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Local atomic structures in grain boundaries of bulk nanocrystalline aluminium: A molecular dynamics simulation study

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ABSTRACT

The microstructures of grain boundaries (GBs) in bulk nanocrystalline aluminium have been investigated by a large-scale molecular dynamics method. Bulk nanocrystalline aluminium is obtained directly by liquid quenching at an appropriate cooling rate, which has narrow grain-size distribution and high-angle GBs. It is found that up to 89.75% GB atoms (named as GB1 atoms) are located at the nearest-neighbour coordination shell around nanograins; others (named as GB2 atoms) are mainly at triple junctions. Local atomic structures in the GBs are quantified in terms of a recently developed method, in which the neighbours of an atom are identified with a parameter-free topological criterion rather than a fixed cut-off distance r_c. The results demonstrate that though there are a large number of different cluster types in both the GB1 and the GB2 regions, only a few ones with FCC-like order appear with high frequency in the GB1 region and play a crucial role in the microstructural feature of the GB1. The GB1 region displays short-to-long range order. The GB2 region presents ICO- and BCC-like short-range orders whose degrees are in between the liquid and amorphous, but the medium-range order at the cluster-scale is very weak.

1. Introduction

Bulk nanocrystalline materials have generated immense scientific interests, due to their superior mechanical and functional properties [1,2]. Owing to their ultrafine grain sizes, a significant fraction of atoms are located at grain boundaries (GBs), and they are believed to play a crucial role in some properties of bulk nanocrystals [3,4]. Therefore, understanding the GB structure is of essential importance for the study of bulk nanocrystalline materials.

Many experiments [5–10] have been carried out to investigate the microstructures of GBs in the nanocrystalline materials. Early experiments [5,6] suggested a highly disordered "gas-like" GB structure in some bulk nanocrystalline metals, without short- and long-range orders. Meanwhile, some experiments [7–9] concluded that they have a short-range order (SRO), similar to that in coarser-grained polycrystalline materials. Recently, Wu et al. [10] reported that the microstructures of GBs in the ZnO nanocrystalline film are gradually disordered from the grains to the outer coordination shells, experiencing a transition from the modestly ordered innermost coordination shell around grains to the partly disordered second coordination shell and then to the completely disordered higher coordination shells. In spite of the large amount of experimental works, our understanding on the local atomic structures in the GB region is still limited due to the difficulty in observing them directly. The GB structure model which can unify the contradictory observations has not been evolved up to now.

Computer simulation is a powerful tool to study the microstructure of nanocrystalline materials, and some "preparation" procedures for bulk nanocrystalline metals have been proposed. First attempt to generate a bulk nanocrystalline metal was proposed by Phillpot et al. [11]. The nanocrystalline structure was obtained by the crystallization of supercooled melt, in which some crystalline seeds were inserted to obtain high-density nuclei. It was found that the GB region exhibited a highly disordered microstructure, based on the analysis of pair distribution function (PDF). But the local atomic structures in the GB region were not demonstrated, since the PDF only reflects the atomic distributions in one-dimension statistical average. At present, most nanocrystalline configurations in simulations are geometrically constructed by the Voronoi cell method [12–16]. There into, single-phase nanograins are separated by the narrow GBs, and this microstructures are close to that produced by inert gas condensation in experiments. Recently, Van Swygenhoven et al. [13,14] further demonstrated that a large percentage of GB atoms are in the environment with significant crystalline order, and they often build into some regular coherent

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patterns. However, the specific local atomic structures in these ordered regions of GBs were not investigated.

The nanocrystalline configurations generated by the above simulation methods are close to experimental results to some degree, but all of their generation processes deviate from the realistic experiments more or less. In this work, in order to avoid the unrealistic manipulation of inserting nuclei in liquids in Ref. [11], a large-scale MD simulation is performed for the rapid solidification process of liquid aluminium to enhance the nucleation density. The bulk nanocrystalline aluminium is obtained at an appropriate cooling rate. Local atomic structures in the GB regions are investigated in terms of a recently developed method of the largest standard cluster analysis (LSCA) [17].

2. Computational methods

2.1. Molecular dynamics simulation

The rapid solidification process of liquid aluminium was simulated using the large-scale atomistic/molecular massively parallel simulator (LAMMPS) [18]. The embedded atoms method (EAM) potential proposed by Mendelev et al. [19] was adopted to describe the atomic interactions in the simulation model. The total energy E_{tot} is given by

$$E_{tot} = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\varphi_{ij}(r_{ij}) + \sum_{i=1}^{N}F_i(\rho_i), \tag{1}$$

where the subscripts i and j label distinct atoms, N is the number of atoms in the system, r_{ij} is the separation between atoms i and j, φ_{ij} is the pair potential between atoms i and j separated by r_{ij}, and $F_i(\rho_i)$ represents the energy to embed an atom in a background charge density ρ_i:

$$\rho_i = \sum_j \psi(r_{ij}), \tag{2}$$

where ψ_i is the contribution to the electron density of atom i from a neighbouring atom j. This EAM potential was optimized for good representations of both crystalline and amorphous phases, and the MD simulations can accurately predict the thermodynamics and structural properties of Al by using this potential [20–22].

The sample initially contained 1,048,576 atoms in their ideal FCC positions ($32 \times 32 \times 32$ FCC unit cells) with periodic boundary conditions in an isothermal–isobaric (NPT) ensemble. The motion equations were integrated by the velocity-Verlet algorithm with a time step 2 fs. The temperature was controlled by the Nose–Hoover thermostat [23,24]. First, the system was heated from 273 K to 1273 K, and then was isothermally relaxed for 50 ps at 1273 K to obtain an equilibrium liquid. Subsequently, the equilibrium liquid was quenched to 273 K at different cooling rates R varying from 1×10^{13} K/s to 1×10^{11} K/s. At each desired temperature, the instantaneous spatial coordinates of atoms were recorded for further analysis.

2.2. Characterization of microstructures

The PDF, i.e., $g(r)$, is widely used to describe the structural characteristics of liquids, amorphous and crystal solids. It is defined as:

$$g(r) = \frac{V}{N^2}\left\langle \sum_{i=1}^{N}\frac{n(r)}{4\pi r^2 \Delta r}\right\rangle, \tag{3}$$

where N is the total number of atoms in the system, V is the volume, and $n(r)$ is the number of atoms which can be found in the shell from r to $r + \Delta r$. $g(r)$ indicates the probability of finding an atom as a function of distance r from an average central atom.

To identify the local atomic structures in the system, a recently developed method of the largest standard cluster analysis (LSCA) [17] is adopted. In LSCA, the neighbours of an atom are determined by a parameter-free topological criterion. The atomic configuration composed of a central atom and its neighbours is called as the largest standard cluster (LSC), as shown in Fig. 1a. In a LSC, a root-pair composed of a neighbour and the central atom, comprises a centre–neighbour–subcluster (CNS, see Fig. 1b), together with their common–near–neighbours (CNNs). According to the topology of CNNs, a CNS can be denoted by a CNS-index ijk, where i is the number of CNNs, j is the number of all bonds among CNNs, and k equals the number of bonds in the longest continuous chain formed by the j bonds. The CNS shown in Fig. 1b is 421. The face-centered cubic (FCC) cluster shown in Fig. 1a includes twelve 421 CNSs, denoted as [12/421]. The topology of the atomic cluster shown in Fig. 2 is similar to the FCC configuration, except that the two atoms labelled 308,990 and 190,944 in the A layer are not neighbour. Thus two 311 CNSs and one 411 CNS are formed besides nine 421 CNSs, and this cluster is denoted as [2/311, 1/411, 9/421]. Similarly, hexagonal close-packed (HCP), body-centred cubic (BCC), truncated decahedron (TDH), and icosahedral (ICO) clusters are [6/421, 6/422], [6/444, 8/666], [10/422, 2/555], and [12/555], respectively.

In this paper, different atoms are classified in terms of their corresponding types of LSCs. For example, the centre of a FCC LSC is denoted as a FCC atom. FCC, HCP and TDH atoms build the bodies of nanograins (shown in the following section), so we call them as crystal-like atoms; others mainly locating at the GB regions are amorphous-like atoms. The four familiar clusters of FCC, BCC, TDH and ICO are composed of different CNSs, respectively, and their corresponding CNSs are regarded as their characteristic CNSs. For example, 421 CNS is the characteristic CNS of FCC cluster, while the characteristic CNS of ICO cluster is 555.

In previous methods, such as the common-neighbour analysis proposed by Honeycutt and Andersen [25], a constant cut-off distance r_c is needed to determine whether two atoms are neighbours or bonded. This may be problematic for nanocrystalline structures, because the r_c in the ordered grain region is shorter than that in the disordered GB region. To overcome this deficiency, a natural and unique r_c for each LSC are determined as follows [17]. Firstly, an initial temporary cluster around an atom is constructed by searching its temporary neighbours within a larger r_c. Then the r_c is gradually decreased to remove its non-standard CNSs having common-neighbour-subring, and the final LSC can be determined until no non-standard CNS can be found. In this way, each LSC may have a unique maximal r_c. Since the r_c only acts as an intermediate parameter in this search process, our method is parameter free and scale independent.

3. Results and discussion

3.1. Formation of nanocrystalline by liquid quenching

Fig. 3 shows the temperature dependence of average potential energy per atom during the rapid solidification processes of Al under three different cooling rates, together with the snapshots of their final solidification structures at 273 K. At the faster cooling rate $R = 1 \times 10^{13}$ K/s, the energy decreases continuously with decreasing temperature, and the amorphous solid with few crystal-like atoms is formed. At the slower cooling rate $R = 1 \times 10^{11}$ K/s, the sudden decrease of energy near 600 K indicates the occurrence of crystallization, and the final crystal structure displays a FCC stacking interspersed few scattered amorphous-like atoms. For the crystalline process at the intermediate cooling rate $R = 1 \times 10^{12}$ K/s, the crystal-like atoms assemble into nanograins separated by the amorphous-like atoms.