The grain refining effect of energy competition and the amorphous phase in nanocomposite materials

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The effect of refining a two-phase nanocrystalline–amorphous (NC–a) nanocomposite microstructure was examined by performing Monte Carlo simulations. The results showed that the ratio of NC–NC grain boundary energy (J_{gb}) and NC–a interfacial energy (J_{int}) determines the two-phase microstructure and controls its stability. The optimal stable microstructure was found with $J_{gb}/J_{int} = 10$ and amorphous fraction $f = 0.15$, where almost all the grains are surrounded by the thinner amorphous phase and the grain size distribution obeys the log-normal form very well.
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Nanocomposite materials exhibit a range of technologically interesting properties, including enhanced hardness, higher fracture toughness, superior ductility, excellent resistance against cracking and lower wear rate compared to their conventional coarse-grained counterparts [1–3]. For example, the hardness of Ti–Si–N nanocomposite films, where nanocrystalline (NC-) TiN grains are surrounded by very thin layers (~1–10 nm) of amorphous (a-) Si_3N_4, can reach up to 70–100 GPa [1,4,5], whereas the maximum hardness of single-phase TiN films is only about 20 GPa [5,6]. These exceptional properties are primarily attributed to their stable microstructure, with NC grains embedded in amorphous matrix. Thus, the most fundamental microstructural information, including NC grain sizes and their distributions, is significant in determining the macroscopic properties. A microstructure with small grains and a high density of grain boundaries per unit volume has been observed in many nanocomposite materials with excellent physical and mechanical properties [7].

Previous experimental studies have focused mainly on the microstructural optimization and amorphous phase control of nanocomposites. The most direct method is to adjust the ratio of additive elements in materials in order to reduce the grain size and enhance the mechanical properties. However, it is noteworthy that microstructures and properties of nanocomposites with the same ratio of additive elements can be different from each other under different experimental conditions. Take NC-TiN/a-Si_3N_4 as an example: different research groups have obtained different values of maximum achievable hardness, and its dependence on the Si content differs considerably [8]. Though it has been found experimentally that the deposition conditions have a significant influence on the microstructures and properties of materials, in-depth theoretical work is very limited. The formation of the nanostructured composite is a self-organization process that occurs via phase separation and the interaction between the different phases, i.e. NC–NC and NC–a interactions [9]. From an energetics point of view, different NC–NC and NC–a interactions are related to different NC–NC grain boundary energies and NC–a interfacial energies, and the competition of these energies plays a key role in forming different microstructures of the system. In this letter, we present systematic calculations and analysis of various energies, which control and refine the material's microstructure, with a Monte Carlo (MC) approach based on a modified Q-state Potts model [10–13].

A two-dimensional MC model with an $N \times N$ ($N = 200$) triangular lattice is used in this work. Both

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NC and a phases are assumed to occupy the lattice sites with periodic boundary conditions. The number of the lattice sites occupied by the NC species is denoted as N_A and the fraction f of a phase is determined by the ratio of $(N^2 - N_A)/N^2$. Each lattice site owns two distinct spin states (S, Q) due to the coexistence of the NC and a phases. Here, S represents the species ($S = 1$ for the NC species and $S = 0$ for the a species) and Q denotes the orientation state, with $Q = 1$ to $Q = 50$ for the NC species and $Q = 0$ for the a species. $Q = 1$ means that the system is a single crystal with only one orientation and no grain boundary, whereas $Q = 2$ indicates that the system is composed of a bicrystal with two orientations and two kinds of grain boundaries: a 90° angle grain boundary and very low angle boundary, as illustrated in Ref. [14]. Microstructures with various orientations will be formed if $Q > 2$. In the grain growth model, a sufficiently large value of Q should be chosen to avoid frequent impingement of grains with identical orientations. Thus, $Q = 50$ is chosen in our simulation, as it has been validated that the simulation results are essentially independent of Q as long as $Q > 36$ [10,11]. Normal grain growth is characterized by two events: successful site reorientation at grain boundaries with neighbors that have the same S value but different Q states or site exchange between neighbors that have different S values. Note that the reorientation event can be omitted for the amorphous phase. The total energy of the system (E) includes the NC–NC grain boundary energy (E_{gb}) and the NC–a interfacial energy (E_{int}) as below [12,13]:

$$E = E_{gb} + E_{int} = \frac{1}{2} J_{gb} \sum_{i=1}^{N^2} \sum_{j=1}^{NN_A} (1 - \delta_{Q_i Q_j})$$

$$+ \frac{1}{2} J_{int} \sum_{i=1}^{N^2} \sum_{j=1}^{NN} (1 - \delta_{S_i S_j}) \quad (1)$$

where NN is the nearest neighbors of a lattice site ($NN = 6$ for the triangular lattice), with NN_A occupied by the NC species. J_{gb} and J_{int} scale the isotropic E_{gb} and E_{int}, respectively. $\delta_{S_i S_j}$ or $\delta_{Q_i Q_j}$ is the Kronecker delta function, with $\delta_{S_i S_j}$ or $\delta_{Q_i Q_j}$ equaling unity if $S_i = S_j$ or $Q_i = Q_j$ and zero otherwise. The site exchange or reorientation probability P is based on the Metropolis algorithm [10]: if $\Delta E \leqslant 0$ then $P = 1$, otherwise $P = \exp(-\Delta E / k_B T)$. Here, ΔE is the energy change of the system associated with the occurring event; k_B is the Boltzman constant; and T is the simulation temperature.

As mentioned in the calculation algorithm, the NC–NC grain boundary energy and NC–a interfacial energy are set by the magnitudes of J_{gb} and J_{int}; therefore, it is simple and convenient to analyze the influence of the NC–NC grain boundary energy and the NC–a interfacial energy based on J_{gb} and J_{int}. Furthermore, the competition between the NC–NC grain boundary energy and the NC–a interfacial energy is illustrated as J_{gb}/J_{int}; our previous work has shown that J_{gb}/J_{int} should not be less than 3 in order to form continuous amorphous matrix in a two-phase system [12]. Thus, we set the ratio of J_{gb}/J_{int} between 3 and 13 in the system with a fixed amorphous fraction value of $f = 0.06$ after a time duration of Monte Carlo steps (MCS) = 2000.

The grain growth process can reach its size plateau in a short time, resulting in a decreased finite grain size D_f (the grain size at the plateau phase) as J_{gb}/J_{int} increases, as shown in Figure 1(a) and (b). For the system with $J_{gb}/J_{int} = 3$, grains initially grow at a high speed, before gradually slowing down. Similar grain growth kinetics is also observed for J_{gb}/J_{int} ranging from 4 to 7. However, the grain growth kinetics changes dramatically to that characteristic of bilinearity from $J_{gb}/J_{int} = 8$, with grains growing rapidly to D_f and then remaining at the same size with increasing time. Increasing the competition (J_{gb}/J_{int}) of the NC–NC grain boundary energy and the NC–a interfacial energy leads to the restricted grain size in a shorter period of time, as can also be seen in Figure 1(b). This result indicates that D_f keeps decreasing up to $J_{gb}/J_{int} = 10$, at which point the grain size becomes constant and remains so with further increasing J_{gb}/J_{int}. The same trend is also found for the time interval to reach D_f. For systems with the same fraction of amorphous phase, the microstructures of systems with larger J_{gb}/J_{int} values have a larger number of smaller grains (Fig. 1(c)) than those with smaller J_{gb}/J_{int} values, which have larger grains (Fig. 1(d)).

From a thermodynamics point of view, a microstructure tends to form an energetically favorable configuration. The microstructural evolution, including the formation of a continuous amorphous matrix around NC grains, and the growth of the NC grains themselves
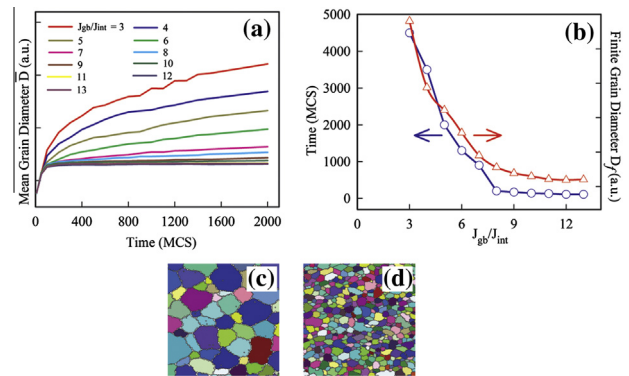

Figure 1. (a) Simulated mean grain diameter ($\overline{D}$) as a function of time, in units of Monte Carlo steps (MCS), at various J_{gb}/J_{int} values. (b) Grain growth processes reach the size plateau in a shorter time and can have a decreased finite grain size (D_f) as J_{gb}/J_{int} increases. (c, d) The simulated microstructures of the system with $J_{gb}/J_{int} = 3$ and $J_{gb}/J_{int} = 10$, respectively, at the grain size plateau.
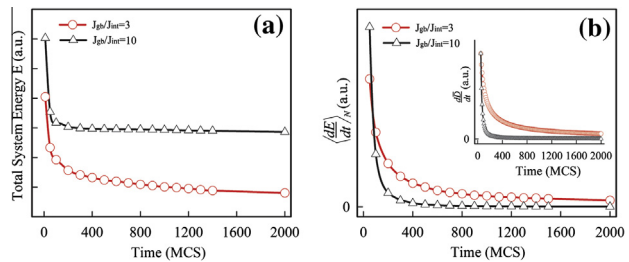

Figure 2. (a) Total system energy E, calculated based on Eq. (1), at the conditions of $J_{gb}/J_{int} = 3$ and $J_{gb}/J_{int} = 10$. (b) Average reduction rate of the total system energy E exerted on each grain $\langle \frac{dE}{dt} \rangle_N$ in the above two systems. The inset shows the corresponding grain growth rate of $\frac{d\overline{D}}{dt}$.