Model-based simulation of normal grain growth in a two-phase nanostructured system

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Abstract

To systematically study normal grain growth in a two-phase volume-conserved system, a modified Potts model is proposed, in which the driving forces for grain boundary migration are the interfacial energy between two phases and the boundary energy inside each phase. Model-based simulation results show that the grain growth kinetics follows a power law with a temperature-independent exponent and that the normalized grain size distribution is lognormal and time invariant. Also, a simple theoretical model is used to predict the potential microstructure in a two-phase system due to the competition between interfacial and grain boundary energies. A critical ratio of the grain boundary energy to the interfacial energy is found for a common two-phase system.

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1. Introduction

Grain growth is a well-known process in the manufacture and use of materials through which various microstructures can be formed. Recent advances in nanostructured materials have shown that, as the average grain size in a material decreases, superior physical and mechanical properties could be achieved. For example, when nanocrystalline TiN is embedded in an amorphous SiN\textsubscript{x} matrix, the hardness of nanostructured Ti–Si–N films reaches a maximum value of more than 40 GPa (defined as superhard) as the average size of TiN grains decreases to several tens of nanometers [1–3]. Similarly, by adding an amount of Al into TiN films, the solid solution (Ti\textsubscript{1-x}Al\textsubscript{x}N) formed has a substantially improved hardness and good thermal stability [4]. Hence, a better understanding towards grain growth processes is of fundamental importance in the fabrication of novel nanostructured materials.

It is commonly believed that the driving force for grain growth is the reduction of total grain boundary energy, achievable by reducing the total grain boundary area of a system. During normal grain growth, the microstructure of a system is expected to reach a steady state, in which only the average grain size increases while the normalized size distribution becomes time invariant [5]. Over the past few decades, a variety of models have been proposed to predict the grain growth kinetics, i.e. time dependence of average grains and their size distribution in single-phase polycrystalline materials [6,7]. Unfortunately, these analytical models are too simple to involve the complexity of grain growth such as topologies, grain boundary interactions, and microstructure evolution. As a result, computer simulation is indispensable and plays a key role in exploring the details of grain growth and validating analytical models. Simulation models for this purpose include the phase field model [5], the Potts model [8], the

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vertex model [9], and others. Among them, the Potts model coupled with the Monte Carlo (MC) procedure is the simplest and most flexible one especially in large system simulation. Originally, the Potts model was proposed to generalize the two-state spin up or spin down ferromagnetic Ising model to systems with arbitrary spin degeneracy [10]. Later, Anderson et al. [8] introduced the model into simulations of grain growth, and Holm et al. [11] used it to study a two-phase volume non-conserved system. Recently, the Potts model has been further extended to explain the grain growth mechanisms of two-phase volume-conserved materials [2,12].

Although great advances have been made in modeling and computer simulations, there is still a lack of systematical studies of grain growth in different systems. In this paper, a general Potts model, an extension of the conventional model, is proposed to investigate single-phase and two-phase (nanocrystalline/amorphous and nanocrystalline/nanocrystalline) grain growth systems. Combined with a MC scheme as in our early work [12], microstructures, growth kinetics, and grain size distributions (GSD) are studied in these systems. Also discussed are the inhibition effects of second phase on grain growth. In addition, the energy anisotropy due to the existence of an electronic, magnetic or mechanical field is introduced in the model, and its effects on grain growth are investigated. Finally, a simple theoretical model is proposed to explain the microstructure transformation induced by the competition between the grain boundary energy and the interfacial energy.

2. Model

In the conventional Potts model, a continuum microstructure is usually mapped onto a discrete lattice [8]. Each lattice site i is assigned a number, $Q_i$, which corresponds to the orientation of the grain in which it is embedded. The grain boundary is defined as one existing between two nearest-neighbor lattice sites with different orientations, which indicates the interaction between these two sites. Thus, the total energy of a two-dimensional $N \times N$ triangular system can be written as

$$E = \frac{1}{2} J \sum_{i=1}^{N^2} \sum_{j=1}^{NN} (1 - \delta_{Q_iQ_j}),$$

where $N^2$ is the total number of lattice sites and $NN$ is the number of nearest neighbors of a lattice site. This simple model is usually used to simulate single-phase grain growth; however, multi-phase grain growth is much more common in the real world, since impurity or second phase particle is usually introduced into the system during preparation of materials. We now modify the Potts model so that it is available to both single- and two-phase systems. In the modified model, an additive attribute $S_i$, indicative of the species A or B, is attached to a lattice site $i$. The interface is assumed to exist between two nearest-neighbor lattice sites with different types and the energy associated with it is denoted by $J_{AB}$. Then, the energy of the whole system becomes

$$E = \frac{1}{2} J_{AB} \sum_{i=1}^{N^2} \sum_{j=1}^{NN} (1 - \delta_{S_iS_j}) + \frac{1}{2} J_A(r_i)$$

$$\times \sum_{i=1}^{N^2} \sum_{j=1}^{NN} (1 - \delta_{Q_iQ_j}) + \frac{1}{2} J_B(r_i) \sum_{i=1}^{N^2} \sum_{j=1}^{NN} (1 - \delta_{P_iP_j}),$$

where $N_A$ and $N_B$ are the numbers of phases A and B with $N_A + N_B = N^2$, $N_{AA}$ and $N_{BB}$ are the numbers of nearest neighbors of a lattice site occupied by A and B, respectively, and $N_{AB}$ is the Kronecker delta function with $\delta_{S_iS_j} = 1$, if $S_i = S_j$, where $Q_i$ (or $Q_j$) and $P_i$ (or $P_j$) are the orientation indices of A and B at site i (or j). Here the orientation indices of A and B at a given site can change in the range of (1, $Q_A$) and (1, $Q_B$), with $Q_A$ and $Q_B$ the total orientation numbers that A and B can choose. The interfacial and grain boundary energies in Eq. (2) are dependent on $r_{ij}$, the direction from site j to site i, which can be induced by external fields such as mechanical, electronic or magnetic fields. In a triangular lattice, $r_{ij}$ may be one of the three directions: $r_1 = 0^\circ$, $r_2 = 60^\circ$ and $r_3 = 120^\circ$. It is obvious that, in the case of $N_A = N$ (or $N_B = 0$), Eq. (2) represents the total energy of a single-phase system. If B has only one orientation, i.e. $Q_B = 1$, the above total energy is reduced to the one proposed by Liu et al. [2], which was used to study grain growth of nanocrystallites in an amorphous matrix. If grain boundaries are isotropic, that is, the direction dependence of $J_{AB}$, $J_A$ and $J_B$ vanishes, Eq. (2) becomes one that can be applied to study two-phase grain growth in nanocrystalline/amorphous materials [12].

3. Computer simulation

As shown in Fig. 1, two events, reorientation and site exchange, are considered in the extended Potts model. The kinetics of boundary and interface migration is simulated by a MC method, in which the probability $P$ of an event being executed is determined using the Metropolis algorithm [13]: if $\Delta E < 0$, then $P = 1$; otherwise, $P = \exp(-\Delta E/kT)$, where $\Delta E = (E_{i+1} - E_i)$ is energy change of the system with $E_i$ and $E_{i+1}$ being energies of the system before and after a selected event occurs, $k$ is Boltzmann constant, and $T$ is temperature. Here, reorientation takes place when two randomly selected sites (i.e. a host site and one of its nearest neighbors) belong to the same phase A or B; whilst site exchange is executed when the states of two selected sites are not identical. Since a grain grows through atom migrations across the grain boundary from one grain to another, it was suggested that the newly attempted orientation should be limited to one of its nearest neighbors to improve the accuracy of the simulations [14,15]. This simple algorithm is adopted in the following MC simulations. Similarly, site exchange is also
limited to one of its nearest neighbors that have different states [2].

3.1. Single-phase system

We first consider the grain growth in a single-phase system that is instructive for a better understanding of such a process in multi-phase systems. Fig. 2 shows the microstructure evolution in a typical single-phase system of $300 \times 300$ and the boundary energy $J_A = 1.0kT_0$, where $T_0$ is a reference temperature that is lower than the melting point. Due to the isotropic grain boundary energy, the direction indices are omitted. Here the initial number of grains immediately after crystallization is about 1400, and after 2000 MC steps there are about 100 grains left. The average grain size vs. time can be described by power-law kinetics: $\bar{R} = Ht^n$, where $H$ is a constant dependent on temperature and $n$ is the grain growth exponent [16]. Such parabolic grain growth kinetics implies that a theoretical grain growth exponent of 0.5 exists for a pure single-phase system [16]. A growth exponent of $\sim 0.49$ was obtained in our simulation, which is supported by experimental results and theoretical predictions [8,16].

During the growth process, a grain boundary tends to migrate towards its curvature center. A small grain has less mobility than its big neighbors, thus it shrinks and finally disappears. This behavior is called the grain annihilation, as demonstrated in Fig. 3(a). In the system, it is found that tri-junctions where three boundaries meet are stable and most favorable; but multi-junctions (where more than three boundaries meet) are unstable and usually decomposed into several tri-junctions. The decomposition is a common feature in the grain growth process. An example is illustrated in Fig. 3(b), where initially grains J and L are neighbors and there is no grain boundary between grains I and K; but, after switching occurs, a new neighbor pair (I and K) forms and the boundary between grains J and L vanishes.

3.2. Two-phase (nanocrystalline/amorphous) system

Provided that some foreign atoms are added into a single-phase system, three kinds of microstructures could
be formed: (1) solid solution, in which the additive atoms replace some of original atoms without changing the lattice structures; (2) two-phase nanocrystalline/amorphous composites, where the additive atoms form an amorphous network; and (3) two-phase nanocrystalline/nanocrystalline composites, in which some crystallites consist of the additive atoms. Actually, solid solution is a single-phase system with similar appearances as shown in Fig. 2. To study the microstructure evolution and grain growth kinetics in a two-phase nanocrystalline/amorphous system, we set $Q_B = 1$, that is, atoms of phase B only have a specified average orientation. As shown by Liu et al. [2] in the simulations of grain growth in superhard Ti–Si–N films, the average TiN grain size was found to decrease with increasing volume fraction of Si consistent with experimental observations. However, it is worth noting that their simulations were performed assuming grain growth is a natural process to reduce the total energy of a system without the imposition of an external field. Generally, mechanical properties such as hardness are measured by indentation, which may induce grain boundary anisotropy.

As shown in Fig. 4, it is obvious that an amorphous phase surrounds TiN grains and the growth kinetics with an exponent of $\sim 0.22$ is almost the same in both isotropic and anisotropic cases. The only difference between these two cases is that grains prefer to grow along a certain direction ($120^\circ$ in Fig. 4(b)) in the anisotropic case. Experiments showed that an amorphous phase always formed a continuous matrix when enough foreign atoms were added [17]. According to our MC simulations (see Figs. 4 (a) and (c)), we found that a continuous amorphous matrix could only be formed when the interfacial energy is much lower than the grain boundary energy.

3.3. Two-phase (nanocrystalline/nanocrystalline) system

Second-phase grains may form by adding a number of foreign atoms during annealing. This process can be studied by setting $Q_B > 1$ in Eq. (2). Fig. 5 shows the
microstructures obtained in two-phase systems with and without an applied external field. The appearance of the microstructures may be different with changes of the boundary energies inside each phase and the interfacial energy between two phases. As the interfacial energy decreases, second-phase grains, similar to the nanocrystal-line/amorphous system, form a continuous band between the grain boundaries of the primary phase. Experiments showed that the grains are uniformly dispersed in Zn–Al [18] and perovskite–periclase systems [19]. Thus, two-phase nanocrystalline/nanocrystalline systems can be formed if the interfacial energy is comparable to the grain boundary energies.

4. Results and discussion

4.1. Grain size distribution

The GSD curves obtained from MC simulations are shown in Fig. 6. In all the three cases, GSDs for each phase can be fitted by a lognormal function

$$f(R) = \frac{1}{\sqrt{2\pi}\sigma R} \exp \left[ -\frac{(\log R - \mu)^2}{2\sigma^2} \right],$$

where $\mu$ and $\sigma$ are the mean value and standard deviation, respectively. The mean values of GSDs sequentially decrease in single-phase, nanocrystalline/amorphous, and nanocrystalline/nanocrystalline systems, so do the standard deviation of GSDs. The GSDs of phases A and B are almost identical in a nanocrystalline/nanocrystalline system. In addition, the shape of GSDs is independent of time, indicating that all the systems lie in a dynamical steady state [5]. The difference between the GSDs of various systems reconfirms that the grain growth of one phase is suppressed due to the presence of the other phase, which results in narrow GSDs in two-phase systems [12]. Also, the relatively narrow distribution of grain sizes and the time-invariant property of GSDs indicate that normal grain growth takes place in these systems [20].

4.2. Inhibition effect of additive atoms

As shown in Figs. 2, 4 and 5, additive atoms work as road blocks that decrease the mobility of other atoms in a two-phase system. This inhibition effect can also be clearly seen in Fig. 6, where the average grain size in a two-phase nanocrystalline/amorphous system is about half of that in a single-phase system (or $\bar{R}_A/\bar{R}_B \approx 1/3$ in a nanocrystalline/nanocrystalline system). It is the inhibition effect that makes the enhancement of mechanical properties such as hardness, which is consistent with the study on their deformation mechanisms in these nanostructured systems under external loads [21]. In contrast to the inhibition effect induced by additive atoms, temperature has a negligible effect on grain growth (see Fig. 7). Furthermore, simulation results showed that the inhibition effect of second phase in a two-phase system may be characterized by a power-law relationship between the grain size ratio, $\bar{R}_A/\bar{R}_B$, and the volume fraction $f_B$ of second phase, $\bar{R}_A/\bar{R}_B = C f_B^q$, where $C$ is a constant and $q$ is a characteristic exponent of $\sim 0.6$ in these two-phase systems [2,12]. The optimal volume
fraction of an additive phase to control grain growth is about 7–11%, which is in agreement with experimental observations [17,22].

4.3. Energy competition

The competition between interfacial and grain boundary energies could result in various microstructures in two-phase systems. For example, in the nanocrystalline/amorphous case, the amorphous phase would be mainly dispersed between grains when the interfacial energy is much lower than the boundary energy and a band structure forms to decrease the total energy of the system. However, when the interfacial energy is comparable to the grain boundary energy, an additive phase may result in second phase particles/grains to ensure the system is in a lower total energy state as in nanocrystalline/nanocrystalline systems. Let us consider a nanocrystalline/amorphous system of triangular grains with a length of \(a\), as shown in Fig. 8(a). For simplicity, we assume that the bands have the same width \(b\) and the particle is a circle with radius \(r\) and is located at the center of the unit cell (see Figs. 8(b) and (c)). Provided that the volume fraction of the amorphous phase is \(f\), the amorphous bandwidth and the total energy in Fig. 8(b) are 

\[
b = a(1 - \sqrt{1-f}) \quad \text{and} \quad E_1 = 6\sqrt{3}(a-b)J_{AB},
\]

respectively. Similarly, the amorphous particle radius and the total energy in Fig. 8(c) are 

\[
r = \frac{3a}{4}\sqrt{\frac{f}{\pi}} \quad \text{and} \quad E_2 = [(3\sqrt{3}a-6r)J_A + 2\pi r J_{AB}],
\]

respectively. The critical energy ratio, defined as \(J_A/J_{AB}\) in the condition of \(E_1 = E_2\), can be represented by

\[
\frac{J_A}{J_{AB}} = \frac{\sqrt{3}\sqrt{3}\sqrt{3}\sqrt{3} - 6\sqrt{3}1 - f \sqrt{3} \pi}{3\sqrt{2}\sqrt{3}f - 3\sqrt{\pi}}.
\]

As depicted in Fig. 9, when \(J_A/J_{AB}\) falls in the shaded region, the amorphous phase prefers to form a particle; otherwise, the band structure is the favorable one due to its lower energy. The critical energy ratios for rectangular and hexagonal grain systems were also given in Fig. 9. It is obvious that the critical energy ratio is dependent on the volume fraction and the maximum critical energy ratio is \(\approx 2.6\) for a general system. That is, a band structure can be formed when \(J_A/J_{AB} > 2.6\) in a two-phase system with arbitrary volume fraction of amorphous phase [3]. Similar results were numerically obtained in a two-phase nanocrystalline/nanocrystalline system.

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Fig. 7. The log-log plots of average grain sizes of phases A and B vs. time at different temperatures.

Fig. 8. Illustration of (a) a cell in a triangular grain system; (b) amorphous phase formed between two grains in a continuous matrix; and (c) a circular particle formed by the amorphous phase.

Fig. 9. Critical energy ratio as a function of the volume fraction of amorphous phase in nanocrystalline/amorphous systems with triangular, rectangular, and hexagonal grains, respectively. Arrow indicates the tendency of curves as the number of faces/boundaries of the grains increases.
5. Conclusion

In this paper, a systematical analysis of grain growth in different systems has been made. The results show that grains in a two-phase system grow slower than those in a single-phase system due to the road-block effect of the amorphous-phase band structure or second-phase grains. The growth exponent is $0.22$ in a two-phase nanocrystalline/amorphous system and $0.16$ in a nanocrystalline/nanocrystalline system, which are much lower than that in the single-phase system ($0.49$). The inhibition effect of additive second-phase has been also qualitatively investigated and an optimal volume fraction within the range of 7–11% was found to control the grain growth. Finally, a simple theoretical model is given to predict the critical energy ratio between grain boundary and interfacial energies in a two-phase system. The value of critical energy ratio predicted by the model implies that, to simulate the grain growth in nanocrystalline/amorphous systems, the interfacial energy should be less than 1/2.6 times the grain boundary energy.

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