Cooling rate dependence of polymorph selection during rapid solidification of liquid metal zinc

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Abstract: The polymorph selection during rapid solidification of zinc melt was investigated by molecular dynamics simulation. Several methods including $g(r)$, energy, CNS, basic cluster and visualization were used to analyze the results. The results reveal that the cooling rate has no observable effect on the microstructure as $T > T_c$ (T_c is the onset temperature of crystallization); and at the first stage of crystallization, although microstructures are different, the morphologies of nucleus are similar, which are composed of HCP and FCC layers; the polymorph selection of cooling rate finally takes place at the second stage of crystallization: at a high cooling rate, the rapid increase of FCC atoms leads to a FCC crystal mixed with less HCP structures; while at a low cooling rate, HCP atoms grow at the expense of FCC atoms, resulting in an almost perfect HCP phase. The results reveal that the cooling rate is one of the important factors for polymorph selection.

Key words: polymorph selection; crystal structure; rapid solidification; metal zinc; molecular dynamics simulation

1 Introduction

Polymorphs have different physical properties [1], e.g., materials solidified into different polymorphs will result in different macro-properties. Therefore, controlling polymorph form is crucial for many applications, and it is also a great technological importance in making of drugs and pigments as well food. So, controlling and designing the polymorphism of crystals have attracted a great deal of attention in various fields [2−5]. The structure of a crystal is developed from the nuclei which often consist of different polymorphic structures. While the nucleation and growth are a very complex process, in which the structure of polymorph is affected by several factors such as impurities, cooling rates and boundary condition. Thus, the control of polymorph selection during crystallization is still a mysterious problem, which demands further explorations [5,6].

Polymorph selection is a complex phenomenon mainly resulted from the competition of kinetics and thermodynamics [7,8]. Much attention has been paid on this issue and great progress was achieved in the past. Both experiment and simulation have shown that nucleation stage is important for controlling polymorph selection [9,10]. In the very recent work of ZHANG et al [4], the Lennard−Jones system often evolves into a polymorphic crystal with either fivefold-symmetric stacking faults or single-direction stacking faults, and such an evolution depends on the configuration of FCC/HCP concomitance in the nucleation stage. For spherical particle system and Lennard−Jones particle system, the polymorphism can be controlled by varying the conditions of crystallization (e.g., the value of the dimensionless screening parameter, the pressure at fixed supercooling) [11,12]. However, experiments have suggested that seeding with the desired polymorph in nucleation stage is not sufficient to ensure the growth of a desired polymorph [10]. Therefore, the polymorphism

control remains a long standing and challenging issue and efforts are still urgently needed to make a comprehensive understanding of this phenomenon.

In this work, we focus on the effect of cooling rate on the polymorph selection during rapid solidification. The molecular dynamics (MD) simulations for the rapid solidification of liquid zinc have been performed at two cooling rates. And several analysis methods including the cluster type index method (CTIM) [13−17] and visual analysis have been adopted to detect the structure evolution during solidification. It is found that via cross nucleation of different layers, the cooling rate plays a critical role in polymorph selection that begins to work at the second stage of crystallization.

2 Computation details

We use the effective pair potential function of the generalized nonlocal model-pesudopotential (GNMP) to model the interactions between atoms [18,19]. The potential is defined as

$$V(r) = (Z_{eff}^2/r)\left[1 - \left(\frac{2}{\pi}\right)\int_0^\infty F(q)\sin(rq)\mathrm{d}q / q\right] \qquad (1)$$

where Z_{eff} is the effective ionic valence and $F(q)$ is the normalized energy wave number characteristic, and both of them were defined in detail in Refs. [18] and [19]. The reliability of the potential for metal zinc has been demonstrated by computing its liquid structure [20]. The pair potential is cut off at 20 a.u., and the time step is 5 fs.

The MD simulation was carried out in a cubic box with 10000 zinc atoms under ambient pressure and three dimensional periodic boundary conditions. In this simulation, the damped force method (also called the Gaussian thermostat) [21,22] is adopted to control the temperature of the system. Subjected to the Maxwell distribution law, the position and velocity of each atom are initialized randomly at 973 K (much higher than the melting point of zinc (692 K)). First of all, let the system run 50000 time steps to obtain equilibrium liquid state determined by the energy change of the system; then, the system is quenched to 73 K at two cooling rates of $Q_1 = 5 \times 10^{11}$ K/s and $Q_2 = 1 \times 10^{11}$ K/s. Finally, the microstructural evolution is analyzed by means of the common neighbor sub-cluster (CNS), the enhanced cluster-type index method (CTIM-2) [13,14] and 3D graph technique.

3 Results and discussion

As well known, the pair distribution function (PDF or $g(r)$) can be obtained by Fourier transformation of X-ray diffraction factor $S(q)$, so the current simulation can be verified by comparing the calculated $g(r)$ curves with the experimental results obtained by WASEDA [23], as shown in Fig. 1. Obviously, the calculated results are perfectly in agreement with the experiment data. This demonstrates that the effective pair potential function adopted here is successful in describing the interactions among zinc atoms.
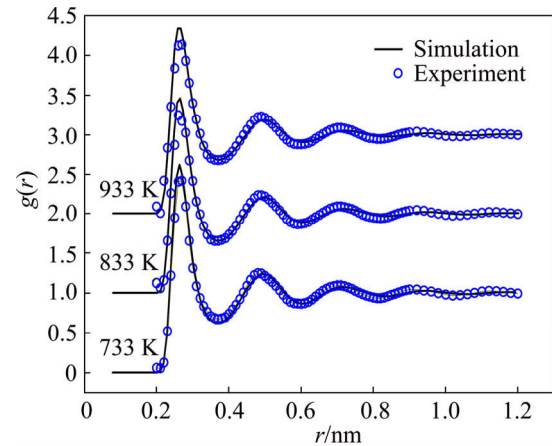

Fig. 1 Comparisons of simulation $g(r)$ curves (solid lines) with experimental data (circles) for zinc at different temperatures

Figure 2 shows the evolution of average energy E per atom with the decrease of temperature at two cooling rates. The slopes of both curves have twice steep jumps, which implies that the solidifications experience first-order phase transitions. And the initial temperatures (T_c) of crystallization can be evaluated to be about 313 K and 353 K at Q_1 and Q_2, respectively. And the end temperatures (T_e) of the phase transition are respectively 213 K and 298 K. Obviously, with the decrease of the cooling rate, T_c increases, while ΔT ($T_c - T_e$) decreases. This is because under a slower cooling rate, for a certain temperature decrease, it needs more time to relax the system. In other words, the slower the cooling rate is, the closer the system is to the equilibrium state at any
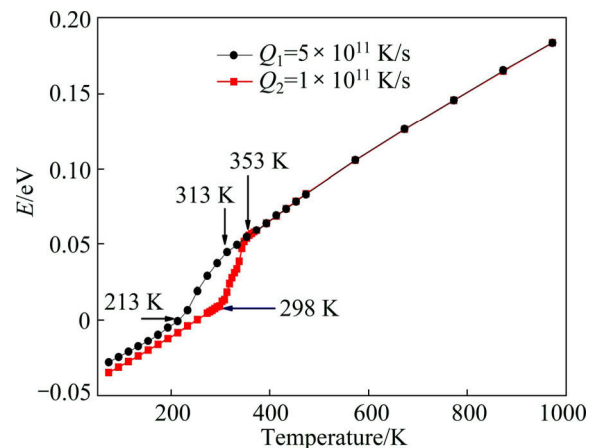

Fig. 2 Relationship between total energy per atom and temperature at different cooling rates