Potts Model Simulation of Grain Size Distributions during Final Stage Sintering

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ABSTRACT

The Potts Monte Carlo model was used to simulate microstructural evolution and characterize grain size distribution during the final stages of sintering. Simultaneous grain growth, pore migration and pore shrinkage were simulated in a system with an initial porosity of 10% with varying ratios of grain boundary mobility to pore shrinkage rates. This investigation shows that the presence of pores changes the grain size distribution and the topological characteristics due to pinning of grains by pores. As pores shrink away, their pinning effect decreases. Once pore shrinkage is complete, normal grain growth is achieved.

INTRODUCTION

During the final stages of sintering, pore channels along grain boundary begin to shrink and pores are isolated on grain boundaries and triple junctions then shrink continuously and may disappear altogether[1]. However, in many cases, pores would break away from grain boundaries and become trapped within grains, resulting in some amount of residual porosity[2]. These observations neglect the importance of surface diffuison and bulk diffusion during final stage sintering. For pore shrinkage in the final stage of sintering, grain boundary diffusion is the most important mechanism. However, surface diffusion is responsible for pore mobility and will affect both sintering microstructure and sintering kinetics.

In this paper, we have developed a modified Potts Monte Carlo simulation algorithm to study final stage sintering, which is based on the previous development on the microstructure evolution such as grain growth and pore migration. Multiple kinetics are incorporated by assigning different Monte Carlo probability to different mechanisms based on the experimental conditions which exist during final stage sintering. Using a 2D Potts model, microstructural evolution, topological distribution and grain size distribution are discussed in detail.

MODEL AND SIMULATION METHOD

The two-dimensional Potts model was used to study simultaneous grain growth, pore migration and pore shrinkage simulation. Grain structure is mapped onto a square lattice with periodic boundary conditions in both the X- and Y-directions. Each lattice is assigned a spin between 1 and q (q=100) which represents the different orientation of the grain in which the site is embedded. Each pore site is assigned a spin = -1. Each grain or pore site may be considered as a discrete domain, consisting of some billions of atoms, which maps to a 400× 400 lattice to form a meso-scale microstructure. In this investigation, we chose the grain boundary energy and surface energy to be isotropic and independent of the grain orientation. Thus, we assign the bond energy, E_0, to be constant with direction and spin. First and second nearest neighbor interactions are considered as this results in lower anisotropy[3]. The equation of state for this system, also know as the Hamiltonian, was defined as

$$E = \frac{1}{2} E_0 \sum_{i=1}^{N} \sum_{j=1}^{8} \left(1 - \delta(S_i, S_j)\right) \qquad \text{eq.1}$$

where E_0 is the bond energy between neighboring sites of unlike spin ($s_i \neq s_j$, e.g. grain boundary or surface). The Hamiltonian counts the number of unlike bonds between all sites i and their 8 1st and 2nd nearest neighbors j.

Grain growth is simulated using Potts model: a grain site is chosen at random from the simulation space, then a new trial spin is chosen at random from q spins. The energy change is evaluated using eq.1. The change in energy for the grain growth step, ΔE, is then used to calculate the transition probability, P, using Boltzmann statistics as

$$P = \begin{cases} \exp(-\frac{\Delta E}{K_B T}) & \text{for } \Delta E > 0 \\ 1 & \text{for } \Delta E \leq 0 \end{cases} \qquad \text{eq.2}$$

where K_B is the Boltzmann constant and T is absolute temperature. The Metropolis algorithm[4] is used to determine if an exchange is accepted or not by choosing a random number between 0 and 1. If the random number is less than or equal to P, then the transition is accepted. If not, the transition is rejected. A Monte Carlo temperature T = 0 is used for grain growth simulation to eliminate the thermal fluctuations and has been shown to simulate grain growth well[5, 6]

Pore migration is simulated using conserved dynamics. A pore site is picked at random, then a neighboring grain site is chosen also at random. A trial exchange of the grain site and the pore site with the grain site assuming the spin which results in the minimum energy is considered. The energy change of this trial exchange is calculated using eq.1. The transition probability is determined by applying eq.2 and the Metropolis algorithm is used to accept or reject the pore migration step. In this simulation, almost all pore migration events happen by grain sites moving along the pore-grain interface, thus, simulating pore migration by surface diffusion as shown by Tikare and Holm[6]. The mobility ratio of pore boundaries to grain boundaries was chosen to be 1:1 based on earlier work. Monte Carlo temperature of $K_BT = 0.5$ was chosen for pore migration also based on earlier work[6].

Pore shrinkage is assumed to occur by grain boundary diffusion only. First, we select a pore site at random. If the pore site is at a grain boundary, pore shrinkage is attempted. If it is an internal pore site then pore shrinkage is not permitted, as it is an intragranular pore. Pore shrinkage is simulated by replacing that pore site with a grain site which has a spin resulting in the minimum energy as calculated by eq. 1. We calculate the change in energy for shrinkage using eq. 1. The transition probability corresponding to this change is calculated using eq. 2 and finally, the Metropolis algorithm is used to accept or reject the transition.

The grain boundary mobility to pore migration ratio was held constant at 1 for all the simulations in this investigation. The pore migration to pore shrinkage ratio, m, was varied from 1,000 to 10,000. This was done by attempting m pore migration events for each pore shrinkage event. Pore migration and shrinkage are simulated under temperature $k_BT=0.5$, this high temperature is necessary to sample higher entropy states required for simulation of pore migration and shrinkage. At lower temperature, pores would not have sufficient energy to diffuse in the microstructure[7].

Time in the Potts model is measured in units of Monte Carlo steps, MCS. At 1 MCS, the number of attempted changes is equal to the total number of lattice sites in the simulation.

DISCLAIMER

Simulations were run up to 10^5 MCS. Data was collected from four independent runs for each set of simulations run under identical conditions to obtain good statistics for grain size distributions and topologies.

RESULTS AND DISCUSSIONS

Previous study of pore migration and grain growth with no pore shrinkage showed that pores grow by coalescence and the grain growth is pinned by pores. In this simulation, we choose initial porosity of 10%, which is considered appropriate for the final stage sintering[8,9]. The starting microstructure for pore shrinkage simulations is obtained by only allowing grain growth and pore migration for a system with constant porosity of 10%. After the average grain size, measured in grain area, reaches 100 sites, pore shrinkage, along with grain growth and pore migration, is allowed to be active. This initial microstructure, Fig. 1a, shows that pores are present at grain triple junctions and almost all the triple junctions are occupied by pores. The pores and grains are equi-axed with smooth, regular interfaces.

A series of simulations with pore migration to pore shrinkage ratios of 1000, 3000, 7000 and 10,000 were run. These ratios were chosen to simulate the surface to grain boundary diffusion ratios typically observed in real materials systems.

For a two dimensional system with constant volume fraction of pores, pore growth rate was predicted by Tikare and Holm to be

$$R \propto t^{0.2} \qquad \text{eq.3}$$

where R is the grain radius and t is time. They obtained this relationship for the case where pores migrate through the microstructure by random walk and grow by coalescence (two or more pores become one large pore when they touch each other). Fig.2 shows that the pore growth curves, pore size vs. time, for systems with (a) grain growth and pore migration and (b-e) grain growth, pore migration and shrinkage at different pore migration to pore shrinkage ratios. For the system with no pore shrinkage, only grain growth and pore migration, pore growth curve shows that the pore growth exponent is about 0.15, which is a good agreement with the predicted pore growth exponent, indicating that pores do grow by coalescence. In the simulation with both pore shrinkage and pore migration, two competing events occur, pore growth by migrating pores which coalesce and pore shrinkage. The smaller pores disappear faster because of their higher curvature, thus increasing the mean distance between pores. This in turn makes pore coalesces via random walk less frequent. The competition between pore growth via coalescence and pore shrinkage via grain boundary diffusion tends to favor shrinkage as surface to grain boundary diffusion rate decreases as shown in Fig.2. However, at the slow shrinkage ratio, the pore coalescence could be seen in the microstructures shown in Fig. 1b to Fig. 1d. Pore breakaway could also been seen in those microstructures as pore shrink and no longer pin grain boundaries.

Fig.3 shows the grain growth curves for (a) grain growth without pores, (b) constant porosity, grain growth and pore migration and (c-f) different pore migration to shrinkage ratios. The grain growth kinetics display power law behavior with a grain growth exponent n, $R \propto t^n$, with $n = 0.5$[10]. In the simulations, the grain growth exponent for normal growth was $n = 0.5$, which is in good agreement with that predicted by the theory of single phase grain growth ($n_G = 0.5$[11]). For grain growth together with pore migration, grain growth is pinned by pores and thus, scales with pore growth with exponent $n_P = 0.2$ as indicated by Eq.3. The grain growth with pore migration simulation shows that $n = 0.25$ as shown in Fig.3, which is a reasonably good agreement. Grain growth with pore migration and shrinkage at different ratios shows that the grain growth is not log-linear. However, the grain growth curves for these simulations fall

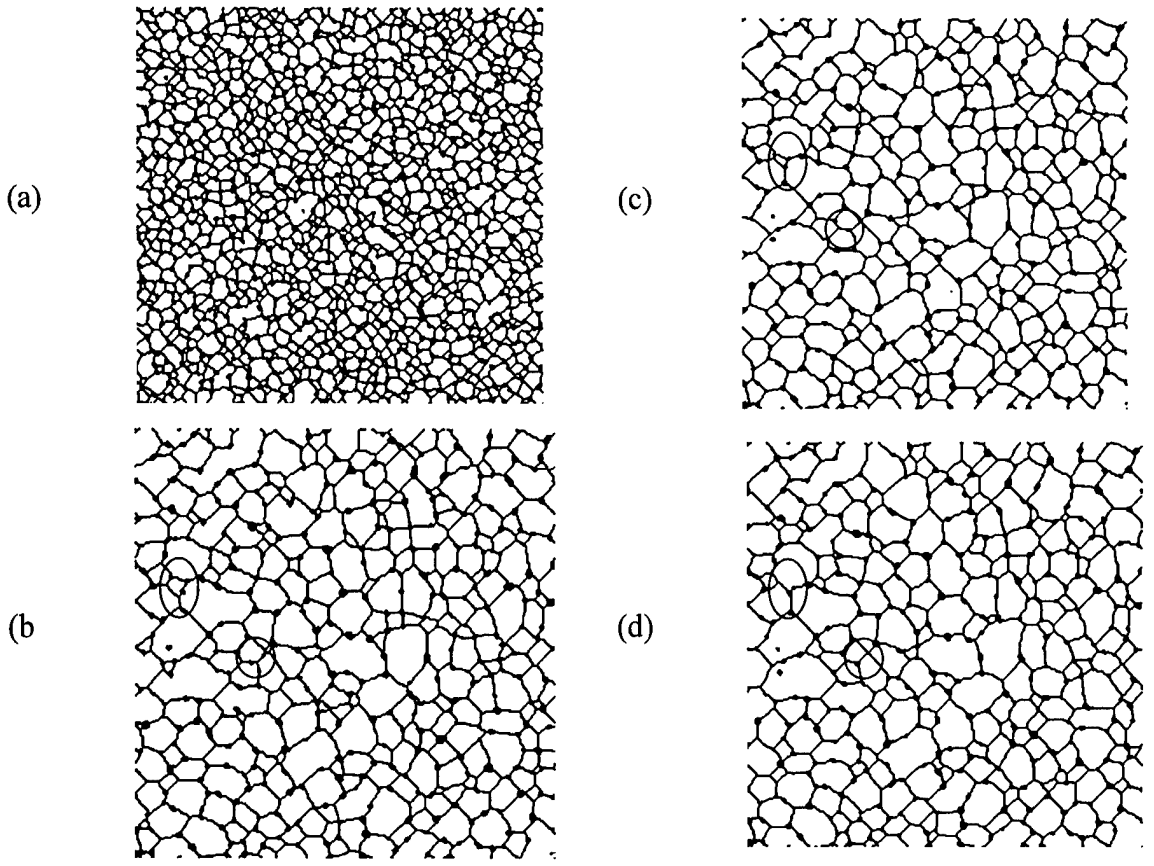

Fig.1 (a) Starting microstructure for pore shrinkage with initial porosity 10%, microstructure at (b) 80,000 (c) 90,000 and (d) 100,000 MCS at pore migration to pore shrinkage ratio m = 10,000. Pore coalescence events are circled.

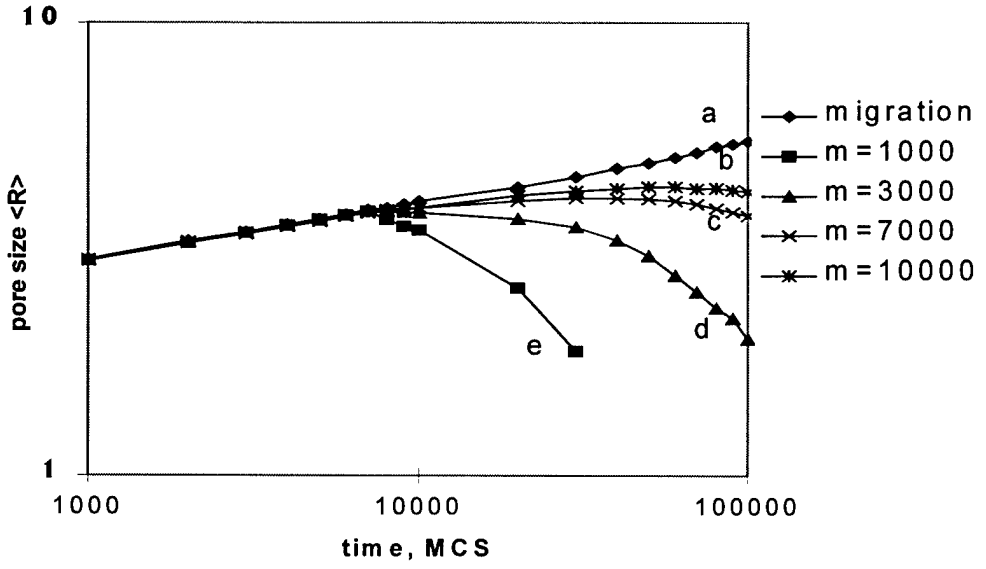

Fig.2 Pore size vs. time for different pore migration to pore shrinkage ratios m.

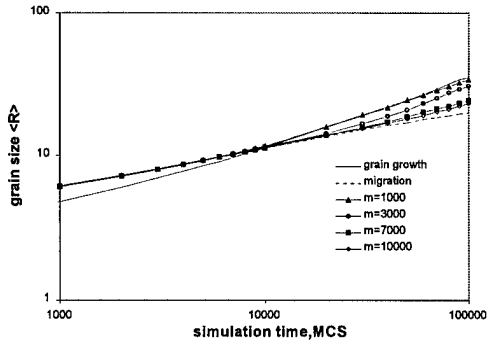

Fig.3 Grain growth curves with different pore migration to pore shrinkage rations m.

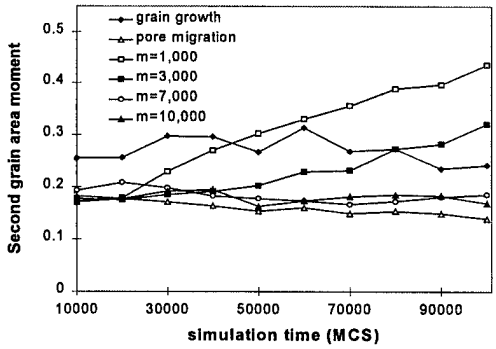

Fig.4 Second moment of grain area at different time for different pore migration to pore shrinkage rations m. For m=1,000, pores disappear at 40,000 MCS.

between those of normal grain growth and grain growth with pore migration. Furthermore, the simulation with highest pore shrinkage rate is closest to the normal grain growth curve with the lower shrinkage rate simulations progressively deviating from the normal grain growth curve. These results indicate that grain growth is pinned by pores in all cases however, the pinning effect is decreasing as the pores shrink and disappear.

Fig.4 is the plot of the second moment of grain area as function of simulation time for all simulations. The second moment is the variance of the grain size distribution and is calculated as

$$\mu_2(A) = \frac{1}{n-1}\sum_{i=1}^{n}\frac{A_i^2}{<A>^2} - 1 \qquad \text{eq. 4}$$

where n is the number of grains, A is the grain area and <A> is the average area. Fig.4 shows that the systems with faster pore shrinkage rates tend to have broader grain size distributions than the normal grain growth size distribution. This effect not only persists after the pores completely disappear, but continues to deviate from the normal grain growth behavior in the case where pore shrinkage rate is highest. To understand this behavior we examined the microstructures of the simulation with the highest pore shrinkage rate and compared them to the others. We found that the initial microstructure for the simulation with the fastest pore shrinkage rate had pores evenly distributes at triple junctions as seen in Fig. 1a. As pore shrinkage was started entire pores would shrink away quickly unpinning a few grain boundaries while most were still pinned. These unpinned grains grew quickly giving abnormal grain growth of a few grains as shown in Fig. 5. At lower pore shrinkage rates, the grain pinning effect of pores is more persistent as well as more even, thus abnormal grain growth did not occur. Furthermore, as the low pore shrinkage rates, the grain size distribution was narrower than that of normal grain growth because the pore pinning.

The changes of average grain sides also indicate that pore shrinkage alters the grain growth, as shown in Fig. 6. For all system, the average grain sides is about 6, which is a consequence of the Euler-Poincare relationship applying to a two-dimensional cellular structures if grains meet only at tri-junctions. The normal grain growth without pore's appearance give the lowest average grain side value and the grain growth in a system which pore only migrates give a

value a little higher. The shrinkage of pores effect greatly in the topologies of the microstructure until the pores shrink away completely.

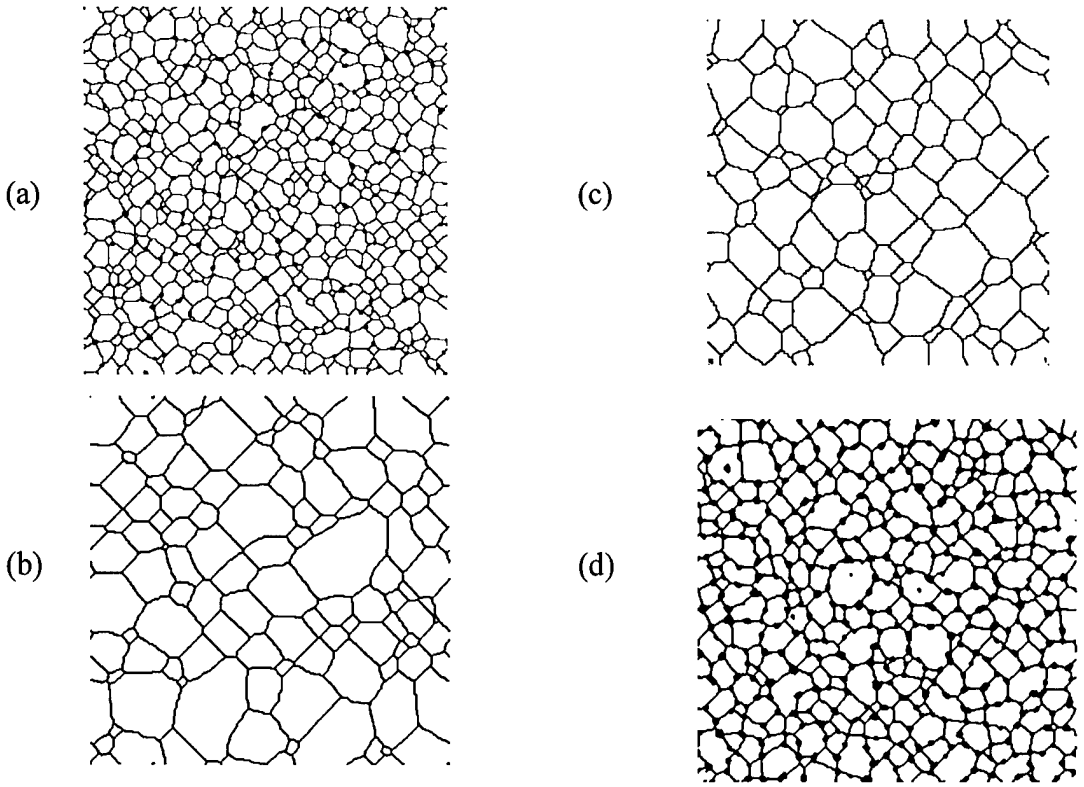

Fig.5 Microstructures from the fast pore shrinkage simulation at (a) 20,000 and (b) 100,000 MCS showing the development of a broad grain size distribution as a result of uneven pinning by pores. (c) Microstructure of a normal grain growth simulation and (d) grain growth and pore migration simulation with no pore shrinkage to show that both result in a narrower grain size distribution.

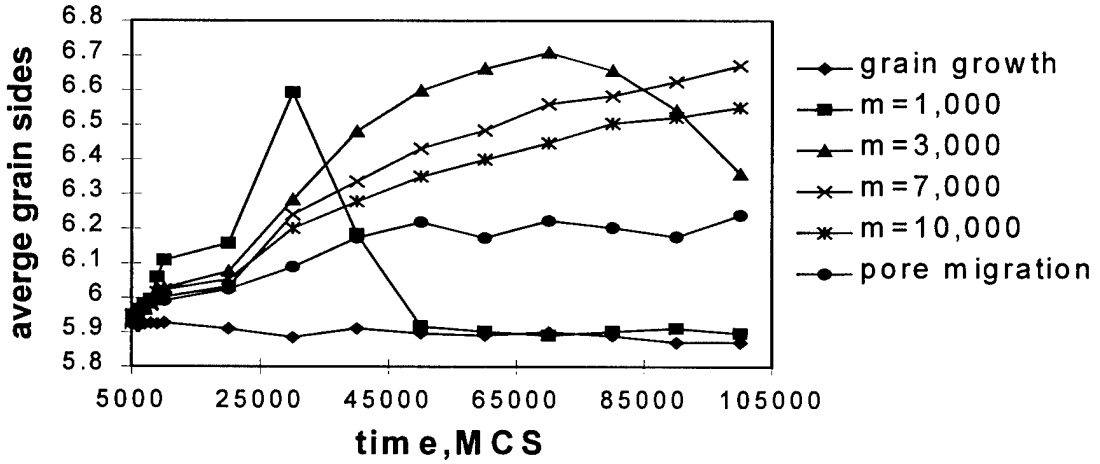

Fig.6 Average grain sides vs. simulation time for different pore migration to pore shrinkage ratios. Pore disappear at 40,000 MCS for m = 1,000.

SUMMARY

The microstructural evolution during the final stage sintering was studied using the Potts model. Grain growth by grain boundary migration, pore migration by surface diffusion and pore shrinkage by grain boundary diffusion were incorporated in the Potts model. An initial porosity of 10% was chosen as a representative microstructure during the final stage sintering. The microstructure evolution shows that pore will migrate along the grain boundaries and coalesce to form larger pores at the triple junctions. Simultaneously, pore shrinkage competed with the pore growth by coalesce especially at the higher shrinkage rates. Simulation results show that the shrinkage of pores and the shrinkage rate effects the topological and grain size distribution. Fast shrinkage results in a broad grain size distribution because some grains are pinned by the pores and will not grow while other grains grow bigger, then the small grains would shrink after all the pores are vanished. In contrast, at the slow pore shrinkage rates, the grain size distribution is narrower because pores hinder grain growth evenly.

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REFERENCES

[1] M.N. Rahaman, Ceramic Processing and Sintering, Marce Dekker, Inc, 1995
[2] J.E. Burke, " Role of Grain boundaries in sintering", J. Am. Ceram. Soc. 40. 80-85 (1957)
[3] E.A. Holm, James A. Glazier, D.J. Srolovitz, G.S. Grest, "Effects of Lattice Anisotropy and Temperature on Domain Growth in the Two-Dimensional Potts Model," Phys. Rev. A, 43 [6] 2662-2668 (1991).
[4] N. Metropolis & S. Ulam, "The Monte Carlo Method", J. Am. Sta. Ass. V44, 335,(1949)
[5] D. J. Srolovitz, M.P. Anderson, P.S.Sahni & G.S. Grest, "Computer simulation of grain growth-II. Grain size distribution, topology, and local dynamics", Acta Metall. V32, No.5, pp792-802 (1984)
[6] E.A. Holm & V. Tikare, "Simulation of Grain Growth and Pore Migration in a Thermal Gradient", J. Am. Ceram. Soc., 81[3] 480-484 (1998).
[7] V. Tikare & J.D. Cawley, "Application of the Potts Model to Oswald Ripening", J. Am. Ceram. Soc., 81[3] 485-491(1998).
[8] R.L. Coble, "Sintering Crystralline Solid. I. Intermediate and Final State Diffusion Models," J. Am. Ceram. Soc., 32[5] 787-792(1961)
[9] G.N. Hassold, I. Chen, D.J. Srolovitz, "Computer Simulation of Final Stage Sintering: I, Model, Kinetics and Microstructure", J. Am. Ceram. Soc., 73[10] 2857-64(1990)
10 E.A. Holm, "Modeling micro-structural Evolution in Single Phase, Composite and Two-phase polycrystals", Dissertation, University of Michigan, 1992
11 M. Hillert, "On the theory of Normal and Abnormal Grain Growth", Acta Metall., 13, 227-231(1965)

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