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TITLE CRAIN GROWTH PHENOMENA IN FILMS: A MONTE CARLO APPROACH

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AUTHOR(S) D. J. Srolovitz

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GRAIN GROWTH PHENOMENA IN FILMS: A MONTE CARLO APPROACH

D. J. Srolovitz

Los Alamos National Laboratory

Los Alamos, NM 87545

ABSTRACT

A statistical model of microstructural evolution is developed for the evolution of grain structure during deposition. In cases where the atomic mobility on the surface greatly exceeds that in the bulk of the film, the bulk microstructure may be viewed as static while all of the evolution is controlled by the free surface. This leads naturally to a two dimensional model of microstructural evolution. Since the surface is advancing at a constant rate during deposition there is a linear relationship between time in the two dimensional model and depth in the film. A Monte Carlo computer simulation technique is described which models the evolution of microstructure in this way. Various driving forces are included. Simulated microstructures in the plane of the film and in the plane perpendicular to the free surface are shown.

I. INTRODUCTION

While grain growth phenomena are routinely exploited in bulk materials as a means of controlling grain size,¹ the grain size and morphology of films are generally determined by the deposition process. Nonetheless, the driving forces for grain growth phenomena in bulk and film geometries are essentially the same. However, the relative importance of the different forces vary. For example, while grain boundary curvature, dislocation density, internal stress gradients and surface energy anisotropy all contribute to forces driving grain boundary migration, surface energy anisotropy is expected to be much more important in films due to their much higher surface to volume ratio.¹ Not surprisingly, the types of grain growth phenomena seen in films are similar to that in bulk materials: normal grain growth, recrystallization, secondary grain growth, etc. Forces tending to retard the rate of grain boundary migration in bulk materials come from such sources as second phase particles and solutes. While such impediments to boundary migration also exist in films, a particularly strong retarding force comes from the grooves formed where the grain boundary meets the free surface.

Grain boundary migration can be thought of as resulting from the diffusion of atoms across the grain boundary region (perpendicular to the plane of the grain boundary). Since diffusion is an activated process, the absolute rate of grain boundary migration will decrease with decreasing temperature or increasing activation energy. Provided that the film is not too thick or the deposition rate too high, we may consider the deposition process as being essentially isothermal. For those restricted sets of deposition conditions for which these constraints are satisfied, the dominant contribution to the anisotropy in

grain boundary mobility comes from spatial variations in the energy. Therefore, even when the temperature is too low for any significant grain boundary migration to occur in the bulk, the diffusion necessary for grain boundary migration can occur readily at the free surface. Therefore, at temperatures below approximately half the melting point, grain boundary migration will effectively be limited to the surface region.

Since both grain boundary migration and deposition are limited to the surface it should be expected that the two processes are coupled. Consider an atom incident on the surface from the vapor. Assuming conditions are such that the atom does not readily escape back into the vapor it diffuses around until it finds a particularly favorable location at which to stick (e.g. a kink on a step).² As it diffuses about, it samples many environments with differing energies. For example, if it lands near a curved grain boundary it will sense that the energy of the side with positive curvature is higher than the side with negative curvature due to the existence of the Gibbs-Thompson effect. The atom, therefore, has a greater probability of sticking on the lower energy (negative curvature) side of the boundary. This corresponds to a bias in the direction of boundary motion during deposition and in fact leads to normal grain growth type behavior (i.e. grain boundary motion towards its center of curvature). Similarly grain boundary migration will occur if the grain on one side of the grain boundary has a lower surface energy than does the grain on the other side (i.e. secondary grain growth).

In the present paper we attempt to formalize some of these ideas about the connection between grain boundary migration and deposition.

In so doing we will show that much of the grain growth phenomena that occurs during the deposition of films is essentially two dimensional. Realizing this we are able to use the simulation techniques which we previously developed to describe grain growth phenomena in two dimensions.³⁻⁵ In Section II we develop a probabilistic argument describing the evolution of grain morphologies in films and show how it is related to our Monte Carlo technique for describing grain growth. In Sections III and IV our results on the kinetic and morphological aspects of grain boundary curvature related grain growth^{3,4} and surface energy driven grain growth⁵ are reviewed. Finally, in Section V the relationship between the two dimensional grain structures and the full three dimensional structures are demonstrated.

II. STATISTICAL ASPECTS OF BOUNDARY MIGRATION

A. Grain Boundary Migration During Deposition

We consider the case where the mobility of atoms on the surface greatly exceeds that in the bulk such that the grain structure interior to the film is quenched in during the deposition process. In this limit we need only be concerned about the dynamics going on at the free surface. We begin by considering the fraction of time an atom spends on different sections of a surface over which there is a variation in energy. The probability of the atom sitting in a region of space where it has an energy E is simply⁶

$$p = A e^{-E/kT} \quad (1)$$

where kT is the thermal energy and A is a normalization factor such that the integral of P over the entire surface is unity. If, for example,

the different crystallographic faces on the free surface have different surface energies, then the atom would tend to spend more time on those faces with lower energies. However as $T \rightarrow 0$, all surfaces become equivalent (i.e. the atom sticks where it lands). For very large T the entropy factor in the free energy is dominant and again all surfaces are equivalent.

The probability of an atom on site 1 (energy $E(1)$) making a transition to an adjacent site 2 (energy $E(2)$) is simply⁶

$$P = B \frac{e^{[E(1)-E(2)]/kT}}{1 + e^{[E(1)-E(2)]/kT}} \quad (2)$$

where B is a normalization constant. If the two surfaces sites have the same energy or T is infinite $P = 1/2$. Equation 2 shows that there is a nonzero probability of a transition from site 1 to site 2 even when $E(2) > E(1)$. The conversion from a transition probability to a transition rate requires the inclusion of a factor which accounts for the rate at which a transition is attempted and the activation barrier in going from site 1 to site 2. Both the attempt frequency and the activation barrier depend sensitively on the detailed atomic structure of the surface in the vicinity of sites 1 and 2.

During deposition an atom arrives at the free surface and diffuses from site to site until it reaches one in which the transition probability in going to any of its neighboring sites is essentially zero. Although the atom is diffusing about in the plane of the nominally flat free surface, its incorporation into the film corresponds to one unit of film growth normal to the plane of the free surface. As the temperature is raised, the atom is able to sample greater portions of the

surface. Since locations where the grain boundary intersects the free surface are generally higher energy than sites on the surface far from a grain boundary, the atom will tend to stick on these non-grain-boundary-surface sites. In fact the atoms will preferentially stick at steps on growth ledges or, preferably at kinks on those steps.² If the atoms completely avoided the grain boundary regions, large grain boundary grooves would be formed. However, for a fixed grain size equilibrium groove depths are finite and atoms also attach in the grain boundary region (to avoid the infinite surface curvatures that would otherwise occur). In deciding to which of the two crystals meeting at the grain boundary to attach, the atom is sensitive to the energy of the potential sites. For example, energy effects such as grain boundary curvature, anisotropic surface energy, and differences in defect density are important in determining the nature of the resultant grain growth process (normal grain growth, secondary grain growth, or recrystallization, respectively).

B. The Monte Carlo implementation

The evolution of the grain structure could be simulated as outlined above⁷ by adding atoms to random locations on the surface and allowing them to move about according to the transition probability defined above (Eq. 2). However, this approach is computationally untractable since it requires the simulation of the evolution of order 10^{17} atoms to simulate a surface as small as a square micron. A suitable simulation procedure must be able to include a large number of grains and be easily implemented on currently available computers. It is clear that such an approach cannot be atomistic in nature. An alternative approach is to

employ a continuum or quasi-continuum model that properly accounts for the statistical nature of the deposition and growth process.

The approach that we have taken³⁻⁵ is essentially that of a continuum model which has been discretized in order to make it computationally tractable while retaining the appropriate statistical framework. We begin by mapping the surface microstructure onto a discrete lattice (Fig. 1). Each lattice point is assigned a number between 1 and Q corresponding to the orientation of the grain in which it is embedded. Q is chosen sufficiently large that grains of like orientation impinge infrequently. Impingement also occurs in real systems during grain growth and corresponds to grain coalescence or the formation of a low angle grain boundary. While Q = 48 is employed in the simulation results presented herein, the results³ are essentially independent of Q > 36. In the present model, a grain boundary segment is defined to lie between two sites of unlike orientation. The grain boundary energy is specified by defining an interaction between nearest neighbor sites. A site i has an energy defined by⁵

$$E_i = -J \sum_{j \neq i} (\delta_{S_i S_j} - 1) + e_{S_i} \quad (3)$$

where S_i is one of the Q orientations on site i ($1 \leq S_i \leq Q$) and δ_{ab} is the Kronecker delta. The sum is taken over all nearest neighbor sites. Thus, nearest neighbor pairs contribute J to the system energy when they are of unlike orientation and zero otherwise. The grain boundary energy is, therefore, set by the magnitude of J and hence is nearly isotropic. The last term in Eq. 3 e_{S_i} , is a site energy term instead of a grain boundary energy term. e_{S_i} could represent the variation of surface energy with grain orientation.

The kinetics of boundary motion are simulated by employing a Monte Carlo technique. In the standard Monte Carlo method,⁶ a lattice site is selected at random, and a new trial orientation is also chosen at random from one of the other (Q-1) possible orientations. Unlike in Eq. 2, the probability of a transition between the old (1) and new (2) orientations is given by

$$P = e^{-[E(2)-E(1)]/kT} \quad (4)$$

While the transition probability of Eq. 2 is dictated by the requirement that individual atoms are neither created nor destroyed, this transition probability refers to change in grain orientation and hence has no conservation requirement.⁶ Successful transitions at the grain boundaries to orientations of nearest neighbor grains corresponds to boundary migration. Such a model results in a description of the grain boundary velocity which is formally equivalent with that derived from classical reaction rate theory.

Since all of the energies in this model are scaled by the thermal energy it is convenient to perform the simulations at $T = 0$. This corresponds to only accepting reorientation attempts which lower the energy of the system. Simulations performed at $T > 0$, show no fundamental difference from the results quoted here.³ The simulations are begun by randomly choosing the orientation of each site and then running for approximately 1000 Monte Carlo steps until each grain contains many sites. The Monte Carlo step (MCS) is the basic unit of time in the present simulation and corresponds to N reorientation attempts, where N is the total number of sites in the system. Since the thickness of the film increases linearly with increasing time, the microstructure of the

film (in the plane parallel with the flat substrate) at different heights (thicknesses) corresponds to the microstructure in the two dimensional simulation at different times. In this sense, time and thickness are equivalent. The present simulations were performed with $N = 40,000$ (i.e. 200×200) on a triangular lattice.

III. NORMAL GRAIN GROWTH

When e_{S_i} in Eq. 3 is identically zero, the only contribution to the energy of the system is due to grain boundaries. If all grain boundaries were straight, any local change in grain orientation would increase the energy of the system. Hence all grain boundary migration can be attributed to grain boundaries with non-zero curvature. Such curvature driven growth is known as normal grain growth. In this section we review the results of our simulations of normal grain growth in two spatial dimensions.

A. Morphology

The temporal evolution of a polycrystalline microstructure³ is shown in Fig. 2. Good correspondence is obtained between the simulated grain structure and that observed during normal grain growth in nearly isotropic metals and ceramics. Grains which are larger than the mean grain size tend to have more than six sides and grow. Grains which are smaller than the mean, on the other hand, tend to have less than six sides and shrink. While not externally required, we find that grain boundaries tend to meet at 120° , as expected on energetic grounds.

B. Kinetics

A simulation of the evolution of an initially circular grain embedded in an infinite medium³ shows that the area decreases linearly with time as

$$A(t) - A(0) = -at \quad (5)$$

where a is a positive constant, t is time and $A(0)$ is the initial grain area. These kinetics are in agreement with earlier theoretical treatments⁸ and other simulation results.⁹

The kinetics for grain growth in the polycrystalline systems show a growth exponent, $n = 0.4 \pm 0.02$, where n is defined by

$$R(t) = bt^n \quad (6)$$

where R is the grain radius. Equation 6 is valid only when $R(t) \gg R(0)$. The quoted value of n is based on approximately 30 simulations. It is found that under appropriate conditions the value of n is independent of temperature and the lattice on which the simulation is run.³ This value of n is in good agreement with measured growth exponents on ultra-high purity materials.³ However, theoretical predictions of n invariably arrive at a value of $1/2$.

C. Grain Size Distribution

The grain radius distribution was examined⁴ by plotting the frequency of occurrence versus the logarithm of the grain radius, normalized by the mean grain radius. Measurements were made at 15 different times during the course of the simulation and are displayed in Fig. 3. After an initial transient stage, it is easily observed that the normalized radius distribution function is time independent. The

distribution data were averaged over time to yield the distribution histogram in Fig. 4. For the sake of comparison, the grain size distributions for cross sections of bulk Al¹⁰ and MgO¹¹ are also included, as is the two dimensional grain size distribution derived by Hillert.⁸ The agreement between the simulation and experimental results are excellent, while the theoretical distribution shows considerably worse agreement.

D. Topology

The grain topology was also examined⁴ by plotting the frequency of occurrence versus the number of grain edges, N_e . It was found that this distribution is time invariant once the steady state grain size distribution is established. The grain edge distribution was also time averaged and the results are plotted in Fig. 5. Grain edge data for the same studies quoted above are also included for comparison. As with the grain size distribution function, excellent correspondence is obtained. The relationship between grain size and topology is indicated in Fig. 6 where the mean grain size for each topological class (grains with the same number of edges) is plotted versus the number of grain edges. A linear relationship is obtained, in agreement with available data on cross sections of bulk MgO,¹¹ Al,¹⁰ Pb¹² and brass.¹³

IV. SECONDARY GRAIN GROWTH

If the surface energy of the grain depends strongly on the exposed crystallographic face, then different grain orientation will have different energies. Secondary grain growth¹⁴ (also known as secondary recrystallization)¹ is the process by which grains of low surface energy

grow at the expense of those with higher surface energy. In the early stages of film growth, secondary grain growth is affected by both the free surface and the film/substrate interface.¹⁴ The anisotropic film/substrate surface energy is responsible for graphoepitaxy. In the Monte Carlo simulation procedure introduced above, the anisotropy in surface energy enters via the e_{S_i} term.⁵

In Fig. 7 we⁵ show an example of secondary grain growth. In this case, normal grain growth was allowed to occur for 1000 MCS. Then e_{S_i} was chosen such that 2% of the grain orientations had lower surface energy than that of the remainder of the grain orientations (the low energy orientations were assigned $e_{S_i} = -0.1J$). The few (2%) favored grains in Fig. 7 grow such that their radius initially increases linearly with time, followed by impingement with other low energy grains. Eventually the entire microstructure consists of grains with low energy orientations. The mean grain size in the microstructure consisting entirely of low energy oriented grains is determined, in part, by the fraction of orientations with low energy (more low energy orientations implies smaller grain size).

The rate at which the grain orientations are changed by secondary grain growth is indicated in Fig. 8 where we plot the fraction of grains with low energy orientations as a function of time. This plot shows a sigmoidal shape which is characteristic of transformation kinetics.¹ A Johnson-Mehl-Avrami type fit¹ to this curve indicates the following type of kinetics:

$$x = 1 - b \exp(-a t^q)$$

where a and b are constants depending on the fraction of orientations which have low energy and q was found to be 1.8 ± 0.3 , which is close to the theoretical value, $q = 2$. Experimental data on SiO_2 encapsulated Ge films by Palmer¹⁵ show similar secondary grain growth behavior.

V. FIIM MICROSTRUCTURES IN CROSS-SECTION

While the simulations described above are two dimensional, the microstructure of the actual film is three dimensional. The correspondence between the simulation and a film relies on the fact that in the temperature range of interest the microstructure below the surface is frozen in and is determined by the microstructural changes occurring at the free surface. Time in the two dimensional simulation corresponds to depth in the film. This relationship comes from the fact that the free surface moves away from the substrate at a fixed rate. Therefore, in order to examine the microstructure in cross-section (i.e. along planes perpendicular to the substrate and free surface), we need only consider the time dependent location of the grain boundaries.

Such cross-sections are shown in Fig 9 for a microstructure developing under the action of curvature driven growth (i.e. normal grain growth). The kinks on the grain boundaries are a results of the discreteness of the model and would be invisible in a micrograph of an actual film. In Fig. 10 we show the in-plane microstructure at a few different thickness, indicated in Fig. 9. Figure 9 shows how the mean grain size increase as one approaches the free surface. Most of the grains that were present at the substrate have long since disappeared by the end of the deposition/growth simulation. Their disappearance is a result of the growth competition between adjacent grains. Some grains

are seen to increase in size, but eventually lose out to the surrounding grains. What appears at nucleation of new grains in these figures is actually the impingement of a grain which did not initially intersect the plane of the figure. Similarly the apparent coalescence of two grains is attributable to either the advance of a curved grain boundary towards its center of curvature (in a plane parallel to the surface) or the real coalescence of two grains of like orientation (this occurs with probability $1/Q$ in this model).

Since the mean grain size during grain growth increases in time as $t^{0.4}$ (see above), the average grain shape in the plane perpendicular to the surface should appear nearly parabolic. Although this predicts an average grain shape, the growth competition makes it impossible to observe such a morphology. The resultant microstructure does, however, appear essentially columnar. If surface energy anisotropy is present during the growth of the film, the grain shape should increase linearly as the surface is approached, eventually turning over to parabolic growth as all of the grains attain the favored surface orientation and normal grain growth sets in. As for the normal grain growth type of evolution, such shapes are only average in nature and hence may not be seen explicitly in the actual micrograph. We have yet to simulate the cross-section of films grown with anisotropic surface energies. However, since the driving force for secondary grain growth is generally much larger than for normal grain growth, we expect surface energy anisotropy to be important only in the initial stages of film growth, because when the film will be highly textured.

VI. SUMMARY

In cases where the microstructure of the film is determined during the deposition process, the grain morphology of a polycrystalline film may be described in terms of grain growth phenomena occurring on the nominally two dimensional surface. Such a description is, however, only valid in the limit that the grain boundary mobility in the bulk of the film is too low to allow any significant microstructure evolution. An atom deposited onto the surface of the film is able to migrate along that surface, eventually becoming incorporated in a relatively low energy position. Increasing the temperature during the deposition has two effects: allowing the atom to sample a greater region of space and smoothing out the effective energy differences between different sites (see Eqs. 1 and 2). Two possible sources of differing site energies are grain boundary curvature and surface energy anisotropy. Grain boundary curvature leads to a normal grain growth-like mode of film growth. Anisotropic surface energies lead to a secondary grain growth-like mode of film growth.

We have developed a Monte Carlo computer simulation procedure to account for the development of microstructure in films in terms of a statistical model that relies on the energy differences of the various surface sites. This model is inherently two dimensional and hence is capable of describing the evolution of microstructure on the surface. The temporal evolution of the surface microstructure is directly related to the microstructure of the three dimensional film. Since deposition occurs at a fixed rate, the microstructure below the free surface is frozen-in and the free surface moves away from the substrate at a fixed rate. Time in the two dimensional simulation is equivalent to depth in

the three dimensional film. The proportionality constant between time and thickness is a function of temperature, deposition rate and grain boundary energy. Using this analogy, we have shown how competition results in observed film microstructures. Simulation of equiaxed grain microstructures could be performed by adding a nucleation mechanism to the current Monte Carlo procedure. Although the relationship between the two dimensional growth phenomena and film microstructures have only recently been recognized, considerable work has already been done on grain growth phenomena in two spatial dimensions. These include simulations of normal grain growth,^{3,4} secondary grain growth,⁵ grain growth in the presence of a dispersed second phase,¹⁶ and recrystallization.¹⁷

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FIGURE CAPTIONS

1. Mapping of a microstructure onto a discrete lattice. The numbers on each lattice point correspond to the local values of S_i .
2. The temporal evolution of a polycrystalline microstructure. The times are in units of Monte Carlo Steps (MCS).
3. The normalized grain size distribution function, plotted at 15 different times during the same simulation.
4. The normalized grain size distribution function. The histogram represents the grain size distribution function for the present simulation. The solid curve is data for high purity Al^{10} ; the dotted curve is for MgO^{11} ; the dashed curve is Hillert's theoretical prediction.⁸
5. The time averaged, normalized grain edge distribution function. The circles are data points from the simulation and the square are experimental data on Al^{10} .
6. Normalized mean grain radius for each edge class vs. N_c , where N_c refers to the number of grain edges. The circles are simulation results, the squares are data for Al^{10} and the triangles represent data on MgO^{11} .
7. Microstructure undergoing second grain growth. The unshaded grains have orientations with lower surface energy.
8. Fractional area of grains with low surface energy, x , versus time. The result of two simulations (filled and open circles) are displayed, in which (a) 2%, (b) 5%, (c) 10% and (d) 20% of the grain orientations have lower surface energy.
9. Cross sections of the film perpendicular to the surface. Views a-d correspond to the slices indicated in Fig. 10d.

10. Cross sections of the film parallel to the substrate. Views a-d correspond to the slices indicated in Fig. 9d.

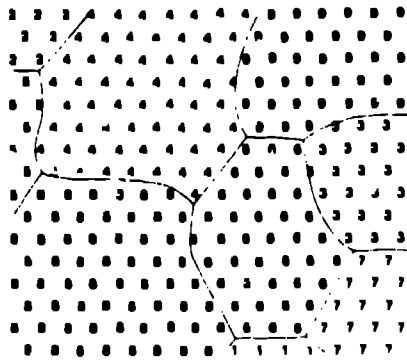


Figure 1

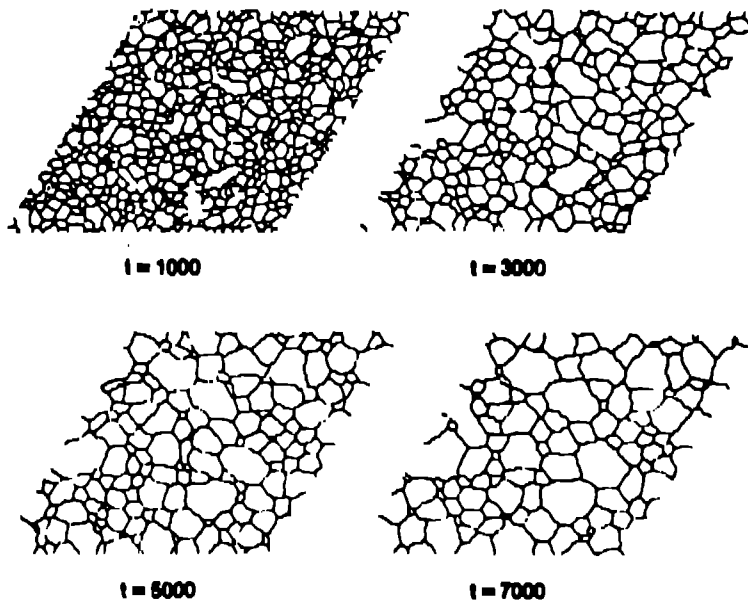


Figure 2

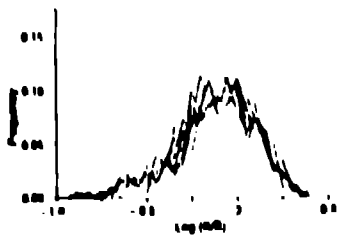


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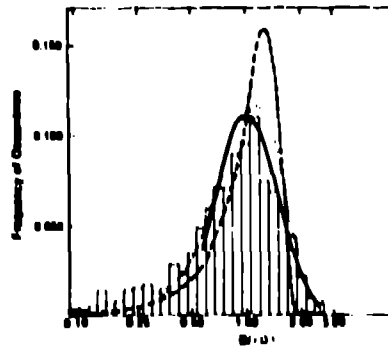


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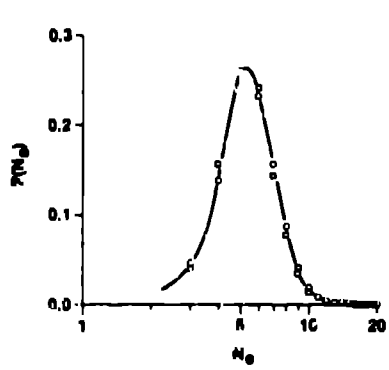


Figure 5

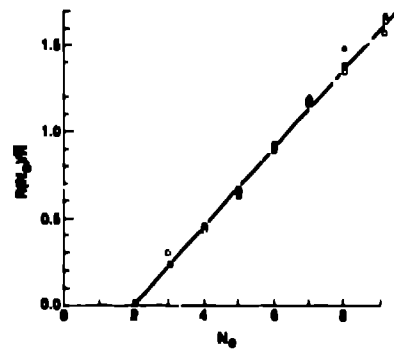


Figure 6

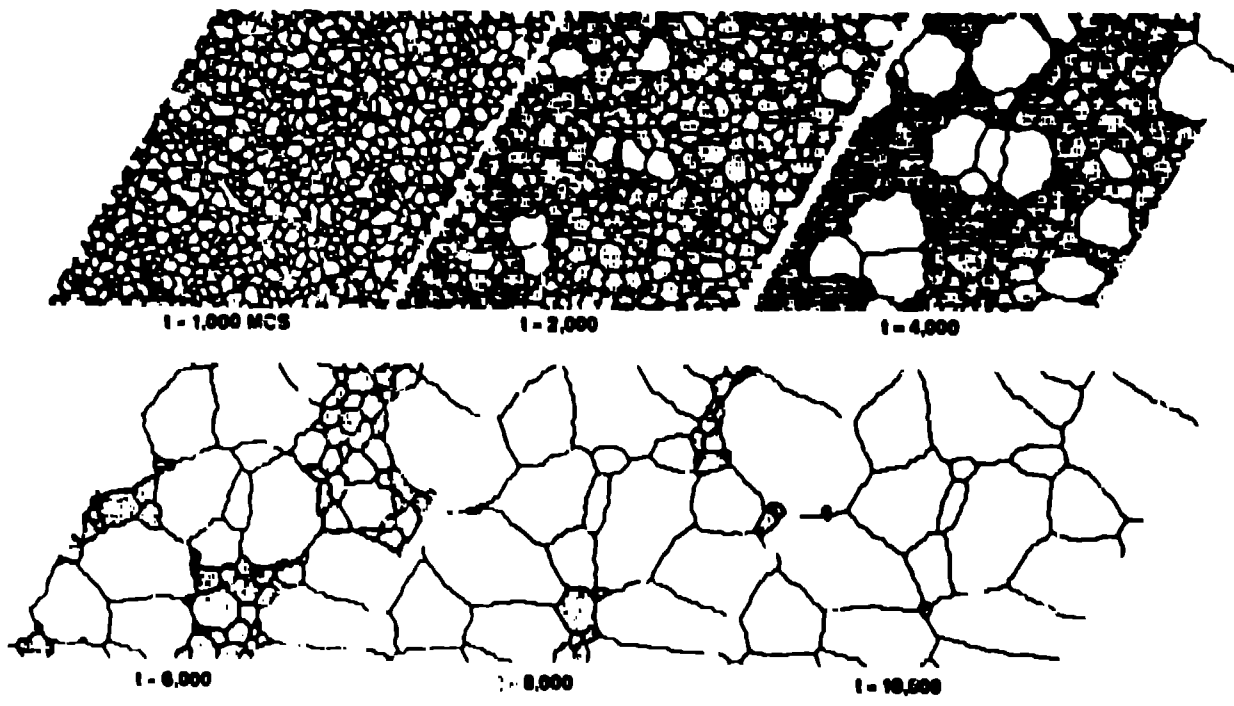


Figure 7

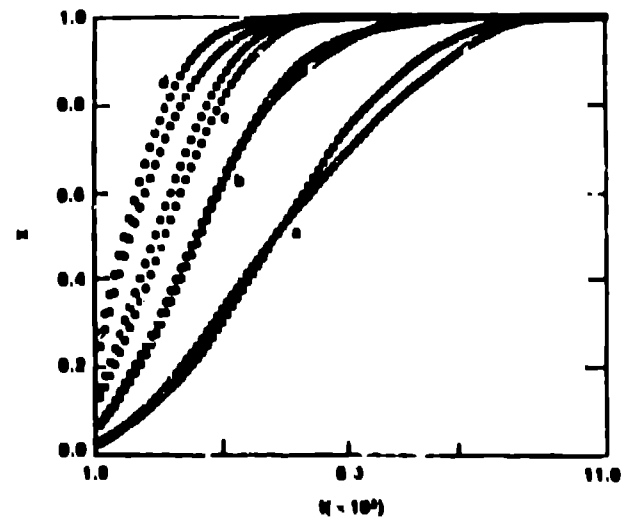


Figure 8

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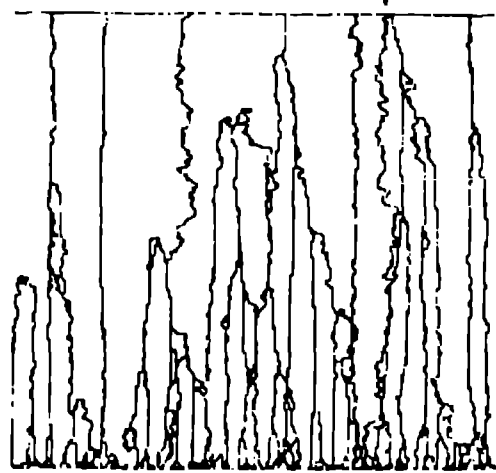
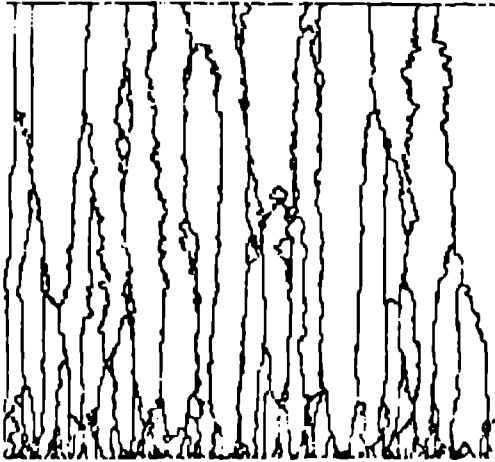
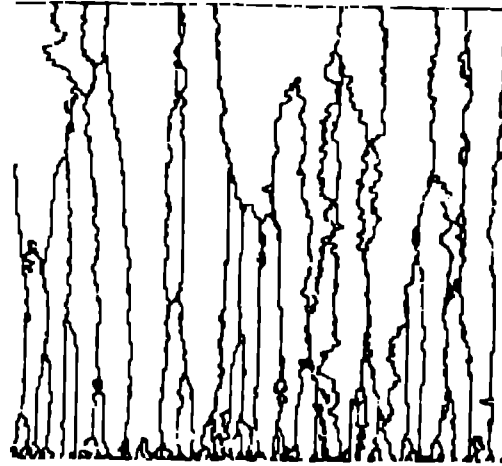
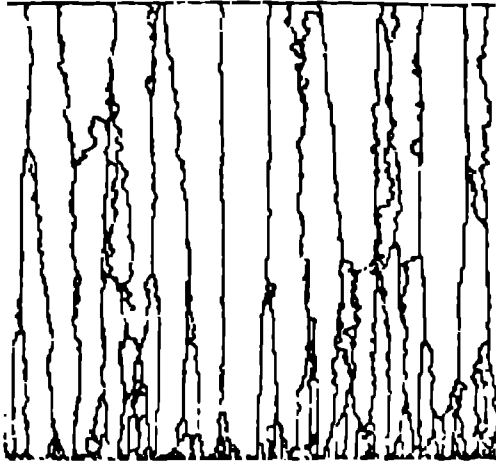


Figure 9

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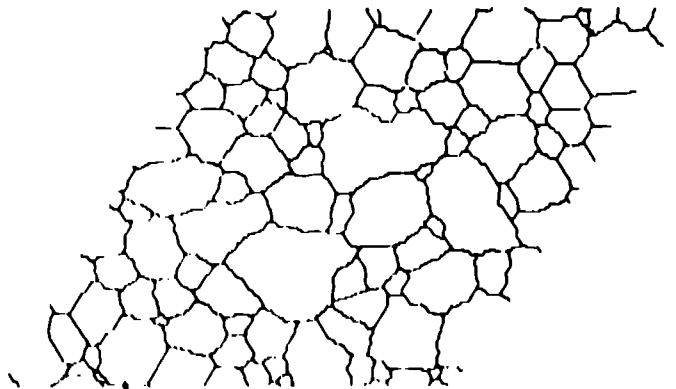


Figure 10