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Molecular Dynamics Simulation of Microstructure of Nanocrystalline Copper

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The microstructure of computer generated nanocrystalline coppers is simulated by using molecular dynamics with the Finnis–Sinclair potential, analysed by means of radial distribution functions, coordination number, atomic energy and local crystalline order. The influence of the grain size on the nanocrystalline structure is studied. The results reveal that as the grain size is reduced, the grain boundary shows no significant structural difference, but the grain interior becomes more disordered, and their structural difference diminishes gradually; however, the density and the atomic average energy of the grain boundary present different tendencies from those of the grain interior.

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The interest in nanostructured materials has rapidly grown since nanocrystals were synthesized nearly two decades ago through consolidation of small clusters formed via gas condensation by Gleiter and co-workers.[1] Nanocrystalline material (NcM), characterized by a typical grain size from 1 to 100 nm, has two remarkable peculiarities, namely, the ultrafine-grain sizes and a large fraction of grain boundaries, which may play a crucial role on its properties. The early structural studies on NcMs, carried out by Gleiter *et al.*,[2] involving x-ray diffraction, Mossbauer spectroscopy and extended x-ray absorption fine structure (EXAFS), suggested a 'frozen-gas-like' atomic structure which was thought to arise from a significant fraction of atoms in highly defected grain boundary environments. However, recent experimental results indicated that the atomic structure of GBs was ordered or disordered, and the fraction of order and disorder structures was related with the generation, synthesis techniques and heat treatment processing.[3] On the other hand, the experimental observations through x-ray, neutron scattering, scanning electron microscope etc, indicated that the atomic structures of GBs in NcMs are similar to those in coarse-grained polycrystalline materials.[4] Computer simulation shows that the structures of GBs are highly ordered and similar to the amorphous structure.[5] However, the researches are rarely concerned with the structure of the grain interior of NcMs.

To computer simulate the microstructure of NcMs, we construct nanocrystalline samples with structures similar to those observed experimentally. Five samples with 8, 27, 64, 125 and 216 grains (Cu_5.27, Cu_3.46, Cu_2.56, Cu_2.01, and Cu_1.65), which represent average grain sizes ranging from 5.27 to 1.65 nm, are constructed by filling the simulation cell volume of an 8.67 nm cube. The grains are produced by a Voronoi polyhedron construction[6] in which a set of grain centres and crystallographic orientation of each grain are chosen at random. Those atoms in the GBs closer than $\sqrt{2}a_0/2$ are removed, where a_0 is the lattice constant of the perfect crystalline copper. In order to eliminate unfavourable configurations in grain boundaries, the samples are relaxed by running a 50 ps at 300 K and 1 atm, using molecular dynamics simulation with a Finnis–Sinclair potential[7,8] in the Berendsen approach,[9] and periodic boundary conditions that replicate the cube infinitely in all three spatial directions. Doubling the duration of relaxing has no significant effect on the structure of the samples. The atomic trajectories were followed by integrating Newton's equation of motion for each atoms with the Frog-Leap algorithm.[10] The time-step in simulation is $\tau_0 = 1.0 \times 10^{-14}$ s, the unit of energy 1.0 eV, and the unit of length $a_0 = 3.615 \times 10^{-10}$ m.

Generally, the characterization of the microstructure may be made in several ways: by the radial distribution function (RDF), by atomic energy and coordination number of the grain interior and the grain boundary region, and by the local crystalline order in terms of a bond analysis technique described in Ref. [11] and suggested to be used in this context by Schiotz *et al.*[12] The following results are obtained by analysing the atomic configurations of the samples at the end of 5000 steps, using these techniques.

According to the model proposed by Kim and Bush,[13] NcM may be divided into four states: grain interior, grain boundary, grain junction and pore. In a sufficiently relaxed sample, the fraction of pore-state, in fact, is very small and negligible, and the structure of grain junction is close to the structure of grain boundary. Thus we may consider NcM to consist of two states: grain interior and grain boundary. If the average grain size is d, the volume fraction of the latter is $f_{gb} \sim 3\delta_{gb}/d$, where δ_{gb} is the width of the GB. In the analysis of their atomic structures, the effective width of $\delta_{\rm gb} = a_0$, suggested by Wang,[14] is used in this letter.

Table 1. Average atomic energy (E/atom in eV), local crystalline order and distribution of coordination number (Z) of the grain boundary/grain interior in the five samples.

	Cu_5.27	Cu_3.46	Cu_2.56	Cu_2.01	Cu_1.65
E/atom (eV)	−3.351/−3.422	−3.357/ − 3.408	−3.361/ − 3.393	−3.361/ − 3.383	−3.356/ − 3.367
Perfect fcc	0.01/36.81	0.06/16.45	0.04/5.60	0.01/1.43	0.0/0.05
Good fcc	17.24/48.49	20.15/53.06	18.22/46.89	14.90/36.94	7.96/19.97
Perfect hcp	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0
Good hcp	1.62/0.28	4.70/2.16	6.15/3.81	7.11/5.18	3.99/4.29
Other $Z = 12$	33.47/ 6.68	34.50/ 13.97	35.58/ 22.13	38.09/ 28.44	43.64/ 37.89
$Z > 12$	10.06/ 1.42	11.19/ 3.93	13.22/ 7.22	14.42/ 10.63	18.44/ 16.05
$Z < 12$	37.60/ 6.31	29.39/ 10.41	26.42/ 14.34	25.33/ 17.36	25.97/ 21.73

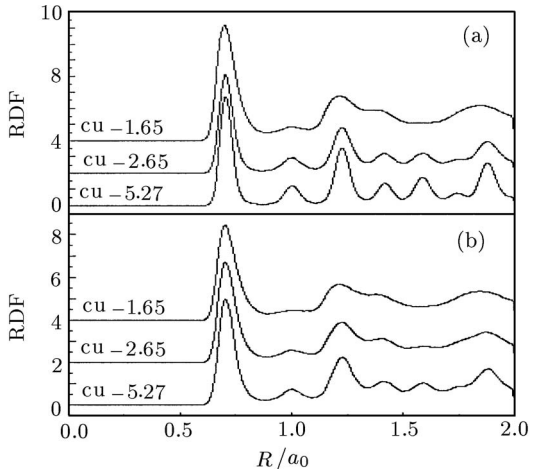

Fig. 1. Radial distribution functions of Cu_5.27, Cu_2.56, and Cu_1.65 samples: (a) grain interior region; (b) grain boundary region.

Figures 1(a) and 1(b) give the radial distribution functions of the grain interior and the GB of Cu_5.27, Cu_2.56 and Cu_1.65 samples, respectively. Figure 1(a) shows that the RDF of the grain interior in the Cu_5.27 sample has seven distinct peaks, and in Cu_2.56 five peaks, but in Cu_1.65 only three peaks, and the second and third peaks have been broadened. This indicates that the order degree of the grain interior is closely related to average grain size. With the average grain size varying from 5.27 to 1.65 nm, the atomic structure of the grain interior deviates gradually from the long-range order of the perfect crystal. In figure 1(b), the atomic structure of the GB shows no significant difference in the three samples; the second peak has already been broadened and presents a low intensity, indicating that the grain boundary is highly disordered but not completely amorphous, which seems not to be consistent with some simulation results.[5] By comparing the two figures, we may find that the structural of the grain interior is close gradually to that of the GB with the decrease of average grain size.

Let us analyse the structure of the five samples by determining the crystalline order. Using the bond analysis, we may define six categories of atoms: 'perfect fcc', atoms having a local fcc order till fourth neighbours; 'good fcc', atoms having a local fcc order till first neighbours; 'perfect hcp', atoms having a local hcp order till fourth neighbours; 'good hcp', atoms having a local hcp order till first neighbours, atoms having other twelve coordinated combinations and finally the non-twelve coordinated atoms, as described in Refs. [15,16]. We use this technique to analyse the structure of GB and grain interior. The distributions of the atoms of different categories in the five samples are given in Table 1.

In Table 1, the 'perfect fcc' atoms are very few in the GBs of the five samples, but the fraction of the 'good fcc' atoms is between 8% and 20%. A large fraction of atoms belong to other twelve coordinated or non-twelve coordinated (about 75% − 88%), suggesting also that the grain boundary is highly disordered but not completely amorphous. Comparing the fraction of atoms of different categories, we find no significant difference in the grain boundary structure of the five samples, which may be seen from their RDF in Fig. 1(a). The percentage difference between under-twelve coordinated and over-twelve coordinated atoms (27.6% in Cu_5.27, 18.2% in Cu_3.46, 13.2% in Cu_2.56, 10.9% in Cu_2.01 and 7.5% in Cu_1.65), decreases with average grain sizes varying from 5.27 to 1.65 nm, and is reflected in the increase of the density of the GB of these samples.

Table 1 also presents the analysis results of the grain interior structures. The 'perfect fcc' atoms decrease sharply when the average grain size decreases. The fraction of the 'good fcc' atoms increases first, and then decreases, and the other twelve coordinated atoms and non-twelve coordinated atoms increase from 14.41% to 75.67%, indicating that the distortion of lattice becomes more severe and the disorder degree of the grain interior higher. The increase of the 'good fcc' atoms is due to the fact that some 'perfect fcc' atoms turn into 'good fcc' atoms with decrease of average grain size. It is worth noticing that the fraction of different categories of the grain interior is close to those of the GB in the Cu_1.65 sample, suggesting that their structural difference diminishes gradually as the average grain size is reduced. This is consistent with the result of their RDF. The difference between the under-twelve coordinated and over-twelve coordinated atoms is higher than 5%, suggesting that the density of the grain interior is lower than that of the

perfect crystal.

There is no 'perfect hcp' atom either in the GB or in the grain interior. The number of 'good hcp' atoms is greater in the GBs than in the grain interior, and most of the 'good hcp' atoms are located in the GBs. This table also shows that the atomic average energy of the GBs, in fact, varies insignificantly with the decrease of the average grain size from 5.27 to 1.65 nm, but that of the grain interior increases distinctly with an increment of 0.055 eV, which may result from the severe lattice distortion in the grain interior. The atomic average energy of the GB is always higher than that of the grain interior for each sample, which is in accordance with the results in Ref. [17].

In summary, molecular dynamics simulations have been carried out for nanocrystalline copper with average grain sizes ranging from 5.27 to 1.65 nm. It is revealed that as the average grain size is reduced: (i) the atomic structure of the GB shows no significant difference but the disorder degree of the grain interior becomes higher, the grain boundary is highly disordered but not completely amorphous, and the difference of the grain interior and the grain boundary diminishes gradually; (ii) the density of the grain boundary increases but the atomic average energy of the grain boundary varies insignificantly, the density of the grain interior is lower than that of the perfect crystal, and the atomic average energy of the grain interior increases distinctly.

References

[1] Gleiter H 1981 *Proc. Second Riso Int. Symp. Metal. Mater. Sci.* ed Hansen N et al (Roskilde, Denmark) p 15

[2] Gleiter H 1989 *Prog. Mater. Sci.* **33** 223

[3] Li D X, Ping D H, Ye H Q, Qin X Y and Wu X J 1993 *Mater. Lett.* **18** 29

[4] Siegel R W 1994 *J. Phys. Chem. Sol.* **55** 1097

[5] Keblinski P et al 1997 *Acta Mater.* **45** 987

[6] Finny J L 1976 *Mater. Sci. Eng.* **23** 199

[7] Finnis M W and Sinclair J E 1984 *Phil. Mag.* A **50** 45

[8] Ackland G J and Vitek V 1990 *Phys. Rev.* B **41** 10324

[9] Berendsen J P C 1983 *J. Chem. Phys.* **81** 3684

[10] Amini M 1990 *Comput. Phys. Commun.* **56** 313

[11] Honeycutt J D et al 1987 *J. Phys. Chem.* **91** 4950

[12] Schiotz J, Tolla D F and Jacobsen K W 1997 *Proc. ISMANAM Conf.* (Barcelona) p 236

[13] Kim H S and Bush M B 1999 *Nanostruct. Mater.* **11** 361

[14] Wang J, Wolf D and Phillpot S R 1996 *Phil. Mag.* A **73** 517

[15] Swygenhoven H V and Caro A 1998 *Mater. Res. Soc. Symp. Proc.* **492** 357

[16] Swygenhoven H V, Spaczer M and Caro A 1998 *Nanostruct. Mater.* **10** 819

[17] Phillpot S R and Wolf D 1995 *J. Appl. Phys.* **78** 847