^{30}\) 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

\[
P = \exp \left( \frac{-\Delta E}{k_B T} \right) \quad \text{(for } \Delta E > 0) \quad \text{(2a)}
\]

\[
P = 1 \quad \text{(for } \Delta E \leq 0) \quad \text{(2b)}
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the simulation temperature, a variable that defines the degree of thermal fluctuation in the system. 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 correctly.\(^{21}\)

Pore migration is simulated using conserved dynamics, so that the total number of pore sites and grain sites is the same after a pore migration step. 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.\(^{25}\) 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 other works.\(^{25, 26}\)

Densification in crystalline solids occurs by uniform annihilation of vacancies at the grain boundaries.\(^{31, 11}\) As vacancies are annihilated, the center of mass of the adjoining grain moves toward

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**Fig. 1.** Simulation results showing microstructural evolution during sintering of three particles. The starting microstructure shown in (a) is of three circular particles touching and the last microstructure, (e), is after the pore disappears.
the grain boundary, thus giving densification. The rate-limiting step in this process is for the vacancies to diffuse along the entire length of the grain boundary. In this model a vacancy is defined as a single, isolated pore site that is not connected to any other pore sites. The algorithm used for pore annihilation is the following. A pore site is chosen. If it happens to be a vacancy (an isolated pore site) on a grain boundary, it is annihilated. Annihilation is simulated as follows. A straight line is drawn from the isolated pore site through the center of mass of the adjacent grain to the outside boundary of that particle. Next, the isolated pore site and the outside grain site are exchanged 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 toward the annihilation site, and annihilates a vacancy. The frequency of the annihilation attempts is adjusted to simulate the diffusion of vacancies to the entire grain boundary. As the grain boundary length increases, time between annihilations also increases as:

\[ t_{\text{ann}} = t_{\text{ann}} \left( \frac{L_{gb}}{L_{gb}} \right)^2 \]  

(3)

where \( t_{\text{ann}} \) is the time between annihilation attempts, \( t_{\text{ann}} \) is the time between annihilation attempts for the initial grain boundary length \( L_{gb} \) at the beginning of sintering, and \( L_{gb} \) is the current grain boundary length. Adjusting the annihilation frequency in this manner simulates uniform annihilation of vacancies along the grain boundary.

Time in the model is measured in units of Monte Carlo step (MCS); 1 MCS corresponds to \( N \) attempted changes where \( N \) is the total number of sites in the system. Monte Carlo time is linearly proportional to real time \( t \) in material systems that have the characteristics simulated by the model. The proportionality constant of a given material can be found by comparing simulated microstructural evolution to that of the material. The starting configuration for the simulation is three circular particles touching each other as shown in Fig. 1. The grain growth, pore migration, and annihilation algorithms are applied as described above to simulate sintering. Three separate simulations were run from the same starting configuration for 150,000 MCS, a time past the disappearance of the center pore. Qualitative microstructural evolution is reported and shrinkage \( y \) at time \( t \) in the simulation is calculated as:

\[ y(t) = \left( \frac{\Delta A}{A_0} \right)(t) = \frac{N_{p0} - N_p(t)}{N_b + N_{p0}} \]  

(4)

where \( A_0 \) is the initial area; \( \Delta A \) is the change in area; \( N_{p0} \) is the initial number of pore sites (the number of pore sites in the middle of the three particles shown in Fig. 1); \( N_p(t) \) is the number of pore sites in the middle of the three particles at time \( t \); and \( N_b \) is the total number of grain sites, which remains constant. In addition to microstructural evolution, the shrinkage results of the three simulation runs are averaged and presented in the following section.

III. Results and Discussion

The microstructural evolution of this three-particle sintering simulation is shown in Fig. 1. Qualitatively, these results are expected. Initially the three particles are just touching and all three pore edges are completely concave. As sintering progress, the necks between the grains grow and the pore corners start to round. The pore edges become increasingly convex as the pores shrink. The centers of mass of the three particles approach each other. No grain growth is observed and none is expected as the grains are all the same size and the grain boundaries between them remain straight as they grow. After the pore in the center disappears, densification continues as the centers of mass of the three particles continue to approach each other.

The morphologic characteristics observed were expected, but we wanted to verify that the model could simulate sintering kinetics as well. The kinetics are verified by comparing the densification curve of the simulation to those predicted by sintering theory. The shrinkage rate of circular particle sintering has been treated analytically by many. They all used a similar approach by equating the flux of the material to the neck with the increase in neck size and solved for the shrinkage as a function of sintering time. They reported the time exponent for shrinkage to vary from 0.31 to 0.50 depending on the details of their derivation such as the transport mechanism and curvature that they assumed for the pore edge. Here we compare our simulation results with the predictions of Johnson, who treated both the three-dimensional case (two-sphere sintering) and the two-dimensional case (two infinitely long wires sintering). He predicted the shrinkage rate by relating the flux of material into the neck to the neck growth for grain boundary diffusion, the same mechanism simulated in this work. The assumptions that he made were that particles were infinitely long cylinders of the same size, that the radius of curvature of the particles remained constant everywhere (the particles remained cylindrical) except at the neck, that the mass transport mechanism is grain boundary diffusion, and that the grain boundary between the particles remains straight as it grows. For the two-dimensional case of infinitely long wires, he obtained the following for shrinkage as a function of time:

\[ y = Br^{-1.32}t^{0.33} \]  

(5)

where \( y \) is shrinkage, \( B \) is a constant related to diffusivity, surface energy, atomic volume, particle radius, and other material parameters, and \( t \) is time. The shrinkage in the simulation was calculated using Eq. (4). The shrinkage was averaged over the three simulation runs. While the simulation was run past the disappearance of the center pore, the shrinkage is calculated from the starting configuration until the center pore disappears. The shrinkage obtained from the simulations is compared with sintering theory in Fig. 2, a plot of shrinkage as a function of time. As one can see, there is very good agreement at early times in the simulation, but at the later time, the simulation shrinks faster than sintering theory would predict. The disagreement in the later time between simulation and theory is due to the assumptions that the pore remained concave as the simulation progressed. Clearly, the pore shape changes from a concave shape to a convex shape as sintering proceeds (see Figs. 1(a–d)). This change in shape of the pore was reported by Alexander and Balluffi in their classic paper studying sintering of copper wires.

To test the hypothesis that the change in pore shape leads to the discrepancy in shrinkage rate between the simulation and analytical prediction of shrinkage, we analytically calculated the shrinkage as a function of time for the convex pore shape. We made the assumptions similar to the ones made in the earlier model. The grains remain circular except for the flattening at grain boundaries.
(have the same radius of curvature everywhere except at the grain boundaries). The pore has the convex shape shown in Fig. 3 with all three segments having the same curvature. The segments meet at a 120° angle since the simulation treats the case of isoenergy surfaces. The pore is assumed to shrink self-similarly with the grain boundaries growing longer as sintering proceeds.

The shrinkage equation was derived for this geometry by equating the flux of material into the pore by grain boundary diffusion to the rate of change in pore area following Johnson’s treatment:  

\[ J \delta = \frac{dA}{dt} \quad (6) \]

where \( J \) is the flux per unit time, \( \delta \) is the grain boundary thickness, \( A \) is the pore area, and \( t \) is time. The flux is  

\[ J = -\left( \frac{D \delta}{18kT} \right) \nabla \mu \quad (7a) \]

where \( D \) is the grain boundary diffusivity, \( \Omega \) is the molar area, \( k \) is Boltzmann’s constant, and \( T \) is temperature. Johnson noted that the quasi-steady-state condition requires  

\[ \nabla J = \text{constant} \quad (7b) \]

and that chemical potential and stress are related as  

\[ \nabla \sigma = \frac{\nabla \mu}{\Omega} \quad (7c) \]

The solution to the stress (or chemical potential) equation is of the form  

\[ \sigma = ax^3 + b \quad (7d) \]

and two boundary conditions are stress at the center of the neck is \( \nabla \sigma(x=0) = 0 \), and stress at the pore surface \( x_p, \sigma(x=x_p) = 2\gamma/R \), where \( \gamma \) is the surface energy and \( R \) is the pore radius of curvature. Finally, the force balance on the grain boundary requires  

\[ \int_0^{x_p} \sigma \, dx = \gamma \sin \left( \frac{\pi}{3} \right) \quad (7e) \]

Using all of the relationships above and noting that the neck size for low porosity is proportional to negative pore radius, it can be shown that the flux is  

\[ J = -\left( \frac{6\gamma \delta D \sin(\pi/3)}{kTR^2} \right) \quad (8) \]

The pore area is also a function of pore radius  

\[ A = \frac{R^2}{2} (\pi - \sqrt{3}) \quad (9) \]

Substituting Eqs. (8) and (9) into Eq. (6) and solving for \( R \) with the boundary condition \( R = R_0 \) at \( t = 0 \), where \( R_0 \) is the initial pore radius, one gets  

\[ R^4 = R_0^4 - \left( \frac{4\Gamma}{\pi - \sqrt{3}} \right) t \quad (10) \]

where  

\[ \Gamma = -\left( \frac{6\gamma \delta D \sin(\pi/3)}{kT} \right) \]

The equation describing shrinkage as a function of time is  

\[ y(t) = \left( \frac{\Delta A}{A_0} \right)(t) = \frac{R_0^4}{R^4} - \frac{\sqrt{R_0^4 - Ct}}{R_0^4} \quad (11) \]

where  

\[ C = \frac{4\Gamma}{\pi - \sqrt{3}} \]

Figure 4 compares the shrinkage Eq. (11) with the results obtained from simulations. There is agreement between the simulation results and the analytically predicted results for this geometry. Furthermore, the microstructures shown in Fig. 1 are labeled in Fig. 4 and correspond well with the concave-pore-shaped region, the transition region, and the convex-pore-shaped region of Fig. 4. Therefore, we conclude that the model presented in this work simulates solid-state sintering in crystalline systems with grain boundary diffusion as the transport mechanism well.

The model presented here simulates a number of microstructural evolution processes that are driven by the reduction of interfacial free energy. While the model is capable of simulating grain growth, no grain growth occurs in this simulation as the three particles are the same size and there is no curvature to the boundaries between them. Single pore sites, analogous to vacancies, are formed at all surfaces. As shown elsewhere the concentration of vacancies near an interface is inversely proportional to its curvature as formalized by the Gibbs–Thompson relation. Thus, more vacancies are formed at the internal pore surface than at the outside boundaries of the particles. When these vacancies diffuse to the grain boundary, they are annihilated and densification occurs. Surface diffusion at the pore surface and the external particle surfaces causes the shape of the system to equilibrate constantly, thus leading to minimum energy shapes in the system.

Fig. 3. Convex-shaped pore used for derivation of densification rate during later times of simulation. The solid line is the shape of the pore at time \( t_1 \) and the dotted outline at a later time \( t_2 \).

Fig. 4. Shrinkage as a function of time measured in the simulation is compared with the shrinkage predicted by sintering theory, Eq. (5), for the concave-pore-shaped region and for the convex-pore-shaped region, Eq. (11). The times corresponding to the microstructures shown in Fig. 1 are labeled.
IV. Conclusions

A kinetic, Potts Monte Carlo model, capable of simulating microstructural evolution during sintering in a two-dimensional system of three particles, has been presented. It has been shown to accurately predict the microstructural evolution in such a system by simulating the expected topological changes and by simulating the kinetics of densification. The topological changes have been compared with experimental evidence found in the sintering literature. The densification kinetics have been compared with predictions of sintering theory.

References