MICROSTRUCTURAL ANALYSIS OF SINTERING BEHAVIOR OF INTRA-GRAIN PORES

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Abstract – A lattice-based Monte Carlo simulation approach has been developed for studying the behavior of intra-grain pores during the intermediate and final stages of sintering. The changes of the microstructures and the resulting properties of intra-grain pores during sintering are easily examined. The sintering behavior such as pore size distribution, average pore size, etc. is in very good agreement with the experimental observations. In addition, the relationships between the number of pores and the average pore volume agree well with theory.

Key words: Sintering, Microstructure, Pore, Grain, Monte Carlo Simulation

INTRODUCTION

One of the major structural characteristics of a specimen is during the intermediate and final stages of sintering, namely, shrinkage and/or growth of the closed pores formed at the end of the initial stage of sintering [Exner, 1979, 1980, 1988]. A typical microstructure at the end of the initial stage of sintering consists of grains and pores. The pores can be classified into two groups: (i) pores between or among the grains, and (ii) pores inside the grains. When gases which resist diffusion through the grains (such as argon or helium) are entrapped in these pores, the shrinkage or growth is strongly influenced by the gas pressure. On the other hand, when the pores are empty or contain diffusible gases (such as hydrogen), the growth will be controlled significantly by lattice-diffusion of atoms or vacancies. In this case material transport will occur either between isolated pores or between the pores and the grain boundaries. If many grain boundaries exist in the sintered material, the material transport between the pores and the grain boundaries will cause the shrinkage of pores and consequently the average size and total number of the pores will be reduced.

Very few systematic studies of the structure of pores and the variations in their geometric properties during the intermediate and final stages of sintering are available. Most of the available literature consists of studies of the sintering behavior of inter-grain pores. In contrast, the sintering behavior of intra-grain pores has received little attention because of the experimental difficulties involved in preparing samples. We mention a few examples here to illustrate the use of our computer simulations for this purpose. Structural changes in pores lying within the grains have been studied optically [Watanabe and Masuda, 1974; Watanabe et al., 1976; Masuda and Watanabe, 1980] by using a single large grain. These authors observe that the porosities remain unchanged during sintering

but that the shapes of the pores become more circular. The literature also contains reports of experiments [Hsueh and Evans, 1982] which show that the intra-grain pores completely separated from grain boundaries cannot be removed easily during the intermediate and final stages of sintering. These features and accompanying changes can be studied readily using our computer simulations [Kim, 1991; Philippou et al., 1995]. In the present work we examine the sintering behavior of intra-grain pores which lie within a large grain.

COMPUTER EXPERIMENTS

1. Computer Simulation Procedure

Two concepts that are universally applicable to all sintering phenomena and are acceptable from a thermodynamic point of view may be stated as follows: (i) a reduction in the net interfacial free energy serves as the driving force for sintering, and (ii) this reduction occurs via several material transport mechanisms [Wong and Pask, 1979]. In the following development, we focus on the interfaces that act either as a source or as a sink for material transport. The individual material transport mechanisms [Kim, 1991] are not considered for this case.

We assume that the material is mapped onto a lattice of suitable topology, where each lattice site may be thought of as an individual atom, a material element, or a pore element. The interaction between particles and pores can be considered as follows: initially, each lattice site is assigned an integer value S which is either 0 or 1. The value S=0 identifies the site as a pore element and S=1 represents a solid element. If a material element is adjacent to at least one pore site, then that element is defined as a surface element.

The energy associated with a site is specified by defining an interaction energy, E, between a site and its neighbors within a given distance. The interaction energy is defined by the equation

$$E_i = \sum_{j=0}^{n} J(S_i, S_j) \tag{1}$$

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(a) 0 MCS   (b) 50 MCS   (c) 100 MCS

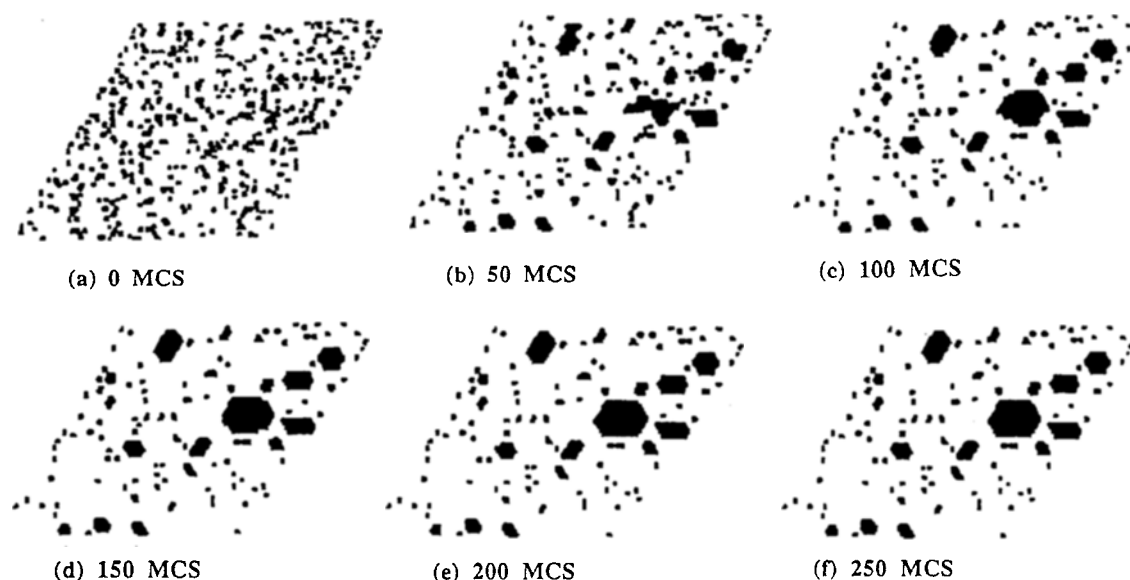(d) 150 MCS   (e) 200 MCS   (f) 250 MCS

Fig. 1. Microstructures showing the growth of pores (black region) in a grain (white region).

where J is positive and sets the scale of interfacial energy, J (0,0) is the pore-pore interaction energy, J(1,1) is the solid-solid interaction energy and J(1,0)=J(0,1) is the solid-pore interaction energy. The pore-pore and solid-solid interaction energy is considered equal to zero. The solid-pore interaction energy is considered equal to one. The sum is taken over all neighbors within a circular neighborhood, with a prespecified radius, located around the site.

During each step, each lattice site is considered sequentially. The energy (E_{old}) of a lattice site is calculated using Eq. (1), then the state of the site is changed. If the site is a pore it is changed to a solid and vice versa. The energy of the new configuration (E_{new}) is then calculated, and the change is accepted or rejected based on the energy difference

$$\Delta E = E_{new} - E_{old} \qquad (2)$$

A reduction in energy leads to acceptance of the change, otherwise the change is rejected. This process is repeated for every lattice site. After all the lattice sites are visited the lattice structure is updated and the process is repeated. The basic time unit is one Monte Carlo step (MCS) and corresponds to a number of change attempts equal to the number of sites in the lattice. A triangular lattice of 100×100 has been used in the simulations reported here. Periodic boundary conditions are applied along the horizontal and vertical directions in order to avoid boundary effects.

2. Analysis of the Microstructure

For analyzing the microstructures, we need to count a 'cluster' of pore elements or solid elements. For this we modify the algorithm of Hoshen and Kopelman [1975], which has been designed to identify and count all clusters in a given percolation configuration and which has been used extensively elsewhere [Stauffer and Aharony, 1992; Binder, 1987]. The algorithm gives all sites within the same cluster the same label, and gives different labels to sites belonging to different clusters, but allows the simulation of large lattices without having to store the whole lattice.

The cluster counting method used in the present work is as follows: First, a given configuration is scanned and all clusters of pore elements or solid (or grain) elements are identified and counted. Then each pore or grain is reassigned a unique number so that it can be distinguished from other pores or grains. Once this is done, a number of properties such as pore size, grain size, density, porosity, coordination number, shrinkage, etc., are determined.

RESULTS AND DISCUSSION

Fig. 1 shows the microstructural changes of a collection of pores within a grain. One clearly sees that the larger pores become larger and smaller ones become smaller as sintering proceeds. In addition, the pores become more circular. This observation is very similar to that observed for the case of inter-grain pores during densification, but, in this case (i.e., for intra-grain pores), the grain does not shrink and therefore the total volume of the pores is conserved. We also emphasize here an important advantage of computer simulations. In the computer simulations, results such as the above can be obtained for specifically identified pores (e.g., for pores lying in a single section of the sample). Therefore, the changes in structural features and sintering kinetics can be studied in a rigorous manner. In contrast, in physical experiments, one usually uses a number of samples, each sintered at a selected set of different conditions. One then takes sections of such samples and studies the structural features. This procedure, which generally cannot be avoided in real experiments, can introduce some uncertainties in the observations.

Additional quantitative observations can be obtained from the changes in pore-size distribution or average pore size as functions of time, as shown in Fig. 2. The figure illustrates that the pore-size distribution becomes broader and the average pore size becomes larger. This is in very good agreement with the experimental observations [Watanabe and Masuda, 1974; Watanabe et al., 1976; Masuda and Watanabe, 1980], which note the
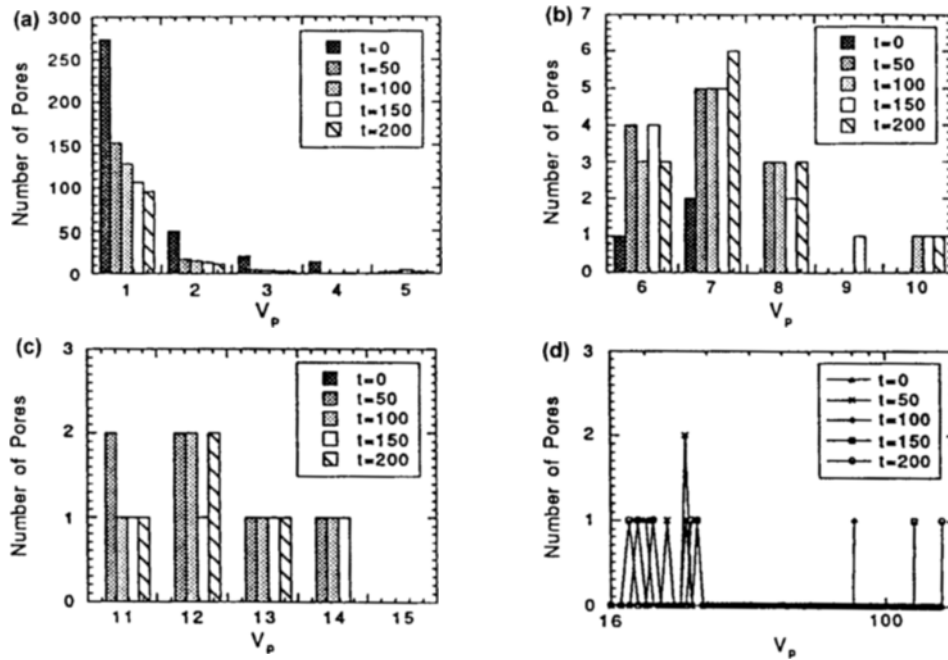
Fig. 2. The change in the size distribution of residual pores during sintering.
(a) $1 \leq V_p \leq 5$, (b) $6 \leq V_p \leq 10$, (c) $11 \leq V_p \leq 15$, and (d) $16 \leq V_p \leq 160$.
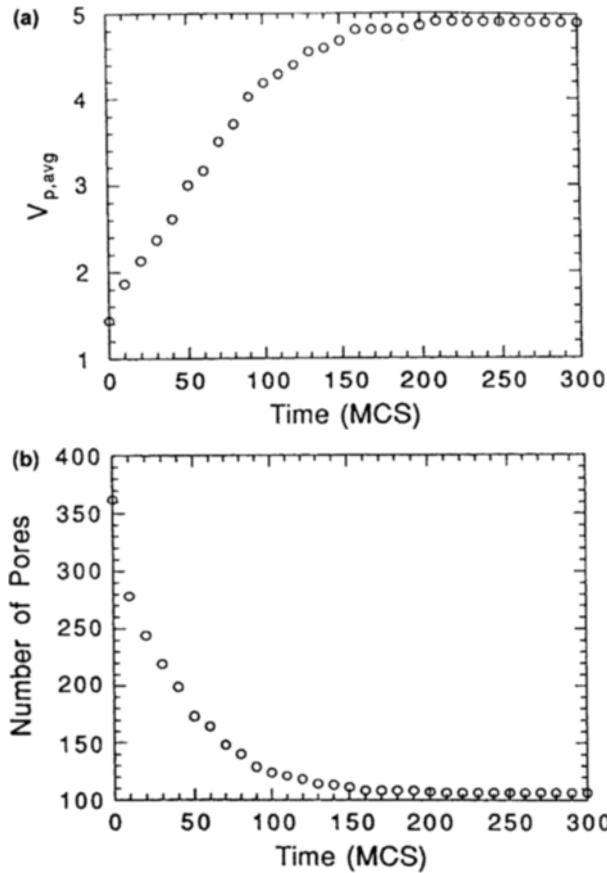

Fig. 3. The change in (a) the average pore volume and (b) the number of pores as a function of time.
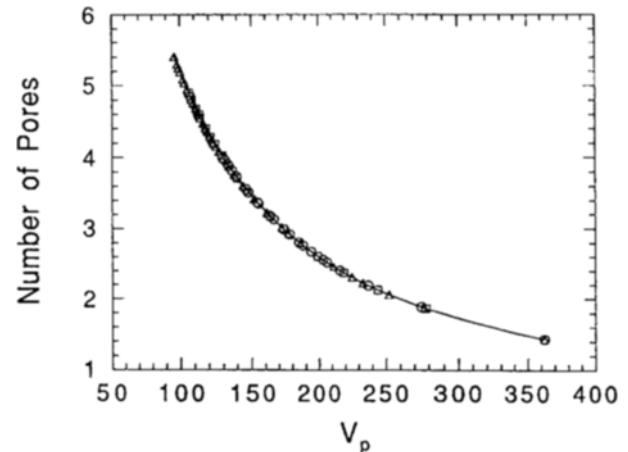

Fig. 4. The relationship between the number of pores and the average pore volume (— theoretical; $\bigcirc$, $\square$, $\triangle$ computer experiment).

same behavior in the experiments. We note that, in practice, one should control the intra-grain pores to be as small as pos-

sible in order to maintain a uniform size of pores in the sintered specimen or to prevent the formation of large pores, which is detrimental to densification.

Fig. 3 shows the change in pore volume and also the changes in the number of pores as functions of time. These are also plotted as number-of-pores versus pore-volume in Fig. 4. The growth of pores in this case may be treated by the theory of diffusion-controlled growth of particles precipitated in a saturated solution [Lifshitz and Slyozov, 1961]. According to this theory the rate of growth of pores can be expressed by the following relations

$$V_{p,avg} \propto d_{avg}^3 \propto t \propto N_v^{-1} \qquad (3)$$

where $V_{p,avg}$ is the average pore volume, d_{avg} is the pore diameter, and N_v is the total number of pores. The correlations between

the number of pores and the average pore volume shown in the above figures have been obtained using three simulations, and they agree well with the above relations.

CONCLUSION

The present computer simulation approach has been applied to the sintering of intra-grain pores. Consistent with what has been observed experimentally, it is shown that the larger pores become larger and the smaller ones become smaller as sintering proceeds and that the pores become more circular. Moreover, the pore-size distribution becomes broader and the average pore size becomes larger. The correlations between the number of pores and the average pore volume also agree well with the theory of diffusion-controlled growth of pores.

ACKNOWLEDGEMENT

NOMENCLATURE

d : particle or pore diameter [nm]
E_i : system energy calculated on the basis of site I [J]
J : unit of interaction energy [J]
n : total number of elements [-]
N_v : total number of pores [-]
S : orientation number of material element [-]
t : time [sec]
V_p : pore volume [nm^3]

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