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Final Structures of Crystallization of Liquid Copper Studied by Molecular Dynamics Simulation *

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Molecular dynamics simulation is performed to study the cooling rate effects on the resulting crystallization microstructure of bulk liquid copper (homogeneous nucleation). Our studies reveal that mixtures of the metastable hcp phase and most-stable fcc phase, in all sorts of proportion and in various forms such as layering and phase separation, can be obtained by controlling the cooling rate. We have also found that, below the glass forming critical cooling rate, the ratio of the number of fcc-type polyhedra to the number of hcp-type polyhedra at 0 K decreases with increase of the cooling rate.

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It is well known that the cooling rate is a critical factor affecting the resulting structure during a liquid–solid transition. Much work has been done on the dependence of the glass structure of both model systems and more realistic systems on the cooling rate.[1] Although the process of crystallization has also been modeled,[2,6–8] the dependence of the resulting structure of crystallization on the cooling rate has seldom been explored. In a previous work[2] about the effects of system size on homogeneous nucleation, there is a suggestion that the resulting crystallization configuration is a mixture of all kinds of crystal structures (hcp, fcc, and bcc), and an fcc phase that is not the most stable can be obtained at zero temperature. In a recent paper giving a computer simulation of free energy barriers in crystal nucleation,[3] it was said that a metastable bcc phase can easily be obtained from the liquid. However, what relationship is there between these results and the cooling rate?

In most previous simulations of crystallization and glass formation, model pair potentials were used.[2] These pair potentials neglected the many-body interaction that is very important for transition and noble metals.[4,5] Recently, many-body potentials have also been adopted to simulate these processes of liquid copper[6] and some other real metal liquids.[7,8] However, the relationship between the final crystallization structure and cooling rate is absent also.

The tight-binding second-moment approximation[5] (TB-SMA) many-body potential is a well-studied semi-empirical many-body interaction potential and has been widely used in numerical simulation in metals and alloys. In this paper we adopt the set of parameters for copper fitted by Cleri and Rosato.[5] The pair correlation functions we obtain have a very good quantitative agreement with the experimental data.[9] Hence, both solid and liquid structures of copper are described well by the TB-SMA.

In our isobaric-isoenthalpic (NPH) classical molecular dynamics simulation, a system with 500 particles in a cubic box subject to periodical boundary conditions is studied. The equations of motion are integrated using the velocity form of the Verlet algorithm for the NPH ensemble of Anderson.[10] The value $\tau = 8.116 \times 10^{-14}$ s is chosen as the time unit and the time step Δt is $0.01\,\tau$. The heating or cooling procedure is realized by scaling the velocity of each particle gradually and proportionally. The well-equilibrated initial liquid is prepared by gradually heating the perfect crystal. In order to guarantee the sufficiency of the relaxation process and the reliability of the final configurations, after a period of temperature drop the system experiences a relaxation process with 10000 steps, which can be regarded as the annealing process.

Six cooling rates, ranging from 10^{11} to 10^{13} K/s ($Q_0 = 8.05 \times 10^{13}$ K/s, $Q_1 = 3.58 \times 10^{13}$ K/s, $Q_2 = 3.58 \times 10^{12}$ K/s, $Q_3 = 7.15 \times 10^{11}$ K/s, $Q_4 = 5.43 \times 10^{11}$ K/s, and $Q_5 = 3.62 \times 10^{11}$ K/s), were selected. From the results of structure analysis we can see that the crystallization processes take place at all selected cooling rates except for Q_0, during which the glass formed. Hence we can estimate that the critical cooling rate below which the crystallization becomes dominant is between Q_0 and Q_1.

To investigate the system microstructure we adopt the pair analysis technique,[11] which has been widely used to monitor liquid, glass and crystalline structures.[6–8,12] In this technique, pairs of atoms can been classified with four integer indices (hence, we call them HA indices for convenience). By counting all types of atom pairs, each of the various phases of the bulk system has its own signature that characterizes

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its local structure.[11] Since the 1421 bond represents the fcc-like structure, 1422 bond characterizes the hcp-like structure, 1441 and 1661 bonds characterize the bcc-like structure, and the 1551 bond characterizes the icosahedron-like structure,[12–14] it is more important to monitor these bonds. Also, with the help of this technique, all sorts of polyhedra can be investigated[13,14] in the system. Here, we define the polyhedra which have 12 pairs of 1421 bonds between central atoms and their near-neighbors as fcc-type polyhedra, and define the central atoms as fcc-type atoms. Similarly, we can define the hcp-type atoms and polyhedra which have 6 pairs of 1421 and 6 pairs of 1422 bonds, the icosahedron-type atoms and polyhedra which have 12 pairs of 1551 bonds, and bcc-type atoms and polyhedra which have 6 pairs of 1441 bonds and 8 pairs of 1661 bonds.

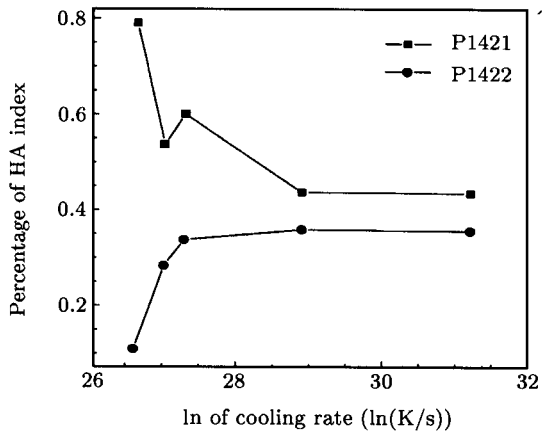

Fig. 1. Percentage of 1421 and 1422 bonds in the final configurations versus natural logarithm of the cooling rate (K/s).

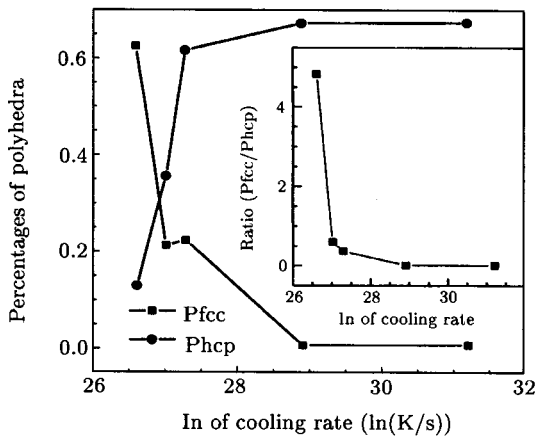

Fig. 2. Final percentage of fcc-type polyhedra, final percentage of hcp-type polyhedra, and final ratio of number of fcc-type polyhedra to number of hcp-type polyhedra versus natural logarithm of the cooling rate.

The curves shown in Fig. 1 describe the 1421 and 1422 bonds at 0 K as a function of cooling rate. With increasing cooling rate, the percentage of 1422 bonds increases, while the percentage of 1421 decreases (except for Q_3). Hence, with the rise of cooling rate, the hcp-like structure will be enforced; on the contrary, the fcc-like structure will decrease. However, there is an anomalous case when the percentage of 1421 bonds violates the trend shown in Fig. 1 from Q_4 to Q_3. It is also worthy to note that both the increase of 1422 bonds and the decrease of 1421 bonds level off with increasing cooling rate because the results of Q_1 and Q_2 show few differences. The other HA indices are rare and not shown here.

For more detailed and direct microstructure information, we count some of the polyhedra defined above. Since the 1421 and 1422 bonds are dominant in percents at all cooling rates except Q_0, we focus on the fcc- and hcp-type polyhedras, which are shown in Fig. 2 polyhedra. The resulting configurations are mixtures of fcc- and hcp-type polyhedra, as well as other polyhedra which are relatively rare and so are ignored. This result agrees with the work of model systems of Lennard-Jones particles.[2] Moreover, we can obtain the effects of cooling rate on the quantities of these polyhedra. The percentage of hcp-type polyhedra has the same tendency as that of the 1422 bond, while the percentage of fcc-type polyhedra has the same tendency as that of the 1421 bond with increasing cooling rate. This indicates that the faster the cooling rate, the more hcp-type polyhedra can be obtained and the less fcc-type can be acquired. At a high cooling rate the number of fcc-type and hcp-type polyhedra can saturate. The cooling rate controls the structure by influencing the nucleation phenomena. Hence, the faster cooling rate benefits the nucleation of the metastable hcp structure whilst the slower cooling rate benefits the nucleation of the most-stable fcc structure.

Figure 2 also shows the ratio of the number of fcc-type polyhedra to the number of hcp-type polyhedra versus the natural logarithm of the cooling rate. A clearer relationship between final structure and cooling rate is shown here. The faster the cooling rate, the smaller the ratio. Therefore we can obtain two critical cooling rates: one is defined as that when the ratio equals 1, which means that there are equal numbers of fcc-type and hcp-type polyhedra; the other is that when the ratio levels off, which means that the number of hcp-type polyhedra will reach a maximum and the number of fcc-type polyhedra will reach a minimum. Accordingly, we can regard the former as the fcc-hcp structure-transition critical cooling rate and the latter as the hcp structure-saturation critical cooling rate. In this paper, the former is between Q_4 and Q_5, the latter between Q_3 and Q_2.

Figure 3 shows the snapshot pictures of hcp-type atoms and fcc-type atoms in one final configuration of twenty samples at five cooling rates. Just as in the work of Swope and Andersen,[2] the distributions

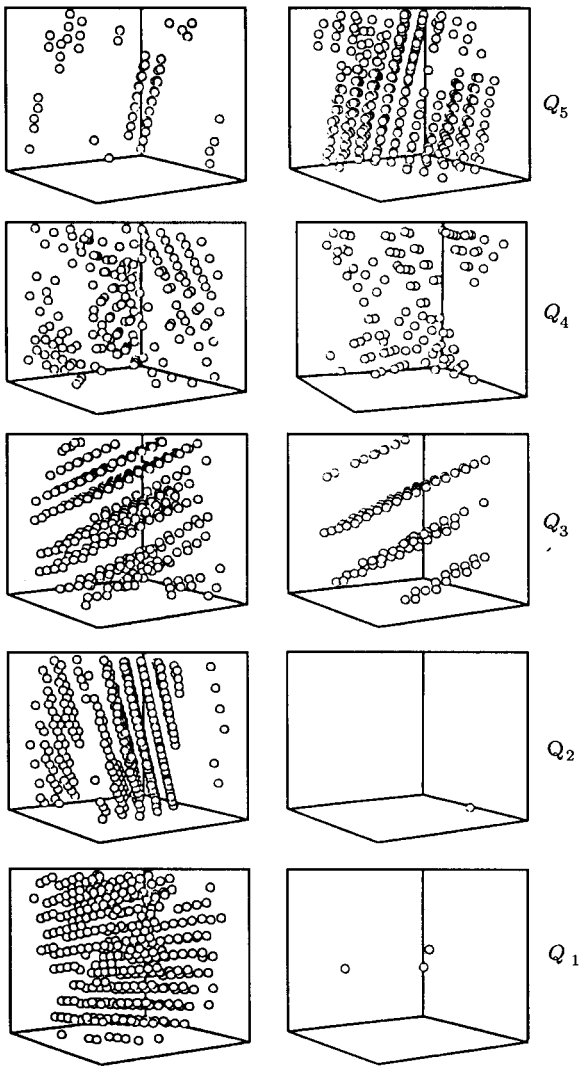

Fig. 3. Snapshot pictures of final distributions of hcp-type and fcc-type atoms at different crystallization cooling rates; left: distribution of hcp-type atoms, right: distribution of fcc-type atoms.

of the two types of atoms are not in a random mixture of the two types of atoms. There is a greater tendency for fcc-type atoms to be surrounded by other fcc-type atoms, and for hcp-type atoms to be surrounded by other hcp-type atoms. Furthermore, our results reveal a cooling rate dependence for the arrangement of atoms. At the high cooling rates Q_1 and Q_2, the fcc-type atoms are few and do not show a clear trend. Then, at Q_3 they exhibit a layer-like distribution. The snapshot picture at Q_4 and Q_5, however, exhibits more similarity to a phase separation. These results explain the anomalous case shown in Fig. 2. From the snapshot pictures, the system with phase separation has more disordered regions, in which the fcc-type polyhedra are rare, than a system with layers. Hence it is natural that there is an anomalous rise in the curve of the fcc-type polyhedra with increase of cooling rate from Q_4 to Q_3, under the condition of limited total number of atoms.

Moreover, there is another anomalous case shown in Fig. 1 to be interpreted. Unlike the 1422 bond, which mainly exists in the hcp-type polyhedron, the 1421 bond exists in both hcp-type and fcc-type polyhedra. Hence, two factors may contribute to this increase of 1421 bond from Q_4 to Q_3: One is the rise in number of hcp-type polyhedra with the increase of cooling rate, the other is the rise in number of fcc-type polyhedra because of layering. Any percentage change of these two types of polyhedra will induce the percentage change of the 1421 bond. We can see that in previous papers[12–14] it is somewhat not accurate enough to say that the 1421 bond represents the fcc-like structure. Strictly speaking, the percentage of 1421 bonds does not decrease progressively and monotonously with the increase of cooling rate, neither does the percentage of fcc-type polyhedra. However the ratio shown in Fig. 2, the percentage of hcp-type polyhedra, and the percentage of 1422 bonds really displays this behavior. So it is more reasonable to describe the cooling rate dependence of the final structure by using this ratio.

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