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Atomic-scale simulation of nano-grains: structure and diffusion properties*

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Abstract: Nanograins are characterized by a typical grain size from 1 to 100 nm. Molecular dynamics simulations have been carried out for the nanograin sphere with the diameters from 1.45 to 10.12 nm. We study the influence of grain size on structure and diffusion properties of the nanograins. The results reveal that as the grain size is reduced, the fraction of grain surface increases significantly, and the surface width is approximately constant; the mean atomic energy of the surface increases distinctly, but that of the grain interior varies insignificantly; the diffusion coefficient is increased sharply, and the relation of the diffusion coefficient and the grain size is close to exponential relation below 10 nm.

Keywords: ; Nano-grain; Structure; Diffustion property; Molecular dynamics simulation

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1 Introduction

Nano-grains, i.e. typical grain sizes from 1 to 100 nm, have two remarkable peculiarities, namely, ultra-fine grain size and a large fraction of surface, and display technologically interesting properties[1], such as dramatically decreased melting point, increasing with decreasing grain size[2]. Nano-grains exhibit some effects, such as surface effect, small size effect, etc., which are considerably different from their coarse-grained counterparts[3,4]. These effects are closely related with the structure of nanograins. However, it is a pity that the structural studies on nanograins are rarely reported.

Due to the small grain size, direct atomic-scale simulations of structure and properties of nano-grains are possible. The atomic-scale calculations provide a useful tool to analyze structural, mechanical properties of nanocrystalline materials[5,6]. Molecular dynamics (MD) approach, as one of most important methods of atomic-scale simulations, provides the phase-space trajectories of particles through the solution of Newton's equation, thereby shedding light on that how atomic level processes lead to macroscopic phenomena, so it can help understanding the relationship between structure and overall properties. MD simulation may display trajectories of atomic motion, and may be used to carry out a variety of observations similar to those in experiment, especially those details, related with atoms, can be easily acquired through MD simulation but can not in experiment.

In this paper, we present molecular dynamics

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simulations of structure and diffusion properties of nanograins. We investigate the nanograin structure, and study the influence of grain size on the structure and diffusion properties of nanograins.

2 Simulations

Molecular dynamics simulations were performed with a Finnis-Sinclair potential[7,8] for copper. To simulate the structure of nanograins with computer, we construct seven nanograin spheres (Cu_1.45, Cu_2.89, Cu_4.38, Cu_5.78, Cu_7.23, Cu_8.68, and Cu_10.12), which represent nanograin of diameters from 1.45 to 10.12 nm, and contain the number of atoms from 141 to 46 049. In order to eliminate unfavourable configurations in nanograins, these nanograin spheres are prerelaxed by running a 60 ps at 300 K. The initial velocities were assigned according to a Maxwell-Boltzmann distribution corresponding to 300 K. Doubling the duration of prerelaxing has no significant effect on the structure of nanograins. The atomic trajectories were followed by integrating the Newton's equation of motion for each atoms with the Frog-Leap algorithm[9]. The time-step in simulation is $\tau_0 = 2.0 \times 10^{-15}$s, the unit of energy 1.0 eV, and the unit of length $a_0 = 3.615 \times 10^{-10}$m.

To facilitate the structural analysis of simulations, we identify which atoms are located at grain surface and which are inside the grains, by determining the local crystalline order in terms of a bond analysis technique described in reference [10]. We may define three categories of atoms: 'fcc', atoms having a local fcc order are considered to be inside the grains; 'hcp'. Atoms having a local hcp order are classified as stacking faults; and all other atoms ('other' atoms) are considered as belonging to grain surface. The atomic energy distribution is a useful way to describe the structure of a system, and is also used in present paper. The following structural results are obtained by analyzing the atomic configurations of the samples at the end of 30 000 steps, using these techniques.

In order to simulate the diffusion properties of nanograins, we define $t = 0$ as the pre-relaxation of nanograins is over, and continue to relax the seven spheres 40 000 steps at 300 K. As the simulation progressed, the trajectory of each atom was generated, and the trajectory information was saved for sequent analysis.

From the coordinate data stored in the trajectory files, the mean-square displacement (MSD) for all the movable atoms were calculated, and the diffusion coefficient, D_{MSD}, computed using Einstein's relation[11]

$$D_{\mathrm{MSD}} = \frac{\sum_{i=1}^{N} (r_i - r_{i0})^2}{6Nt} \tag{1}$$

where N is the number of moving atoms in nanograin, and t the relaxed time elapsed in the simulation, r_{i0} is the original time $t = 0$ position of atom i, and r_i its current position.

3 Results and discussion

3.1 Structure and atomic energy

The atom structure of nanograin Cu_10.22 sphere, pre-relaxed by running a 60 ps at 300 K, is illustrated in cross section in Fig. 1 through the center of the grain. It may be clearly seen that all 'fcc' atoms are located in grain interiors and 'other' atoms are uniformly distributed in the fringe of grains. There is no 'hcp' atom in the grain. This shows that the structural analysis is appropriate, and the computer-generated nanograins are accordant with those observed experimentally.

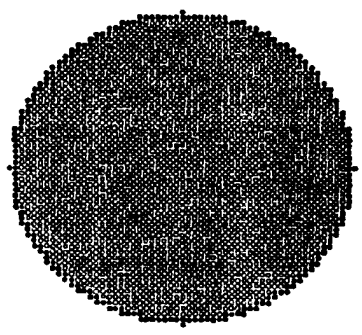

Fig. 1 Snapshots of the simulated nanograin Cu_10.12 sphere. which contains 46 049 atoms. Open circles, and solid circles denote 'fcc' atoms, and 'other' atoms, respectively. There is no 'hcp' atoms in the grain

Fig. 2 displays the structural analysis results of seven spheres. From this figure, we see an decrease of the fraction of the 'fcc' atoms (from 86.8% to 30.5%) and a corresponding increase of that of the 'other' atoms (from 13.2% to 69.5%) as grain sizes is reduced, but there is no 'hcp' atom. This indicates that the fraction of grain surface increases significantly with decrease of grain sizes if we consider 'other' atoms as belonging to grain surface. Fig. 2 also exhibits the grain size dependence of the fraction of surface atoms with surface width of $\delta_{GS} = 0.65\ a_0$, which is very close to that of 'other' atoms, indicative of the surface width being approximately constant with decrease of grain size. Fig. 3 shows the mean energy per atom as a function of grain size. As we would expect, the mean atomic energy of the surface is higher than that of grain interior. With the decrease of grain size, the former increases distinctly, but the latter varies insignificantly, and slightly higher than that of the perfect crystal.

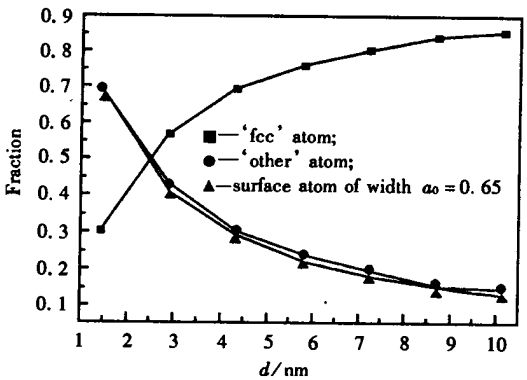

Fig. 2 The structural variation of nanograin Cu as a function of grain size

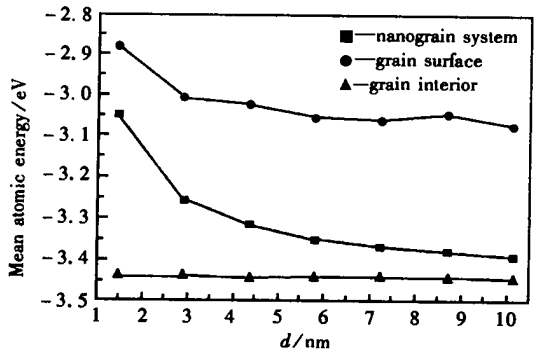

Fig. 3 Ths grain size dependence of the mean atomic energy of system, grain surface and grain interior

3.2 The diffusion properties

With the decrease of grain size, the fraction of surface as well as the mean atomic energy of surface is increased significantly, which may provide a high density of short diffusion paths. Thus the nanograins are expected to exhibit an enhanced self diffusivity in comparison to single crystal or coarse-grained counterpart. The diffusion coefficients were obtained from a linear least square fit of mean-squared displacement (MSD) to Einstein's relation. A typical MSD curve is shown in Fig. 4, representing the time evolution of ensemble average of each atom diffusing inside the grain.

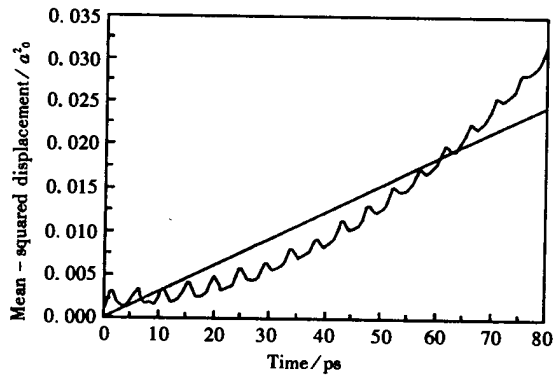

Fig. 4 Mean square displacement of atoms in nanograin Cu–10.12 vs simulation time at 300 K. The linear data mean random – walk diffusion is taking place; the slopes of straight – line fit is proportional to the diffusion coefficient

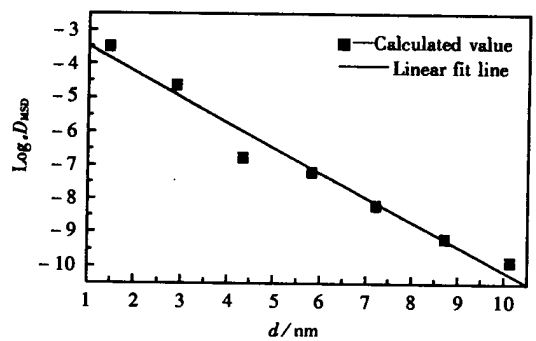

Fig. 5 The grain size dependence of the natural logarithm of the diffusion coefficients. The straight line is the linear fit line of the natural logarithm of the diffusion coefficients to the grain size. This indicates the strong influence of grain sizes on the diffusion properties

Fig. 5 shows the results for the diffusion coefficients of the nanograins studied. The diffusion coefficients, D_{MSD}, is sharply increased when the grain size is

decreased. If we use the exponential function to fit the relation of the diffusion coefficient and the grain size, as shown in fig.5, we may get the following expression

$$D_{MSD} = 0.063\ 1\ e^{-0.735d} \quad (2)$$

where d is the grain size, e the exponential constant (base of natural logarithms). This indicates the strong influence of the grain size on the diffusion properties. In order to calculate the activation energy Q for atomic motion and the prefactor D_0, it is necessary to simulate D_{MSD} at various temperatures and to fit to the general diffusion relation

$$D_{MSD} = D_0 \exp[-\frac{Q}{k_B T}] \quad (3)$$

where k_B is Boltzmann constant, T the absolute temperature, but the related simulations remain to be made.

4 Conclusions

We perform molecular dynamics simulations of the nanograin spheres with the grain diameters ranging from 1.45 to 10.12 nm, and study the influence of grain size on the structure and diffusion properties of the nanograins. It is revealed that as the grain sizes is reduced, (ⅰ) the fraction of grain surface increases significantly, and the surface width is approximately constant (about 0.65 a_0); (ⅱ) the mean atomic energy of the surface increases distinctly, but that of the grain interior varies insignificantly, and slightly higher than that of the perfect crystal; (ⅲ) the diffusion coefficients is increased sharply, and the relationship of the diffusion coefficient and the grain size is close to exponential relation in nanometer scales we study.

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