



Molecular dynamics study on microstructural evolution during crystallization of rapidly supercooled zirconium melts



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ABSTRACT

Molecular dynamics simulations have been performed to explore the crystallization mechanism under rapid cooling for Zirconium that has body-centred cubic (bcc) and hexagonal close-packed (hcp) phases separated at 1136 K. The structural evolution was analysed in terms of the system energy, the pair (and angular) distribution function, and the largest standard cluster analysis. It is found that the critical cooling rate (γ_c) for vitrification is about 5.0×10^{13} K/s, and the Ostwald's step rule is applied to Zr. Crystallization always takes the pathway of supercooled-liquid (scl) \rightarrow bcc \rightarrow hcp, determined by the competition between thermodynamics and kinetics at different conditions. Particularly with γ decrease both the onset temperature of scl \rightarrow bcc and the maximal number of bcc atoms increase; while both the onset temperature of the bcc \rightarrow hcp transition and the rate of different crystalline atoms in the final solids are randomly. A rather perfect bcc phase can be obtained at $\gamma < 1.0 \times 10^{12}$ K/s, however, it is unstable and always transforms to the stable hcp phase under all conditions examined here. In the final solids, most of face-centred cubic (fcc) structures act as the hcp crystalline boundaries not comprises individual fcc phase. These findings are useful for understanding the crystallization of metals, especially for those that have a high-temperature-stabled phase.

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1. Introduction

The structure of materials determines its properties. Changing processing of materials could result in different structures, and get specific properties satisfying desired application [1–3]. The metallic glasses can be obtained by enhancing the cooling rate to suppress the formation of crystalline phase from molten metals [4–6]. Theoretically, all metals can be vitrified under a sufficiently high cooling rate, for example, the monatomic metallic glasses of Ta, W, Mo and V are recently obtained experimentally [7]. While for the materials that have different crystalline phases stabilizing at different temperature ranges under conventional conditions, what path will they adopt during a rapid cooling? Can the metastable phase be frozen to the final solid with some approaches? A good

sample for this issue is Zirconium (Zr) that has a body-centred cubic (bcc) phase β -Zr, stabilized between $T_\beta = 1136$ K and $T_m = 2127$ K on prevailing condition.

The stable hexagonal close-packed (hcp) phase of Zr (α -Zr) will transform into bcc phase (β -Zr) when $T > T_\beta$ under conventional conditions [8,9]. Under high pressure a distorted bcc phase was observed and can persist when pressure is released [10]. Both simulation and experiment indicated that β -Zr is formed firstly during rapid cooling. For example, the *ab initio* molecular dynamics (AIMD) study on the structural properties of liquid and undercooled liquid Zr revealed that the bcc-type rather than hcp-type short range order (SRO) increases with the increase of undercooling degree [11–13]. Another AIMD simulation at the quenching rate of 4.3×10^{13} K/s found out that the β -Zr phase is formed at about $T = 1000$ K [14]. When modelling the atomistic interactions in liquid and undercooled liquid Zr, Gheribi et al. demonstrated that the modified embedded atom model (MEAM) based on bcc lattice is more successful than that based on hcp lattice [15].

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As bcc crystal is the high temperature phase of Zr, the aforementioned results are consistent with the “step rule” proposed by Ostwald: an unstable system could transform into transient states till reaching a stable state [16]. The “step rule” is testified for silver and copper, with a intermediate stage predominated by bcc structures [17–19]. However, the final state is not bcc crystal under the cooling conditions examined. This may because silver and copper have no stable bcc phase under prevailing conditions. As an intrinsic phase stable at high temperature, could β -Zr be obtained at room temperature by rapid cooling?

In this paper, the molecular dynamics (MD) simulations for the rapid cooling of Zr at different conditions are performed. The structural evolution in the vicinity of solidification has been quantified by employing several microstructural characterization methods, including the recently proposed LSCA (the largest standard cluster analysis) [18–23]. The results reveal that when the cooling rate is high enough to 5×10^{13} K/s, the system will be vitrified into metallic glasses. And in all crystallization processes, the bcc clusters are always the first crystalline structures formed from super-cooled liquids. However the metastable bcc phase cannot be captured at room temperature under all approaches explored here. Generally the slower the cooling rate, the more perfect the intermediate bcc phase, whereas the percentage of hcp structures in the final solids seems no certain relationship with cooling rate.

The rest of this paper is organized as follows. In sec 2, the force field, simulation details, and several structural analysis methods used in the present work are described briefly. In sec 3, the existence of bcc phase is first identified by several statistic methods, and then the stability of β -Zr and the structure of the final solid are examined; finally we discussed the mechanism of bcc-hcp transformation and the effect of thermodynamic and kinetics factors on crystallization pathway. The summary is presented in sec 4.

2. Computational method

2.1. EAM potential and MD simulation details

The MD simulation of the rapid cooling of liquid Zr is conducted by employing the large-scale atomic/molecular massively parallel simulator (LAMMPS) [24]. The EAM potential is here adopted, which is highly optimized by fitting the potential-energy surfaces derived from high-precision first-principles calculations. A number of properties such as lattice dynamics, mechanical properties, thermal behaviours, defects, deformation paths and liquid structures have been considered in this EAM potential. The high accuracy and wide applicability of such EAM potential have been illustrated in previous studies [7,18,25–30]. Although no simulation based on EAM potential for Zr has been reported, the specific parameters for this element have been shared by the developer and can be found in Ref. [31]. In our present work, the accuracy and validation of EAM potential for metal Zr are confirmed by comparing the simulated results with the experimental ones, such as the pair distribution function $g(r)$ and mass density (see Supplementary Material Figs. S1 and S2).

Our simulations are subjected to the three dimensional periodic boundary conditions with a time step of 1.0 fs. After the positions and velocities of 10,000 Zr atoms are randomly generated in a cubic box, the equilibrium liquids are firstly obtained by relaxing 1.0 ns at 2600 K that is much higher than the experimental melting temperature, $T_m \sim 2127$ K (see Refs. [11,32,33]). Then the simulated system is quenched to 100 K at the cooling rates of $[10^{14}, 10^{10}]$ K/s under the NPT ensemble [34]. The atoms' velocity and position as well as other necessary information of the systems are recorded per Kelvin for further analysis.

2.2. Structural analysis methods

In the present work, three methods are used to identify the structural characteristic of the simulated system. As a one-dimensional (1D) method, the pair distribution function (PDF or $g(r)$) provides the probability to find other atoms at the distance r from a given atom, and the overall structural characteristic can be identified in terms of the shape and position of peaks on PDF curves. For example, a split second peak is usually resulted from an amorphous state. The second method is the 2D angular distribution function (ADF) [17,19,35,36]. Focusing on three-body correlation, ADF uncovers the local rotational symmetry of microstructures in a system. The largest standard cluster analysis (LSCA) is set to quantify 3D structures according to their spatial configurations. LSCA can characterize all kinds of local clusters beyond the nearest neighbour independent with any pre-set parameters [18–23].

In LSCA, the basic local structure is called a cluster that is composed of a central atom and its all neighbours. Around a given atom, the largest cluster that satisfies a topological criterion is unique and called as the largest standard cluster (LSC). In a LSC (see Fig. 1), a reference-pair (composed of one neighbour and the centre) and their common near neighbours (CNNs) comprise a common-neighbour-subcluster (CNS). The details about the topological criterion and an implementing algorithm can be found in Refs. [18–23]. For convenience, Fig. 1 demonstrates the major LSCs that will be further discussed in the following sections. Fig. 1(a) shows an hcp LSC around atom 4349 that comprise six S421 and six S422 with the 12 neighbours. One S421 in this hcp LSC is depicted in Fig. 1(b), which is composed of a reference-pair of 4263–4349 and their 4 CNNs, labelled 5721, 4535, 633 and 1432; and one S422 in Fig. 1(d), composed of the reference-pair of 5721–4349 and their 4 CNNs of 4535, 4263, 640 and 1004. Fig. 1(f)–(j) illustrate the topology of a bcc LSC that includes six S444 and eight S666. Thus the compact denotations for hcp and bcc LSCs are $[6/421, 6/422]$ and $[6/444, 8/666]$ respectively. Similarly, the compact denotations for face-centred cubic (fcc) LSCs (not shown here) is $[12/421]$, in which totally twelve S421 can be found. For convenience, the centre of a hcp LSC is called a hcp atom, such as the atom 4349; and similarly atom-121 is a bcc atom.

3. Results and discussions

3.1. Phase transition and intermediate stage

Fig. 2 shows the relationship between the average potential per atom and temperature (E - T) at six cooling rates. From Fig. 2(a) it can be found that the critical cooling rate for vitrification is about 5×10^{13} K/s. Hereafter we will focus on the structural evolution during the crystallization processes at four cooling rates of $\gamma_1 = 1 \times 10^{13}$ K/s, $\gamma_2 = 5 \times 10^{12}$ K/s, $\gamma_3 = 1 \times 10^{12}$ K/s and $\gamma_4 = 1 \times 10^{11}$ K/s. For clarity the four crystallization E - T plots are depicted in Fig. 2(b)–(e) respectively, together with the linear fitting and the marks for several critical temperatures. It is easy to find that the slower the cooling rate, the more distinct the characteristic of first order phase transition. Similar to the case for the silver system [17], a metastable phase can be clearly identified by the twice drop-offs on the E - T curves at the two slowest cooling rates of γ_3 and γ_4 . The onset temperature of crystallization (T_c) can be obtained as 986 K (γ_1), 1000 K (γ_2), 1112 K (γ_3) and 1186 K (γ_4) respectively (see Fig. 2(b)–(e)); and the end temperatures of crystallization (T_e) are 554, 740, 928 and 804 K respectively. Obviously the slower the cooling rate, the higher the T_c . This is consistent with the classic nucleation theory [37]. However, T_e does not monotonically increases with the decrease of cooling rate. The different dependence of T_c and T_e on cooling rate (and system size) has been

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