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Simulation study of size distributions and magic number sequences of clusters during the solidification process in liquid metal Na

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ABSTRACT

To investigate the size distributions of various clusters formed during solidification processes, a molecular dynamics (MD) simulation study has been performed for a system consisting of 10^6 liquid metal Na atoms. With the cluster-type index method (CTIM), it is demonstrated that the basic clusters of (13 3 6 4), (13 1 10 2), (14 2 8 4), (14 4 4 6) and (12 0 12 0) and their combinations play a critical role in the microstructure transitions. Also, using a new method to classify all the clusters in the system, the size distributions of various clusters clearly reveal magic number characteristics. The total magic number sequence can be regarded as the superposition of all partial magic numbers corresponding to the related group levels of clusters. The first 10 magic numbers are present in order 14, 22, 28, 34, 41(43), 46(48), 52(54), 57(59), 61(66), 70(74),... (the numbers in the parentheses are the second magic numbers corresponding to the same group level of clusters). This magic number sequence is compared with the experimental and computational results of other authors.

1. Introduction

In the last decades, magic numbers and magic number clusters have been studied as important parts of cluster physics and science. A lot of works on the characteristics of magic numbers and the formation mechanisms of magic number clusters have been reported, both experimentally [1–10] and theoretically [11–16].

However, up to now, for the clusters formed during the cooling processes of liquid metals [17–21], their size distribution characteristics are still unresolved. Recently, we have investigated the formation mechanisms of the clusters formed during rapid cooling processes in liquid metal Al by molecular dynamics simulation. The magic number sequence has been found for the first time in the system as shown in detail in Ref. [20]. To obtain a deeper understanding of the magic number characteristics of the clusters in the solidification process of liquid metals, in this paper, we explore the size distribution and magic number characteristics of clusters formed during the rapid solidification processing of liquid metal Na for a large-scale system consisting of 10^6 atoms.

2. Simulation conditions and methods

The conditions for the simulation are as follows: 10^6 Na atoms are placed in a cubic box and the system runs under constant pressure and periodic boundary conditions. The size of the cubic box is determined by both the number of atoms in the system and the mean volume of each atom at each given temperature under constant pressure, so the box size will change with temperature. The equations of motion are solved using the leap-frog algorithm. The interacting interatomic potential adopted here is the effective pair potential function of the generalized energy independent non-local model-pseudopotential theory developed by Wang et al. [22,23], the potential function is:

$$V(r) = \left(Z_{eff}^2/r\right)\left[1 - \left(\frac{2}{\pi}\right)\int_0^\infty dqF(q)\sin(rq)/q\right], \quad (1)$$

where Z_{eff} and $F(q)$ are, respectively, the effective ionic valence and the normalized energy wave number characteristics, which were defined in detail in Refs. [22,23]. This pair potential was cut off at 1.06 nm (namely 20 a.u.). The time step was chosen as 10^{-15} s, and the cooling rate was 1.00×10^{13} K/s.

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The simulation calculation was started at 973 K (the melting point of Na is 371 K). The system was first equilibrated at the same temperature (the criterion of equilibrium state is the changing degree of energy in the system close to zero). In this simulation, the damped force method (which is also called Gaussian thermostat, because the Gauss's principle of least constraint is used in this algorithm. See Refs. [24,25] for details) was adopted to control the temperature of the system. Then, the system was decreased at the cooling rate of 1.00×10^{13} K/s to some given temperatures: 973, 923, 873, 823,... 273 and 223 K. At each given temperature, the instantaneous structural configurations of the system, i.e., the space coordinates of each atom, were recorded. The Honeycutt–Andersen (HA) bond-type index method [26], the center-atom method [17] and the cluster-type index method [17–21] were used to detect and analyze the bond-types and the cluster-types of the relevant atoms in the system, and then to further investigate the size distributions of clusters formed during the cooling processes of liquid metal Na.

3. Simulation results

3.1. Pair distribution function analysis

We inspect the pair distribution functions $g(r)$ of the system at 573, 473 and 373 K obtained from this simulation and compare them with the experimental results at 573, 473 and 378 K by Waseda [27], respectively, as shown in Fig. 1. The simulation results are in good agreement with the experimental results, even though the last one is at 378 K. This means that the effective pair potential adopted here is rather successful in describing the objective physical nature of this system.

It is well-known that the pair distribution function $g(r)$ can only be used to describe the statistical distributions of the atoms in the system, but not be used to describe and discern the concrete relationship of an atom with its near neighbors.

3.2. Bond-type index analysis

To have a deep understanding of the formation and evolution mechanisms of clusters in liquid metals, it is crucial for us to know the concrete relationship of an atom with its near neighbors. At present, an important method is the pair analysis technique, especially, the bond-type index method of Honeycutt–Andersen (HA) [26], which has been widely used to describe and analyze the microstructure transitions in liquid and amorphous metal systems (see Refs. [17–21,26] for details). In this simulation, various bond-types are also described by HA indices, as shown in Table 1.

Table 1 shows obviously that:

The relative numbers of 1551 and 1541 bond-types, related to the icosahedral configurations, especially to amorphous structures, represent 6.0% and 9.0%, respectively, of all bond-types at 973 K. Highly interesting is that the relative number of 1551 bond-type increases remarkably with the decrease of temperature, reaching 31.2% at 223 K, where the sum of the 1551 and 1541 bond-types occupies 45.8% of all bond-types, increasing by about 30.8%. The changing trends of the 1551 and 1541 bond-types are similar to those obtained in our previous works for different-sized liquid metal Al systems [17,18,20].

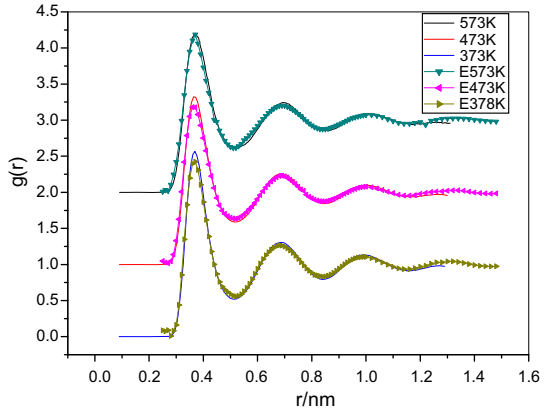

Fig. 1. Pair distribution functions of liquid Na at 573, 473 and 373 K.

The relative numbers of 1441, 1431, 1421 and 1422 bond-types, related to the tetrahedral structures, represent 4.0%, 16.7%, 3.4% and 7.1% of bonds at 973 K, respectively, and their sum accounts for 31.2% of all bond-types. However, these four bond-types change slightly with the decreasing temperature, and their sum still remains 24.3% at 223 K.

It is worth noting that the relative number of the 1661 bond-type, related to bcc structures, increases rapidly from 2.4% at 973 K to 14.2% at 223 K. This is very important for the final structure.

The above-mentioned discussion reveals that different liquid metal systems can be clearly distinguished by the relative numbers of bond-types.

3.3. Cluster-type index analysis

However, the HA bond-type indices cannot be used to describe and discern the different basic clusters formed by an atom with its nearest neighbors, especially, the different nano-clusters formed by some different basic clusters. In order to overcome this difficulty, the authors have proposed a cluster-type index method (CTIM), based on the work of Qi and Wang [28], as shown in detail in Ref. [20].

According to the definition of CTIM, four integers are used to describe a basic cluster. The meaning of the four integers are as follows: the first integer denotes the total number of surrounding atoms (i.e., the coordination number Z of the central atom), which form a cluster along with the central atom; the second, third and fourth integers denote, respectively, the numbers of 1441, 1551 and 1661 bond-types by which the surrounding atoms are connected with the central atom of the basic cluster. For example, the (12 0 12 0) indicates an icosahedral cluster that is composed of 13 atoms (one is the central atom, the coordination number $Z = 12$), the central atom connected to the surrounding atoms only with 12 1551 bonds; the (13 1 10 2) stands for an defective polyhedron cluster composed of 14 atoms (the coordination number $Z = 13$), the central atom connected to the surrounding atoms with one 1441, ten 1551 and two 1661 bonds. For convenience of discussion, six main basic clusters in this simulation system are selected as shown in Fig. 2.

By the CTIM, the statistical results for various cluster-types in this system at each given temperature are obtained. There are 63 different basic cluster-types, among which only 34 main types are listed in Table 2. However, during the whole solidification process, only 17 types appearing more than 1000 times play a critical role. For convenience of discussion, only the relations of the former 10 main basic clusters with temperature are given in Fig. 3.

Fig. 3(a) shows clearly that the first three basic clusters (13 3 6 4), (13 1 10 2) and (14 2 8 4) increase rapidly with the decrease of temperature, and play almost an equally important role in the microstructure transitions of liquid metal Na. And the basic cluster (12 0 12 0) ranks six and only plays a secondary role, but in the liquid metal Al, it is the first one and plays the most important role in the microstructure transitions [20].

3.4. Size distribution and magic number characteristics of clusters

To investigate the size distribution characteristics of various clusters with different sizes in the system, all the clusters should